

STUDY WEEK

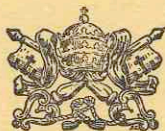
ON:

CHEMICAL EVENTS IN THE  
ATMOSPHERE AND THEIR  
IMPACT ON THE ENVIRONMENT

November 7-11, 1983

EDITED BY

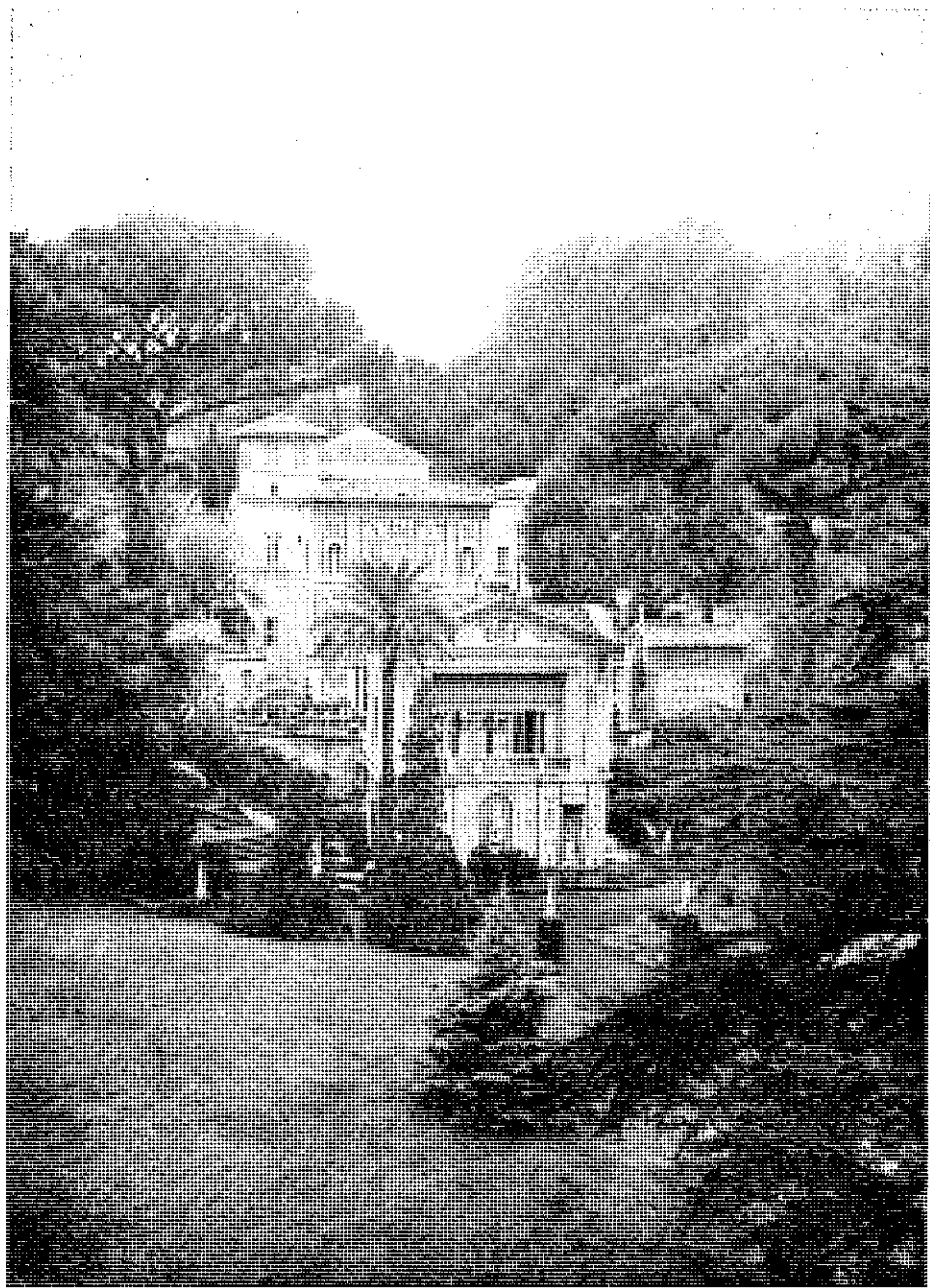
G. B. MARINI-BETTÒLO



PONTIFICIA  
ACADEMIA  
SCIENTIARVM

EX AEDIBVS ACADEMICIS IN CIVITATE VATICANA

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MCMLXXXV



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## FOREWORD

*It is a great honour and joy for me to present the volume of "Scripta Varia" which publishes the papers presented during the Study Week on "Chemical Events and their Impact on Environment" held at the seat of the Academy from the 7th to the 11th of November, 1983. In the volume are included the discussions which followed each presentation. These proceedings are of great interest; they touch problems which may seem diverse for a non-knowledgeable person, or insignificant to those who flee the reality of our present world. Nevertheless, the problems dealt with are a menace to humankind and challenge our future. Only those who are not aware of the questions herein treated are not preoccupied by the picture we see around us. These problems are a part of our daily life but they are not visible to the general public, either because they are hidden by concealed interests or because they have such slow effects that even their additive results are difficult to perceive.*

*The danger of a nuclear war after the terrifying effect of the remembrance of Hiroshima and Nagasaki brings to us easily fear and the desire to act in any way in order to avoid it. The subtle effect of the chemical events occurring in the atmosphere on the biosphere, because they are not instantaneous, cannot be easily perceived; unless an event of great proportions occupies for a few days the first page of our daily paper it is followed by oblivion. Their handicapping and deathly effect, however, can in a not so distant future destroy the quality of life, or life itself. Should we be pessimistic? Yes, certainly, unless we can change the mentality of many of the developmental processes of our society. This can be done only if scientists, technologists, sociologists and economists working together can change many of the priorities of our present times and, by the recognition of the facts, convince policy makers and the industrialists of the urgency to take measures to prevent the every-day increasing menace of slow destruction of the wonders of our world, which if protected will conserve the joy everyone experiences admiring*

*the blue sky, the non-smoked air, the clear water of a waterfall, the greenness of our mountains, prairies and forests.*

*The success of our Study Week is due to the hard work Giovanni Battista Marini-Bettòlo has given to its preparation, a zeal which was felt by all participants, a task which has been pursued in editing this volume. As always, Professor Marini-Bettòlo brought perfection to his activity. It is my honour to renew to my colleague my deep gratitude. I wish also to extend my thanks to Father Enrico di Rovasenda, Madame Michelle Porcelli, Mrs. Gilda Massa and Silvio Devoto. It is only through their devotion to the work of the Academy that our activity is made possible.*

CARLOS CHAGAS

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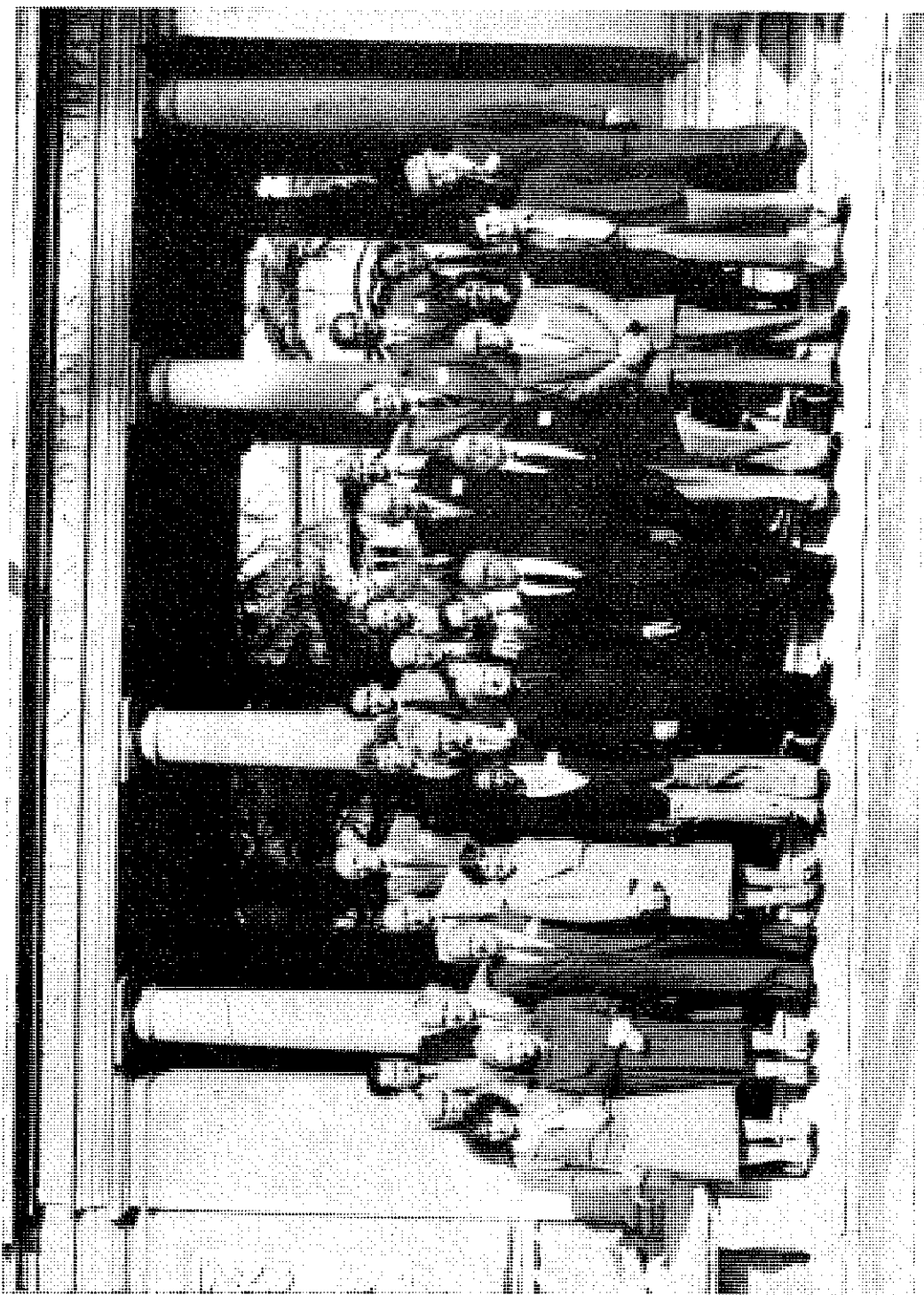
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## PONTIFICAL AUDIENCE

On November 12, 1983, His Holiness John Paul II granted an Audience in the "Sala Regia" of the Apostolic Palace in the Vatican to 45 Members of the Pontifical Academy of Sciences gathered in Plenary Session to discuss the subject "Science in the Service of Peace", to 20 scientists participating in the Study Week organized by the Academy on "Chemical Events in the Atmosphere and their Impact on the Environment", and to 15 scientists of a Working Group convened by the Academy to discuss "Specificity in Biological Interactions".

His Holiness John Paul II addressed to the participants an important speech on the role of Science for Peace and in particular the role of scientific community extended to all nations, concluding:

*Gentlemen, as men of thought and science, as pilgrims of the truth, as explorers in the different branches of science and knowledge, about man and the universe, who submit yourselves to the labour of observing, thinking, searching, so that man may be ever more man and may find in nature the proper environment for his development: I ask you to work for justice, love and peace, and to believe that today more than ever the Catholic Church is your ally, this Church which loves true science and right thinking, this Church which prays for you and which in my person, respecting your beliefs, invokes upon each one of you the blessing of God.*

## SCIENTIFIC PAPERS

## INTRODUCTION

# CHEMICAL EVENTS IN THE ATMOSPHERE AND THEIR IMPACT ON THE ENVIRONMENT

## INTRODUCTORY REMARKS

G. B. MARINI-BETTÒLO

I am glad to greet here today all you distinguished scientists from all over the world who have accepted the invitation of the Pontifical Academy of Sciences for the Study Week on "Chemical Events in the Atmosphere and Their Impact on the Environment".

As the scientist responsible for the organization of the Study Week, I should like to present some information about the philosophy, the methodology and the scope of the present meeting, that is, the guidelines followed by all the previous Study Weeks.

The main object of the Pontifical Academy of Sciences is to invite to the Vatican distinguished scientists of different disciplines from all over the world to discuss problems which are of importance both for their scientific aspect and for their impact on society.

The subjects that will be discussed this week have been in recent years the object of several conferences, round tables, and seminars at various levels all over the world. Many of you know each other well, having participated in specific and specialized discussions which have taken place even in the last months on some of the topics we will discuss here.

I think that a particular aspect of our Study Week is the multidisciplinary approach to the problem, in the presence of scholars of different disciplines: physicists, geologists, chemists, meteorologists, biologists, botanists, ecologists.

The problem of the impact on the environment, or better, on the biosphere, of chemical events occurring in the atmosphere is at present

of considerable importance. I hope that the discussions which will follow the presentations can develop new ideas and even indicate new lines of action.

In the last decade many experiments have been made in stratosphere and troposphere chemistry, as well as in the laboratory on models, on *the causes of acid depositions* and on the role of fluorocarbons on the *ozone layer* and *the impact of the CO<sub>2</sub> increase in the atmosphere on the climate and on oceans*. The studies have given important results for our knowledge and for the advancement of science.

Nevertheless, not all scientists fully agree on the interpretations of the above data since the phenomena are numerous and complex. This appears very clearly if one goes through the literature of the last years, and even of the last weeks, where many discrepant interpretations are found of the chemical events which occur in the atmosphere. I believe that a discussion which could help to clear some of the controversial interpretations could be of interest.

I wish to call your attention to the fact that the discussions, which will be published in a rather extensive form, constitute one of the most interesting aspects of these Study Weeks.

The assessment and interpretation of the impact on the biosphere of chemicals produced in the atmosphere under different conditions may lead to a better diagnosis of the present state of degradation of some environments and thus make it possible to establish new strategies.

The various steps of the discussion could be:

1. the present knowledge regarding chemical events in the atmosphere, both of common components and man-made substances or natural emissions;
2. a critical review of the interpretation of the results so far obtained;
3. the identification of the gaps which make it impossible to complete our diagnosis;
4. the discussion regarding future strategies in order to reduce noxious effects on biosphere of the chemical events in the atmosphere.

The conclusions reached should be condensed in a document, together with a critical examination of our present knowledge in this field.

It is our hope that the Study Week may suggest some new approaches to solve the problems involved in our discussions and that in any case it may lead to a better understanding of the chemical events in the atmosphere for the progress of science and the benefit of humankind.

I.

STRUCTURE, COMPONENTS AND PRIMARY PROCESSES  
IN THE ATMOSPHERE

# PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

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This review presents both a view of unresolved problems relating to the photochemistry of atmospheric constituents of global importance and some more parochial assessments of problems particular to the U.K.

To begin with the latter, while it is right that there should be concern over the quality of air, and the subsequent effects of polluted air on the environment, it should be remembered that the air quality in cities in the U.K. is probably better now than at any time in the previous several hundred years. Thus John Evelyn, in 1611, said:

"It is this horrid smoake which obscures our churches, and makes our palaces look old, which fouls our clothes and corrupts the waters"

Matters really did not improve much until after the disaster of December 5th, December 8th 1952, when the combined effects of a temperature inversion, particulate matter and sulphur dioxide emissions, largely from domestic coal fires, resulted in the premature deaths of some 4000 people, mainly elderly and those suffering from respiratory problems. This led directly to the Clean Air Act of 1953, which on a fairly rapid timescale led to the control of particulate matter emissions, and is a good example of the speed with which Governments can act if suitably motivated. As a child in urban Tyneside, it never occurred to me that the colour of buildings was anything other than jet-black. Indeed, if you visit many urban buildings nowadays which had been repaired prior to 1952 and have subsequently been cleaned you will find pieces of stone which do not match the originals. There was no need, since within twelve months, the colour



would in any case be black. No one could argue that the environment has been significantly improved by the control of particulate matter, the days of the London "pea-souper" are now long gone, but it could be said that the success of this legislation may have led to complacency with regard to the other, invisible emissions, most notably that of  $\text{SO}_2$ .

Again, this is not a new phenomenon. In 1846 Michael Faraday was asked by his club, the Athenaeum, to explain why new leather arm-chairs were disintegrating rapidly, and it did not take him long to diagnose that the cause was atmospheric  $\text{SO}_2$  from domestic coal fires denaturing the leather.

The emission of tropospheric sulphur oxide, and that of  $\text{NO}_x$  emission, is now of great concern, known colloquially, but inaccurately as "acid rain". Acid deposition would be a better description of the phenomenon.

The immediate consequences of emission of  $\text{SO}_2$  and  $\text{NO}_x$  are of course simply stated, the production downwind, either locally, or more often nowadays far away, of sulphuric acid and nitric acid, which may be deposited dry or in precipitation on the ground.

An attempt is made here to identify some of the remaining problems in understanding the chemistry, particularly the photochemistry, of these processes.

### *Photochemistry associated with acid rain*

There is clear evidence that the photochemical conversion of sulphur dioxide to acid is a minor but significant process. The possible mechanisms for the photochemical oxidation have been dealt with by many authors, but the review by Cox provides a basis for discussion [1].

The possible mechanisms are:

(i) Homogeneous direct photolysis of sulphur dioxide in the presence of oxygen.

(ii) Homogeneous gas-phase oxidation by hydroxyl radicals,  $\text{OH}$ ,  $\text{HO}_2$ , and peroxy radicals, of photochemical origin.

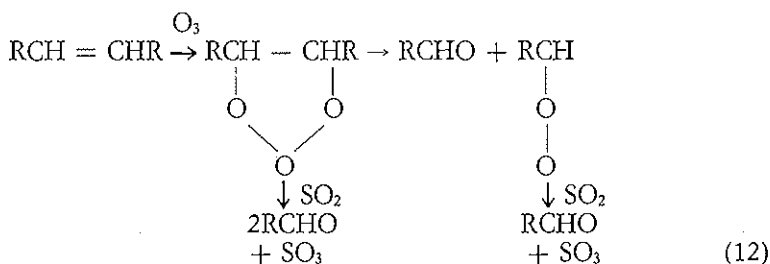
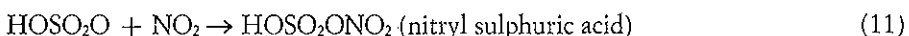
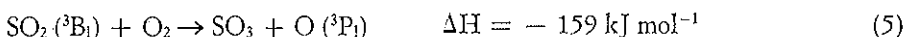
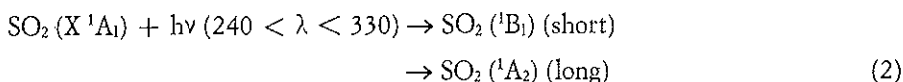
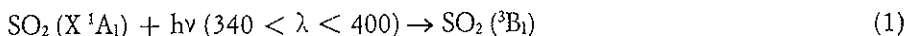
(iii) Homogeneous gas-phase reactions involving ozone-olefin interactions in urban atmospheres.

(iv) Heterogeneous reactions on the surface of particulate matter.

(v) Homogeneous aqueous phase reactions in water droplets in the atmosphere.

The mechanisms of direct photolysis, reaction (1) – (5), oxidation by OH, HO<sub>2</sub>, RO, and RO<sub>2</sub>, reactions (6) – (11), and ozone-olefin reactions, (12) lead to the estimated rates of SO<sub>2</sub> conversion shown in Table 1.

### Reactions



TAB. 1 [1] - *Rates of Homogeneous SO<sub>2</sub> Oxidation.*

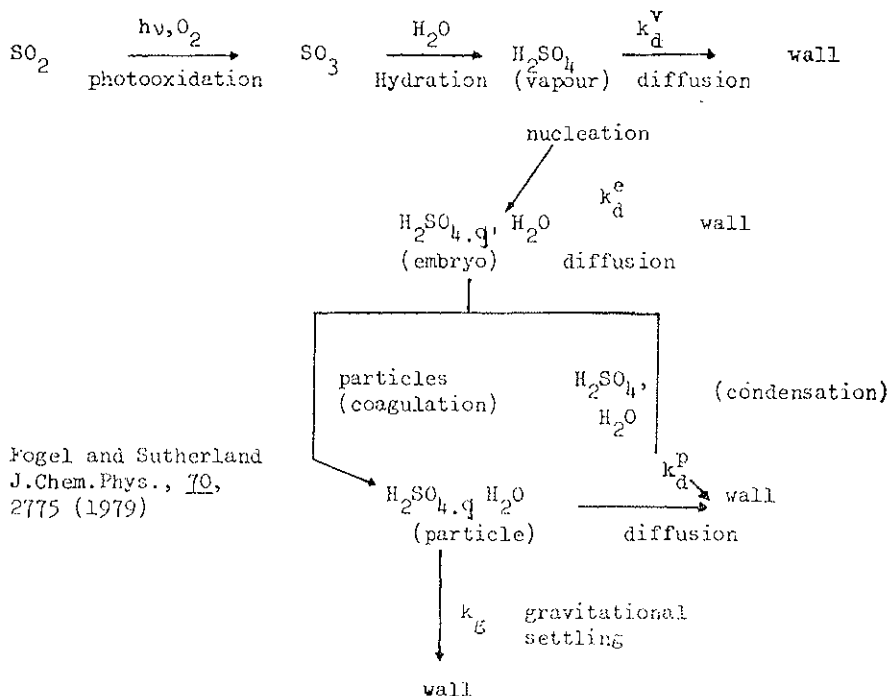
|                                | k<br>cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> | active species<br>molecules cm <sup>-3</sup>     | 100 × SO <sub>2</sub><br>oxidn rate<br>h <sup>-1</sup>         |
|--------------------------------|---|--|--|
| DIRECT                         | $1.6 \times 10^{-15}$                                       | 2.3 (SO <sub>2</sub> <sup>3B<sub>1</sub></sup> ) | 0.026  |
| OH                             | $8 \times 10^{-13}$   | $7 \times 10^6$<br>( $7 \times 10^5$ )           | 2.0<br>0.2   |
| HO <sub>2</sub>                | $9 \times 10^{-16}$   | $2 \times 10^9$<br>( $1 \times 10^8$ )           | 0.6<br>(0.03)  |
| CH <sub>3</sub> O <sub>2</sub> | $5 \times 10^{-15}$   | $2 \times 10^9$<br>( $1.5 \times 10^7$ )         | 1.7<br>(0.03)  |
| O <sub>3</sub> /alkene         |   | $2.5 \times 10^{12}$<br>$2.5 \times 10^{11}$     | (O <sub>3</sub> )<br>(CH <sub>3</sub> H <sub>6</sub> )<br>0.07 |

It is clear from this work that the homogeneous free radical reactions are probably the most significant, but the role of aqueous phase oxidation by H<sub>2</sub>O<sub>2</sub> and of heterogeneous oxidation are still in doubt, and require further investigation. The formation of aerosols is also of some importance. It has been suggested that in clouds, the rate of droplet formation may be proportional to the light intensity, which clearly deserves further attention. The formation of particles in the atmosphere is also very poorly understood, and requires much further work. The sole paper [2] dealing with this phenomenon in any quantitative way investigates the processes occurring, summarized in Scheme 1, upon the direct excitation of SO<sub>2</sub> into the second singlet state at wavelengths > 190 nm, a process clearly not of importance in the troposphere.

Before passing on to other aspects of atmospheric *photochemistry*, we might just anticipate later discussion of the effects of acid deposition, and indeed the location of this. From the parochial UK viewpoint the region most affected is southern Scandinavia, Tables 2 and 3 giving the total contributions by country to deposition in this region [3].

Other later papers in this volume will comment upon the effects on soil and water in lakes and rivers, of this acid deposition, but it may be noted in passing that the Royal Society of London, the Norwegian Academy of Science and Letters, and the Royal Swedish Academy of Sciences have recently agreed to initiate a further long term collaborative programme of research into the effects of acidification of surface waters in Norway

# SCHEME 1



TAB. 2 [3] - Average Contributions of Deposition in S. Norway (1972-1974).

| region        | distribution<br>of wet<br>deposition<br>(%) | distribution<br>of dry<br>deposition<br>(%) | distribution<br>of total<br>deposition<br>(%) | total deposition<br>mg SO <sub>2</sub> m <sup>-2</sup> a <sup>-1</sup> |                        |
|---------------|---|---|---|--|------------------------|
|               |   |   |   | annual average   | per 100 kt<br>emission |
| British Isles | 34.3  | 22.2  | 30.7  | 895  | 15.0                   |
| Norway        | 10.9  | 32.2  | 17.4  | 507  | 323                    |
| G.D.R.        | 11.0  | 9.9   | 10.7  | 312  | 6.3                    |
| F.R.G.        | 11.4  | 7.2   | 10.1  | 295  | 7.3                    |
| Sweden        | 4.4   | 6.9   | 5.2   | 152  | 14.8                   |
| Holland       | 4.3   | 2.9   | 3.9   | 114  | 9.5                    |
| Poland        | 3.4   | 3.9   | 3.5   | 102  | 2.7                    |
| Denmark       | 3.3   | 3.7   | 3.4   | 99   | 26.2                   |
| France        | 4.1   | 1.9   | 3.4   | 99   | 4.1                    |
| Belg./Lux.    | 3.9   | 2.3   | 3.4   | 99   | 8.1                    |
| Czech.        | 3.5   | 2.7   | 3.2   | 93   | 2.9                    |
| U.S.S.R.      | 2.3   | 2.4   | 2.4   | 70   | 0.7                    |
| Italy         | 1.1   | 0.5   | 0.9   | 26   | 0.9                    |
| Finland       | 0.5   | 0.5   | 0.5   | 14   | 3.0                    |
| Others        | 1.5   | 0.8   | 1.3   | 38   | 1.0                    |
| TOTAL         | 100.0                                       | 100.0                                       | 100.0   | 2915   |                        |

Annual average wet deposition 2022 mg SO<sub>2</sub> m<sup>-2</sup> a<sup>-1</sup>

Annual average dry deposition 893 mg SO<sub>2</sub> m<sup>-2</sup> a<sup>-1</sup>

TAB. 3 [3] - *Deposition by Regions for Each Year 1972-1974* (percentages of grand total for each year).

| region        | 1972 total:<br>3698 mg m <sup>-2</sup> |                       | 1973 total:<br>2231 mg m <sup>-2</sup> |                       | 1974 total:<br>2883 mg m <sup>-2</sup> |                       |
|---------------|--|-----------------------|--|-----------------------|--|-----------------------|
|               | dry<br>deposition                      | deposition<br>in rain | dry<br>deposition                      | deposition<br>in rain | dry<br>deposition                      | deposition<br>in rain |
| British Isles | 5.3                                    | 20.9                  | 7.2                                    | 22.6                  | 8.5                                    | 28.7                  |
| Norway        | 7.8                                    | 5.5                   | 12.7                                   | 11.3                  | 10.3                                   | 7.5                   |
| G.D.R.        | 3.9                                    | 11.3                  | 2.5                                    | 5.1                   | 2.3                                    | 4.9                   |
| F.R.G.        | 2.2                                    | 8.5                   | 1.8                                    | 6.9                   | 2.5                                    | 7.9                   |
| Sweden        | 1.9                                    | 3.1                   | 2.1                                    | 3.5                   | 2.4                                    | 2.7                   |
| Holland       | 0.9                                    | 3.4                   | 1.0                                    | 3.2                   | 0.9                                    | 2.4                   |
| Poland        | 1.1                                    | 2.9                   | 0.8                                    | 2.0                   | 1.6                                    | 1.8                   |
| Denmark       | 1.4                                    | 3.1                   | 1.0                                    | 2.1                   | 0.9                                    | 1.4                   |
| France        | 0.7                                    | 3.2                   | 0.5                                    | 2.3                   | 0.5                                    | 2.9                   |
| Belg./Lux.    | 0.7                                    | 2.9                   | 0.8                                    | 2.6                   | 0.6                                    | 2.4                   |
| Czech.        | 1.1                                    | 3.9                   | 0.8                                    | 1.7                   | 0.5                                    | 1.1                   |
| U.S.S.R.      | 0.5                                    | 1.0                   | 0.5                                    | 3.3                   | 1.2                                    | 1.1                   |
| Italy         | 0.2                                    | 1.0                   | 0.1                                    | 0.0                   | 0.1                                    | 1.0                   |
| Finland       | 0.1                                    | 0.1                   | 0.1                                    | 0.3                   | 0.3                                    | 0.6                   |
| others        | 0.2                                    | 1.2                   | 0.2                                    | 1.0                   | 0.3                                    | 0.7                   |
| TOTAL         | 28.0                                   | 72.0                  | 32.1                                   | 67.9                  | 32.9                                   | 67.1                  |

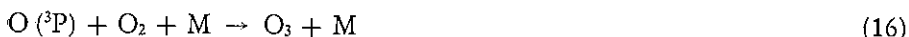
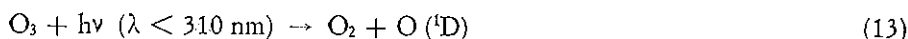
Europe presently emits ~ 33 M Tonnes/yr.

and Sweden and the implication for fisheries. Specifically excluded, however, from this programme will be the questions of how industrial discharges create acid deposition, and to what degree reductions in UK sulphur dioxide emissions would change the acidity of rainfall over affected areas of Scandinavia. The questions to be addressed are:

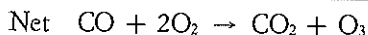
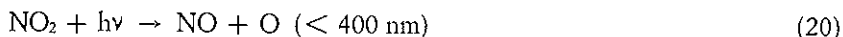
1. In the affected areas of Norway and Sweden, what are the factors, in addition to pH, that in practice determine the fishery status of lakes?
2. What are the biological, chemical and hydrogeological characteristics of catchments which determine whether the composition of surface waters falls within a range acceptable to fish?
3. In Norway and Sweden, to what extent are these characteristics being adversely affected by the acid deposition itself?
4. What changes would be brought about in water chemistry and fishery status in Norway and Sweden by given levels of reduction of man-made sulphur deposition?

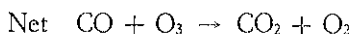
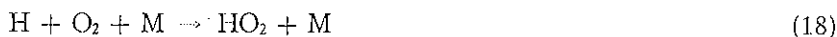
Photochemistry of course plays a crucial role in the whole of tropospheric atmospheric chemistry, not just in locally confined events such as those involving acid deposition discussed above, and in the well-documented "photochemical smog" of Californian cities, which is now a local problem of very widespread incidence throughout the world.

The key intermediate chemical species in the troposphere is undoubtedly the hydroxyl radical OH, the major source being the photolysis of tropospheric ozone, and subsequent reaction of the product O(<sup>1</sup>D) with water (13), (14), in competition with collisional quenching to give O(<sup>3</sup>P) (15), which subsequently reforms ozone (16).



The hydroxyl radical so produced is the major oxidising species in the troposphere, and a complete picture of its chemistry holds the key to furthering progress in understanding tropospheric chemistry. The chemistry discussed in detail elsewhere, is of course very complex. To take, for example, the cycle of reactions with carbon monoxide, which may be net producers or destroyers of tropospheric ozone depending upon the concentration of oxides of nitrogen present. In the presence of NO, the cycle (16)-(20) occurs, without loss of OH or NO, whereas at low NO concentrations, the cycle (17), (18) and (21), again without loss of OH.





Thus ozone may be correlated positively with carbon monoxide or negatively with carbon monoxide, depending upon local oxide of nitrogen concentrations, as indicated in Figure 1 [4].

Since methane reacts with hydroxyl, the level of methane in the troposphere is of great interest. There are some indications that the methane level is increasing, which could be due to an increased methane release rate, or a decrease in hydroxyl concentration. Clearly it will be of great importance to establish which of these possibilities is occurring.

Despite progress in understanding tropospheric chemistry, there is still a pressing need for improvements, with the following problems requiring attention

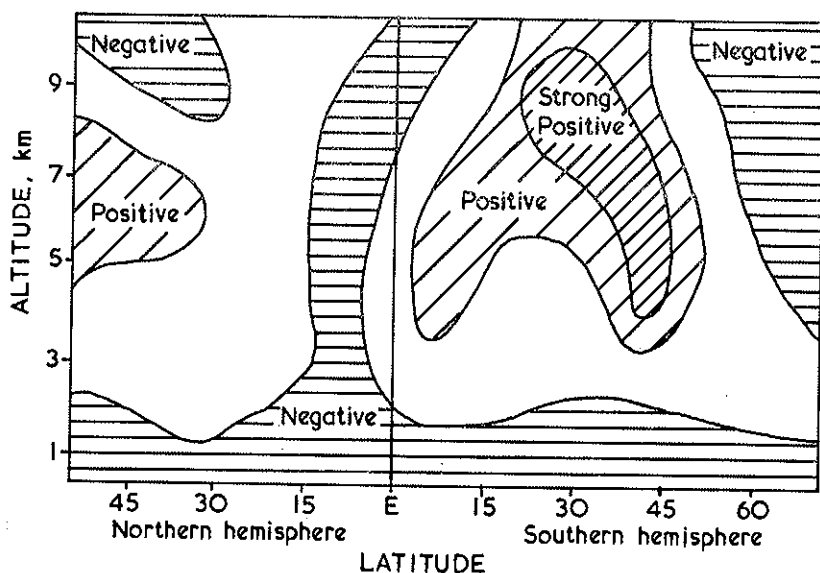


FIG. 1. Latitude-altitude depiction of regions where  $\text{O}_3$  and  $\text{CO}$  variability are positively and negatively correlated (after Figure 3, ref. 4).

(i) understanding the sources and sinks of minor constituents, such as  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{OH}$ ,  $\text{HO}_2$  etc., and their detailed geographical location and intensities on a global scale. On a very parochial level this will improve understanding of local conditions such as photochemical smog, which can be considered merely to be an exaggerated or perturbed normal troposphere.

(ii) in situ measurements of radical intermediates, particularly  $\text{OH}$  on a global scale, a problem which has to date been barely tackled.

(iii) laboratory measurements of rate-constants, particularly those of organic reactions involving peroxy and oxy-radicals.

(iv) modelling of the chemistry, transport, dynamics, radiative transfer, etc., of the troposphere. Here 3D models are desirable, but as yet too expensive in computer time.

On the whole it is probably true to say that tropospheric chemistry is rather less well understood than that of the stratosphere, although of course, since the input of material from the troposphere to the stratosphere must affect the chemistry of the latter, the uncertainties in tropospheric chemistry are reflected in that of the stratosphere.

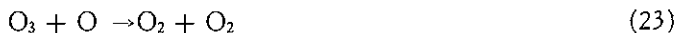
## STRATOSPHERIC CHEMISTRY

In this introductory paper there is no attempt to preempt the discussions by later authors concerning these problems. However, an attempt is made here to pin-point some remaining problems.

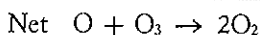
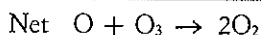
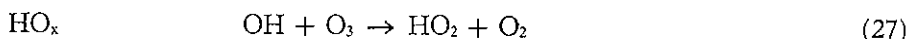
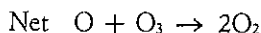
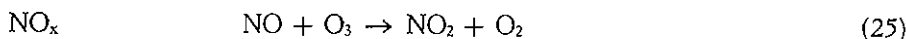
On the simplest possible level, the ozone in the stratosphere is maintained by the Chapman mechanism, (13), (16), (22-24) plus the catalytic cycles which in cryptic form are shown as (25)-(30)



Chapman  
mechanism





*Catalytic cycles*

These cycles are of importance in the unpolluted atmosphere and the concern for the past decade has been

- 1) To understand the chemistry of the unpolluted stratosphere.
- 2) To predict the effects of release of man-made chemical species in the stratosphere.

The latter question will of course become clearer in time as accurate measurements of the ozone concentration are made, and can be compared both with release rates of pollutants, and models. Until relatively recently only local columnar concentrations of ozone had been measured, typified by the Arosa data, shown in Figure 2.

However, since April 1970, *global* measurements have been available from the Nimbus 4 backscatter UV measurements, and Nimbus 7 (SBUV) has been gathering data since 1978. This set of data may be extensive enough soon to allow statistical analysis of long-term trends. Ground-based measurements of the critical 34-36 km layer suggest virtually no change in ozone in north temperature latitudes over the decade 1970-1980. A comparison of the satellite SBUV data for March 1979 with BUUV results for the same month in 1971 or 1972 show a negative trend of  $0.4 \rightarrow 0.7\%$  per year at 38 km. If the comparisons are valid, this is not inconsistent with recent model predictions.

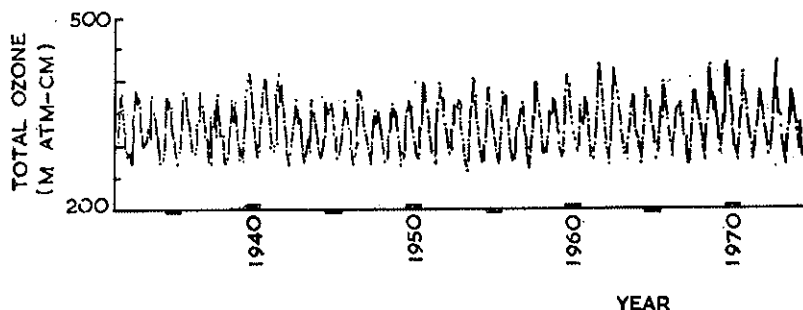
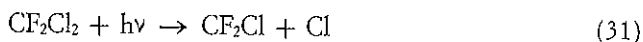


Fig. 2. Columnar ozone concentration variation, Arosa data.

The recent solar mesosphere explorer (SME) satellite (Oct. 1981) measures simultaneously  $[O_3]$ ,  $T$ , and solar uv intensity in the upper stratosphere [5, 6, 7]. This is a good altitude to test photochemical theories since photochemical lifetimes of species here are appreciably shorter than the time-scale for horizontal North to South redistribution. In the mesosphere, the results show quite clearly that the temperature (rather than solar flux) determines the  $O_3$  concentration, although the results of other physical phenomena such as the solar flare of July 13, 1982 were clearly observable.

The anthropogenic perturbations to the stratosphere include inputs of  $NO_x$  from nuclear weapons testing, high flying aircraft, and of Cl from the photolysis of chlorofluorocarbons, discussed in detail in a later article, but represented by



followed by the complex sequence of reactions involving the catalytic cycles represented by (25) – (30), but in fact involving a very large number of interconnected chemical reactions.

Since predicted effects upon ozone concentration due to chlorofluorocarbons, for example, cannot yet be identified unambiguously from measurements of  $O_3$ , modelling is still vital. This requires

- a) Accurate rate data for critical reactions.
- b) Stringent testing of models against *measured* concentrations of atmospheric species.

What of rate data? It is surely true to say that thermal rate data are on a more secure footing than the photochemical, where the rate of a photochemical reaction is given by a pseudo rate-constant  $j$  multiplied by concentration of reactants. Accurate assessments of  $j$  require knowledge of absorption coefficients, solar flux, quantum yields of photodecomposition and of course since  $j$  varies diurnally, seasonally and geographically, values thus represent averages. As an example of the insecurity of photochemical rate-data, it can be said that even as basic a mechanism as the Chapman mechanism given earlier is the subject of recent conflict. Thus it has been suggested that the  $O_2$  absorption cross-sections for absorption in the Herzberg continuum between 200-220 nm widely used in models until recently are significantly in excess of correct values [8]. The use of the wrong  $O_2$  cross-section would greatly affect the rate of photodissociation of a number of species which must be used in modelling. The adjustment of the downward adjustment of the absorption coefficient of  $O_2$ , hence  $j_2$ , has a profound effect upon calculated concentrations of other species absorbing competitively; thus at 30 km, the concentration of  $N_2O$ ,  $CF_2Cl_2$ ,  $CFCI_3$  are reduced by factors of 0.70, 0.62, and 0.19 respectively, whereas  $CH_4$ ,  $H_2$  and  $CO$  profiles are essentially unchanged. The predicted concentration of  $HNO_3$  above 30 km is 50% less, yielding better agreement with observation. The result of these adjustments is to cause a 10-20% decrease in computed ozone concentration above about 35 km, but a fairly large increase ( $\sim 30\%$ ) around 20-25 km. This uncertainty in absorption cross-sections also extends to  $NO_3$ , where recent measurements by Wayne and Cox, independently, give results much less than those of Johnston or Wine.

The effect that adjustment of other rate parameters has upon modelling is further illustrated by the paper of Ko and Sze [9]. The revised rate constants are shown in Table 4.

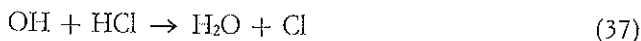
Adaptation of the new rate for reaction 31, a factor of 2 greater than the previous recommendation, results in a factor of 1.3 increase in the concentrations of OH above 40 km. This higher OH reduces the concentration of  $CH_4$  above 40 km by  $\sim 20\%$ .

TABLE 4

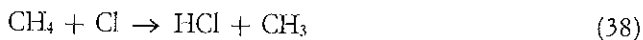
| REACTIONS                                  |      | NASA-JPL (1982)                                   | WMO/NASA (1982)           |
|--|------|---|---------------------------|
| $O + HO_2 \rightarrow OH + O_2$            | (32) | $3.0 (-11) \exp(200/T)$                           | $3.5 (-11)$               |
| $OH + HO_2 \rightarrow H_2O + O_2$         | (33) | $(7 + 4P_{at}) \times 10^{-11}$                   | $8.0 (-11)$               |
| $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$     | (34) | $(3.4 + 2.5P_{atm}) \times 10^{-14} \exp(1150/T)$ | $3.0 (-12)$               |
| $OH + HNO_3 \rightarrow H_2O + NO_2 + O_2$ | (35) | $1.3 (-12) \exp(380/T)$                           | $4.0 (-12)$               |
| $ClO + NO_2 \xrightarrow{M} ClONO_2$       |      | $4.5 (-32) (T/300)^{-3.8*}$                       |                           |
|  | (36) | $1.8 (-31) (T/300)^{-3.4*}$                       | $4.5(-32)(T/300)^{-3.8*}$ |

\* Low-pressure limit rate-constant.

Consequently reaction (37)



is more efficient, while the recycling of Cl to HCl via (38)



is less efficient, resulting in a factor of 1.4 inverse in concentrations of Cl and ClO around 40 km.

The effect of change in (36) is restricted to the region below 30 km where the concentration of ClONO<sub>2</sub> is appreciable. The agreement of the model with some in-situ measurements of ClO seems reasonable (but see below).

For a given concentration of ClY, (Cl + ClO + HCl + ClONO<sub>2</sub> + HOCl) partition between Cl, ClO and HCl is determined mainly by reactions (37) and (38). The choice of rate for (36) clearly has an impact on the concentration of ClONO<sub>2</sub> calculated. Using the fast rate, a chlorine nitrate concentration of 0.6 ppbv at 30 km is calculated, in agreement with measurements by Murray.

While on this subject, further comment concerning chlorine nitrate, ClONO<sub>2</sub> is required. Postulated isomers such as ClOONO, OClONO are now discounted [10], although the rate-constant for formation is still in doubt, as we have seen.

To return to the models of Ko and Sze [9], calculated ozone profiles can now be compared. (Table 5)

TAB. 5 -  $[O_3]$  at altitudes 20-50 km. (10 [11] molecule  $cm^{-3}$ ).

| ALTITUDE | CALCULATED |      |      | OBSERVED     |       |        |       |
|----------|------------|------|------|--------------|-------|--------|-------|
|          | WMA/NASA   | A    | B    | US std. 1976 | STRAT | SABE-2 | IOR 1 |
| 50       | 0.58       | 0.49 | 0.45 | 0.66         | —     | —      | 0.57  |
| 45       | 1.8        | 1.5  | 1.3  | 2.2          | —     | 1.8    | 2.0   |
| 40       | 5.4        | 4.9  | 4.3  | 6.1          | 6.3   | 5.5    | 6.3   |
| 35       | 16         | 15   | 14   | 14           | 14    | 17     | 16    |
| 30       | 34         | 35   | 34   | 25           | 28    | 31     | 31    |
| 25       | 51         | 51   | 54   | 43           | 45    | 38     | 54    |
| 20       | 50         | 50   | 57   | 48           | 31    | 36     | —     |

Ko and Sze, Geophys. Res. Letters, 1983, 10, 341.

In Model A (high  $\sigma(O_2)$ ) there is 10-20% lower  $[O_3]$  above 40 km than in the previous model (WMO/NASA).

In Model B (lower  $\sigma(O_2)$ ). Above 40,  $[O_3]$  is further reduced by 10%.

In the lower stratosphere, there is more ozone in model B than in model A due to an increase in the photolysis rate of  $O_2$  resulting from the greater solar flux. The net effect is an approximate 7% increase in column density of  $O_3$  when the smaller cross-section for oxygen absorption  $\sigma(O_2)$  is used (Model B).

Above 40 km altitude the observed concentration of  $O_3$  is greater than that calculated with a faster rate for reaction 32, and a low  $\sigma(O_2)$ , the agreement is significantly *worsened* in this 1-D model.

Other papers will no doubt comment on this, but here we merely wish to point out the need for very accurate rate data.

At steady-state, as we noted before the downward revision of  $\sigma(O_2)$  causes the ozone depletion —  $\Delta O_3$  to diminish, (Table 6) no doubt due to the smaller peak value of CIY as a result of the shorter lifetime of the chlorofluorocarbons.

### *Correlation of models with measurements*

The crucial test of a model must be the ability to assess correctly the concentrations of trace species as well as that of ozone. Unfortunately,

TAB. 6 - *Calculated steady-state O<sub>3</sub> depletion.*

| MODEL    | Peak ClY<br>(ppbv) | -ΔO <sub>3</sub> (%)<br>slow ClNO <sub>3</sub> | -ΔO <sub>3</sub> (%)<br>fast ClNO <sub>3</sub> |
|----------|--------------------|--|--|
| A        | 9.3                | 5.9  | 4.5  |
| B        | 8.0                | 4.4  | 3.2  |
| WMO/NASA | 9.4                | 6.1  | —  |

as yet there are few global measurements of trace gases or radical intermediates. Some progress has been made in the simultaneous measurement of, for example OH, ClO, HO<sub>2</sub> together with O<sub>3</sub>, NO<sub>x</sub>, but these generally refer to one geographical location, and to one launch day. It is to be hoped that Professor Anderson's experiments and the MAP-GLOBUS campaign might do much to help in this area.

It should be noted that a recent paper by Mumma *et al.* [11] using a ground-based ir heterodyne method to measure the concentration of the important species ClO failed totally to observe any ClO, putting a limit of a factor of 1/7 of the "accepted" value, based upon "in situ" measurements. Professor Anderson will comment on this.

In conclusion then, it seems evident that better laboratory rate constants are required for some reactions, and particularly photochemical data on quantum yields, channels, and cross-sections, and wavelength dependencies of such species as NO<sub>3</sub>, HNO<sub>4</sub>, HOCl, ClNO<sub>2</sub>, while global measurements of trace species are equally vital for the understanding of this complex chemistry.

It is hoped that this introductory article will have identified some of the problems remaining in atmospheric chemistry, with particular emphasis on the photochemistry.

#### ACKNOWLEDGEMENTS

It is a particular pleasure to acknowledge the detailed advice and help given to me in preparing this paper by Dr. Richard Wayne, Oxford University, Dr. John Sodeau, University of East Anglia, and Dr. Tony Cox, AERE Harwell, who are however, absolved of any blame for the opinions expressed here.

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## DISCUSSION

ANDERSON

The subject of ClO will be one that comes up fairly frequently this week and perhaps this is not the time to summarize the situation completely, but I should add that there are a number of elements in this case which were not brought up here. A significant amount of work has been done in other areas, in particular the microwave millimeter emission experiments which detected the purely rotational emission of ClO from the ground at both 204 and 278 nm, and the millimeter emission work of Waters, who has detected that emission from a balloon. The background subtraction which is involved in the 1/10 to 1 percent of the level expected in the laser heterodyne work, coupled with the absorption measurement and the calculation of line strengths together with one other measurement in a laboratory of the kind that could be accepted in this level of discussion is not simply an academic issue since no ClO implies no fluorocarbon problem. The laser heterodyne method is a very, very good one. There is very little that competes with the absence or presence of an observed feature, particularly in this case the absence of that absorption at the proper frequency; and the wave length here is not the issue, rather the difficulty of the observation, the very small signal to noise ratios and the issue of the line strength. The conclusion, or the next step, I should say, in this process will be one of mixing the laser heterodyne method with the laboratory observation of the free radical, a step that most people would require before accepting and presenting the information publicly, and a step that has not been taken. So I think in the next six months the resolution of this issue will probably take place. I respect greatly the basic method applied here and I do not think there have been serious errors in its application. The interpretation of it is the issue, and the homework that precedes the release of the information publicly is the issue at point.

LIBERTY

You pointed out the importance of photochemical reactions in the atmosphere related to pollution, and you described the SO<sub>2</sub> oxidation, giving great emphasis to the homogeneous oxidation through free radicals. I definitely agree these are important processes; however, I strongly believe and



there is experimental evidence that heterogeneous processes are also of great importance. Particulate matter is a natural component of the troposphere and it is well established that particulate matter is always absorbing most of the species in the air and also  $\text{SO}_2$ . The presence of soot in the particles responsible for the so-called "blackness index", which is usually taken as a measure of pollution, being related to particulate concentration, indicates a catalytic reaction can occur for the oxidation of  $\text{SO}_2$ . I wish to emphasize this point because most effects related to the formation of acid rain are due to the formation of strong acids, and these species are found in the aerosol fraction of the atmosphere.

PHILLIPS

I would simply echo what you said. Although I have said that the homogeneous reaction has hitherto been held to be most responsible, there is some evidence that the heterogeneous reaction is of great importance, and I think it is an area which is worthy of further research.

CHAMEIDES

There is another class of reactions. I do not know whether you want to call them homogeneous or heterogeneous as the aqueous phase: homogeneous reactions which involve heterogeneous processes in solution, and these I think can be quite important, involving peroxide as well as radicals. I'll have something to say about that during my talk.

LIBERTY

We are having in the atmosphere gases, liquids and solids. It is a common practice for scientists to tackle the problem separately by considering homogeneous and heterogeneous processes. This approach can be correct as it permits us to obtain measurements of rate of conversion, equilibrium constants and other thermodynamic data. In the environment all reactions occur simultaneously and the relative rates of reactions might be affected. So it is difficult to attribute a greater importance to one process than to another one unless some reactions are completely prevented.

# QUANTUM-MECHANICAL STUDIES ON THE BINDING PROPERTIES OF SMALL ATMOSPHERE MOLECULES

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## SUMMARY.

It will be shown on selected examples that the methods of quantum chemistry can help to obtain useful information on problems related to atmospheric chemistry.

Model examples will be the study of the competitive clustering of ammonia and water on the ammonium ion and the determination of the characteristics of binding of water, carbon dioxide and sulfur dioxide on the nitrite ion, in relation to gas phase experimental measurements.

A brief account of recent applications to space molecules will be given.

## I. INTRODUCTION

Quantum Chemistry can be utilized in atmospheric research in the same way as in other fields involving molecules and their transformations. Atmospheric chemistry is in fact much more favorable than the usual chemist's chemistry for applying quantum chemical methods since it occurs in the gas phase. From that point of view, of course, space chemistry, where temperature and pressure are very low, is even closer to the ideal conditions! Quantum theory in atmospheric research can be useful in various areas: i) pure spectroscopic calculations of frequencies and intensities, helping the identification and understanding of observations, ii) es-

tablishment of potentials for use in collision theory, iii) calculations of the characteristics of clusters (either between neutral molecules or between neutral molecules and positive or negative ions), iv) determination of the energetics and pathways of formation of species and of their properties, etc...

I would like to indicate, on some examples, the kind of information which can be obtained in these calculations. We shall consider first, in some details, the domain of clusters, then make a brief excursion into interstellar space, where a similar approach will give us an insight into recent spectroscopic and reactivity applications.

## II. ENERGETICS AND PROPERTIES OF IONIC CLUSTERS

Clustering reactions of neutral species around positive and negative ions play a considerable role in the atmosphere (Castleman Jr., 1983; Ferguson and Arnold, 1981). Thus knowledge of the energetics and properties of ion clusters is a prerequisite for an elaboration of proper theories of such phenomena as nucleation and condensation.

A considerable progress towards the understanding of ion-molecule interactions has been made possible in the last decade due to two simultaneous developments: one concerns the establishment of experimental methods for measuring, in the gas-phase, the characteristics of association in high pressure mass spectroscopy (Kearle, 1977; Tang *et al.*, 1972), ion-cyclotron resonance spectroscopy (Beauchamp, 1971), flowing-afterglow systems (Ferguson *et al.*, 1969). The second development which occurred simultaneously, is the progress made in the non-empirical techniques of quantum chemistry which rendered possible the calculation to a fair accuracy, of the energies of interaction between ions and ligands. The comparison of the computed energies with the measured enthalpies of binding provides a unique way to test the accuracy of the theoretical calculations; at the same time, the interest of performing such calculations in connection with gas-phase measurements resides in the fact that, aside from binding energies, they furnish, as subproducts, quantities which are not attainable by direct measurements, such as for instance, the equilibrium structure of the adduct (distance, angles), the lability of the binding (how much energy is lost upon displacement from equilibrium), as well as informations on the nature of the interaction, since it is possible to define and evaluate explicitly, inside the binding energy, the separate values of its main components (electrostatic, polarization, repulsion, charge-transfer and dis-

persion). Thus the conjunction of the two developments mentioned above renders possible a clearer rationalization of the phenomenon of cluster formation.

To illustrate the kind of information obtained let us consider two examples.

The first concerns the clustering of ammonia and water molecules around the ammonium ion, which was one of the first successes of theory in this domain. The extent to which the conclusions drawn at the beginning have remained stable throughout the refinements of the theoretical methodology is a good illustration of what can and what cannot be asked from calculations at different levels of accuracy. It must be said that although the presence of  $\text{NH}_3$  in the low atmosphere is suspected, due to the biological activity of soils (Fehsenfeld and Ferguson, 1973 and references therein) and the presence of  $\text{NH}_4^+$  mixed clusters advocated (*ibidem*), there do not seem to be direct *in situ* measurements to support it. Thus our example has more didactic value than direct bearing on an observed atmospheric chain of events.

Early mass-spectrometer studies (Hogg and Kebarle, 1965; Hogg *et al.*, 1966; Searles and Kebarle, 1968), confirmed later by different groups and techniques (Payzant *et al.*, 1973; Fehsenfeld and Ferguson, 1973; Tang and Castleman, 1975) of the competitive solvation of  $\text{NH}_4^+$  by water and ammonia vapors had shown that  $\text{NH}_3$  molecules were taken up preferentially to water, up to an addition of four molecules in the first solvation shell, while water seemed to be preferred over ammonia in the second solvation shell.

The situation was viewed at first as somewhat surprising since, in such interactions, considered to be essentially ion-dipole interactions, the molecule with the larger dipole moment, water ( $\mu = 1.85$  debye units) should have been taken up preferentially to ammonia ( $\mu = 1.47$ ).

Considerations on the possible importance of polarizability, larger for ammonia than for water, led to require a very small radius for  $\text{NH}_4^+$ . Hence it was suggested that the arrangement of the ammonia molecules around the ion might be of type I (inclusion between  $\text{N}^+\text{H}$  directions) instead of II (hydrogen bonding along  $\text{N}^+\text{H}$  bonds), although no definite choice could be made (fig. 1).

Three problems were immediately considered by theoretical calculations: i) the structure of the adduct; in other words, the answer to the question whether there is preference for binding along an  $\text{NH}$  bond or to the central nitrogen; ii) the reasons for the energetical preference for

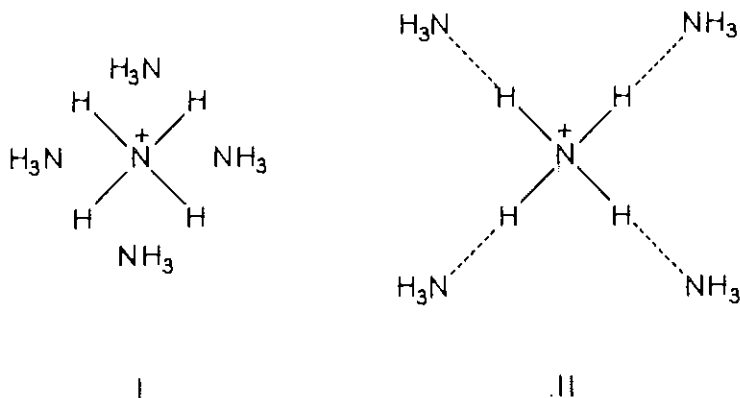
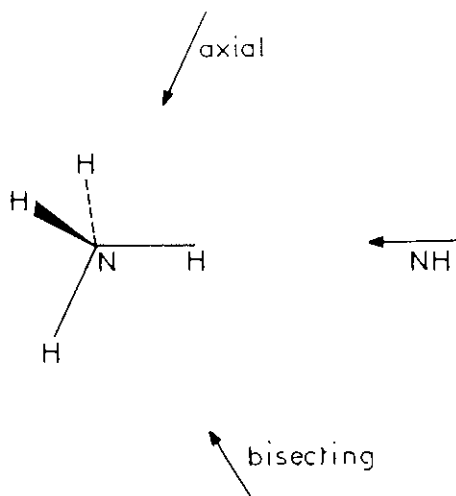


FIG. 1. The two possible structures proposed for the  $\text{NH}_4^+$  clusters.

$\text{NH}_3$  rather than water in the first shell; iii) the reasons for the reversed preference in the second shell. In supermolecule *ab initio* calculations using STO 3G and 4-31G basis sets, (Pullman and Armbruster, 1974) the approach of one molecule (water or ammonia) to  $\text{NH}_4^+$  was first considered, optimizing the energy with respect to the distance and the relative orientation of the ion and solvent molecules. Three directions of approach were selected: one along the NH bonds, one bisecting two NH bonds in their plane, and one bisecting the angle made by three NH bonds. Rotation of water or ammonia about the direction of approach was allowed in each case so as to obtain the most stable arrangement.

The results summarized in figures 2 and 3 allowed two clear-cut conclusions: a) for both  $\text{NH}_3$  and  $\text{H}_2\text{O}$  the most stable adduct is, by far, the one which involves fixation along an NH bond, in strong preference to a bisecting position, b) the affinity of  $\text{NH}_4^+$  for  $\text{NH}_3$  is clearly larger than its affinity for water.

Further computations on the polyadducts (Pullman and Armbruster, 1975; Pullman, 1976), up to five molecules of  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , gave the results indicated in Table 1 and figure 4 on the evolution of the binding energies upon progressive solvation. The reversal of the ammonia-water preference after  $n = 4$  appears very clearly in the results. The parallelism in evolution of the theoretical and experimental data is quite striking, in spite of the numerical overestimation of the values of the binding energies, particularly for small  $n$ . This overestimation is a well-documented effect of the STO 3G basis. It was shown later that improvement of the values



| Values of $-\Delta E$ (kcal/mole) and $R(\text{\AA})$ (STO 3G) |                 |      |           |       |      |
|--|-----------------|------|-----------|-------|------|
| Solvent  |                 | NH   | Bisecting | Axial | Exp. |
| $\text{NH}_3$  | $-\Delta E$     | 42.2 | 16.2      | 14.3  | 24.8 |
|  | $R_{\text{NN}}$ | 2.5  | 2.8       | 2.75  | .    |
| $\text{H}_2\text{O}$   | $-\Delta E$     | 37.3 | 16.0      | —     | 17.3 |
|  | $R_{\text{NO}}$ | 2.4  | 2.6       | —     |      |

FIG. 2. The three directions of approach and their binding energies.

occur, upon enlarging the basis, without altering the rest of the afore-mentioned conclusions. An illustration of the situation is given in Table II. It shows in particular that the preference for the direct NH binding is conserved in all, up to the most refined very recent, calculations. This may be considered as a reflection of the distribution of the positive charge in the ammonium ion among the four hydrogens as exemplified in figure 5.

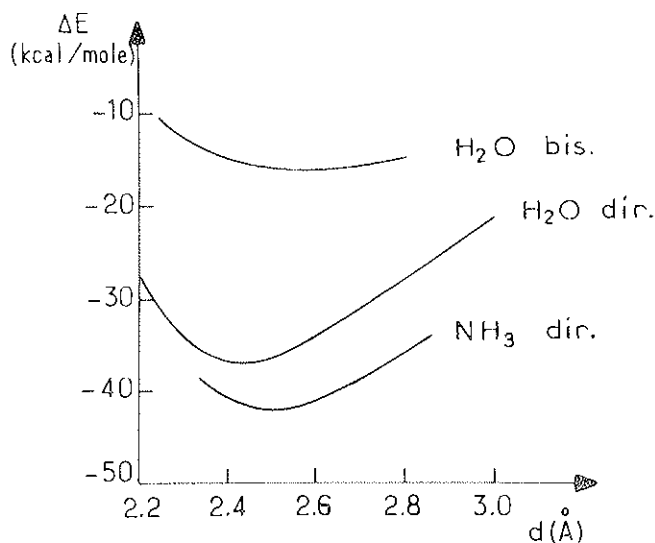


FIG. 3. Evolution of the binding energies of  $\text{NH}_3$  or  $\text{H}_2\text{O}$  along the approach in different positions as indicated. (dir. = approach to  $\text{NH}$ ; bis. = along bisectrix).

TABLE I - *Stepwise solvation of  $\text{NH}_4^+$ .*

|             | n                | (a)<br>d | (b)<br>$-\Delta E_{n-1,n}$ | (c)<br>$-\Delta H_{n-1,n}$ |
|-------------|------------------|----------|----------------------------|----------------------------|
| Ammoniation | 1                | 2.50     | 42.2                       | 24.8                       |
|             | 2                | 2.60     | 32.0                       | 17.5                       |
|             | 3                | 2.65     | 23.1                       | 13.8                       |
|             | 4                | 2.70     | 17.6                       | 12.5                       |
|             | 5 <sup>(d)</sup> | 2.90     | 10.3                       | 7.5                        |
| Hydration   | 1                | 2.40     | 37.2                       | 17.3                       |
|             | 2                | 2.45     | 28.4                       | 14.7                       |
|             | 3                | 2.55     | 22.1                       | 13.4                       |
|             | 4                | 2.60     | 17.6                       | 12.2                       |
|             | 5 <sup>(d)</sup> | 2.62     | 12.6                       | 9.7                        |

(a) Computed  $\text{N} \dots \text{N}$  or  $\text{N} \dots \text{O}$  distance ( $\text{\AA}$ ).

(b) Computed (STO 3G), kcal/mole.

(c) Experimental enthalpy, kcal/mole.

(d) With the first four molecules fixed at the equilibrium distance of the tetrasolvate.

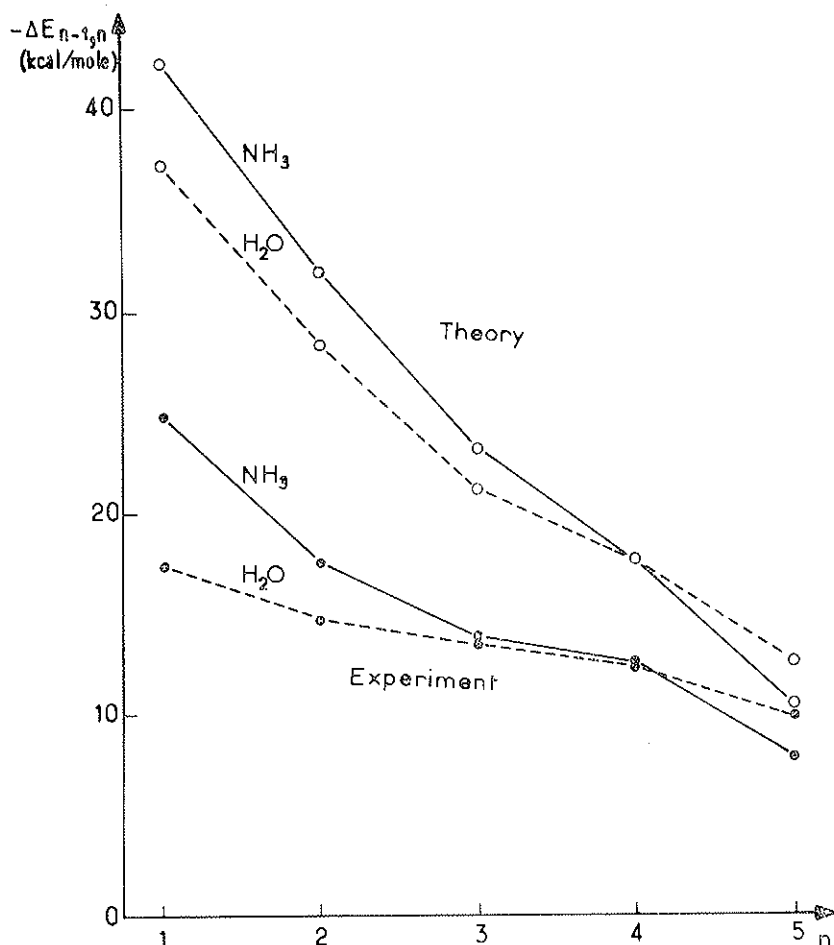


FIG. 4. Evolution of the computed and measured binding energies upon progressive solvation for  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .

by the distribution of the net electron populations. (STO 3G and most accurate calculation of Table II). A still more accurate view of the distribution of the attractive character of the ion towards an incoming nucleophile is given by the distribution of its electrostatic molecular potential (see Scrocco and Tomasi, 1978, for definition) on spheres centered on the nitrogen atom. The values of Table III are seen to be on all spheres in the order: direct > bisecting > axial.



TABLE II - SCF Binding energies ( $-\Delta E$ ) of  $\text{NH}_4^+ \dots \text{H}_2\text{O}$  in different basis sets for the positions defined in figure 2 (kcal/mole).

|         |     | direct | bisecting | axial |
|---------|-----|--------|-----------|-------|
| 4-31G   | (a) | 27.3   | 21.8      | 20.4  |
| PBG     | (b) | 22.7   | 16.3      | 14.9  |
| D**     | (c) | 20.19  | 17.16     | 16.17 |
| 6-31G** |     | 21.6   | —         | —     |
| DK      | (d) | 19.7   | —         | —     |
| PCC     | (e) | 18.51  | 15.41     | 14.56 |

(a) Pullman and Armbruster, 1974; Kollman *et al.*, 1977.

(b) Minimal basis set defined in Pullman *et al.*, 1976.

(c) Dunning polarized (details in Berthod and Pullman, 1980).

(d) Diercksen analog. (details as in (c)).

(e) Pullman *et al.*, 1984.

The underlying features which command the order  $\text{NH}_3 > \text{H}_2\text{O}$  in the binding to  $\text{NH}_4^+$  and the reverse order in the second shell were tentatively rationalized (Payzant *et al.*, 1973) on the basis that the proton affinity of  $\text{NH}_3$  being larger than that of  $\text{H}_2\text{O}$ , its attraction for the positively charged hydrogen of  $\text{NH}_4^+$  should be larger, an effect which would be superseded in the second shell by the better H-bonding properties of water. Calculations permit a more precise rationalization: the (exact) computation of the Coulomb component of the binding energy shows that

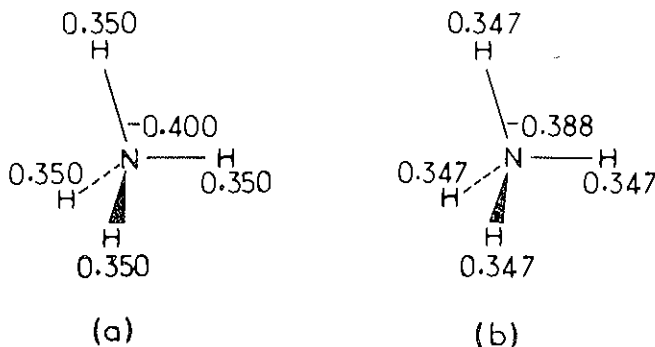


FIG. 5. Net atomic populations in  $\text{NH}_4^+$  (a) STO 3G, (b) best basis set.

TABLE III - *Molecular electrostatic potential,  $V(P)$ , of  $\text{NH}_4^+$  on spheres centered on nitrogen (large basis set, see (e) of table II).*

| d (NP) Å | V (P) kcal/mole |           |        |
|----------|-----------------|-----------|--------|
|          | direct          | bisecting | axial  |
| 2.0      | 203.70          | 158.95    | 152.03 |
| 2.5      | 145.41          | 130.13    | 126.23 |
| 3.0      | 116.23          | 109.53    | 107.27 |
| 3.5      | 97.73           | 94.32     | 92.95  |
| 4.0      | 84.64           | 82.73     | 81.85  |
| 4.5      | 74.79           | 73.63     | 73.05  |

it is the major component of the binding energy and that it commands the order  $\text{NH}_3 > \text{H}_2\text{O}$  (see Table IV). (Note that this is true in spite of the order  $\text{NH}_3 < \text{H}_2\text{O}$  of the dipole moments, because electrostatic interaction cannot be reduced only to the ion-dipole term). On the other hand, in the second shell the new ligands attach themselves to molecules of  $\text{NH}_3$  or  $\text{H}_2\text{O}$  which, although partially polarized, are more and more similar to "normal"  $\text{NH}_3$  or  $\text{H}_2\text{O}$  molecules when  $n$  increases. In the limit, the respective  $\Delta E_{n-1,n}$  must converge towards the binding energies of the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  homodimers. These energies (also dominated by the Coulomb energy) as shown in table IV, are in favor of water binding, hence the reversal in tendency. In the homodimers the hydrogen to be bound is

TABLE IV - *The role of Coulomb energy in  $\text{NH}_4^+$  binding and in the homodimers (STO 3G) (kcal/mole).*

|   | $-\Delta E$ | $-\Delta E_c$ |
|---|-------------|---------------|
| $\text{NH}_4^+$ - binding                 |             |               |
| $\text{NH}_4^+ \dots \text{NH}_3$         | 42.3        | 46.4          |
| $\text{NH}_4^+ \dots \text{H}_2\text{O}$  | 37.2        | 38.5          |
| Homodimer                                 |             |               |
| $\text{NH}_3 - \text{NH}_3$               | 3.7         | 4.8           |
| $\text{H}_2\text{O} - \text{H}_2\text{O}$ | 5.6         | 6.8           |

appreciably less positive in  $\text{NH}_3$  (0.160e), than in  $\text{H}_2\text{O}$  (0.183e) so that the fundamentally larger attractive character of  $\text{NH}_3$  exerts itself on a smaller charge whereas the smaller attractive character of  $\text{H}_2\text{O}$  acts on a larger positive charge: the two effects playing in reverse order, only explicit computations can give a decision. (In fact for  $n = 5$ , binding occurs to a hydrogen of charge 0.200 in the tetraammoniate and 0.233 in the tetrahydrate, and these charges are much closer to those of the neutral monomers than to the charge of the hydrogen in  $\text{NH}_4^+$  (figure 5a).

Aside from  $\text{NH}_4^+$  and apart from the pioneer work on the  $\text{H}_3\text{O}^+$  hydrates (Newton and Ehrenson, 1971), few non-metal positive ions have been studied as extensively by theoretical computations. Very recently, calculations have been done on the proton solvation by methanol and dimethylether (Hirao *et al.*, 1982), and  $\text{N}_2$ , CO and  $\text{O}_2$  (Yamabe, 1981). In our laboratory, a study of the hydrates of  $\text{NO}^+$  in view of understanding the mechanism of production of  $\text{NO}_2\text{H}$  is in progress (Pullman and Ranganathan, 1984).

As concerns clustering around negative ions, nearly no theoretical work has been done until very recently on the molecular ions of atmospheric interest other than the water clusters of the spherical halogens. The recent accumulation of gas-phase experimental data on the clustering of neutral molecules on small negative ions (Castleman *et al.*, 1982; Keese *et al.*, 1980) renews the interest in this area by the intriguing regularities (and irregularities) observed. Having studied earlier in some details the binding properties of the phosphate and carboxylate ions, which are of biological interest, (Berthod and Pullman, 1981 and references therein) but for which there are no gas-phase data, we decided to undertake theoretical work on the set of newly measured clusters.

As a first step in this area we have considered the clustering of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  to the nitrite ion  $\text{NO}_2^-$ . The experimental data (Keese *et al.*, 1980) show striking differences between the three ligands, their enthalpies of attachment on  $\text{NO}_2^-$  being  $-15.2$ ,  $-9.3$  and  $-25.9$  kcal/mole respectively for the first clustering molecule. The rationalization of these results on the simple basis of ion-dipole interaction is obviously not possible. Although ion-ligand interactions are likely to be dominated by electrostatic forces, it was interesting to try and evaluate in the case of these three quite different molecules the relative weights of the components of the binding energies which are perhaps the source of their different behavior. On the other hand, the building up of polymolecular clusters around polyatomic ions strongly depends not only on the structural properties of the

ion itself and on the distribution in space of its attractive character but also on the most advantageous location of the first molecule in the cluster, which itself depends on the properties of the ligand. Owing to the differences between water, carbon dioxide and sulfur dioxide, the question of the location of the first molecule is not purely academic.

For this exploratory study we used a minimal but good quality basis set, which we found could reproduce, to a fair accuracy, the results of much more extended basis for anion binding (Berthod and Pullman, 1981). Technical details for the present problem can be found in the original paper (Pullman and Berthod, 1981).

Concerning the structure of the anion itself, the image given by the computed electron populations indicates a slightly positive nitrogen atom (global charge  $6.983 e^-$ ), the negative charge being essentially shared by the two oxygens ( $8.508 e^-$  each). This excess negative charge is essentially of  $\pi$  character ( $1.512 e^-$  on each oxygen,  $0.976 e^-$  on the nitrogen). A somewhat more informative view of the structural properties of  $\text{NO}_2^-$  is given by the distribution of its molecular electrostatic potential (fig. 6). It is seen that the negative potential entirely surrounds the ion. Quite striking is the fact that a very deep minimum faces the nitrogen atom ( $-200$  kcal/mole), very close in value to the two minima associated with each oxygen atom. This shows once more that reasoning purely on electronic charges can be misleading.

The overall distribution of the negative potential indicates that the whole molecular periphery will be able to present a favorable attractive interaction with an electrophile, with perhaps a small advantage in favor of the oxygen regions. In order to gain more information on the role of the pure electrostatic energy in the binding, the search for the binding characteristics was done in two steps: first using a procedure developed in our laboratory (Pullman and Perahia, 1978, and references therein) where a good approximation of only the electrostatic part of the interaction is calculated, then by complete supermolecule calculations to find the energy and the most stable positions. The results of the calculations led to the following major conclusions:

- 1) The binding energies computed for single attachment in the most favorable positions for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  (Table V) are in very good agreement with the measured enthalpy values. The agreement is sufficiently good to lend credence to the conclusions concerning the binding positions. For water, a calculation with a better basis set (Banerjee *et al.*, 1980) confirms entirely our data with a somewhat less good binding

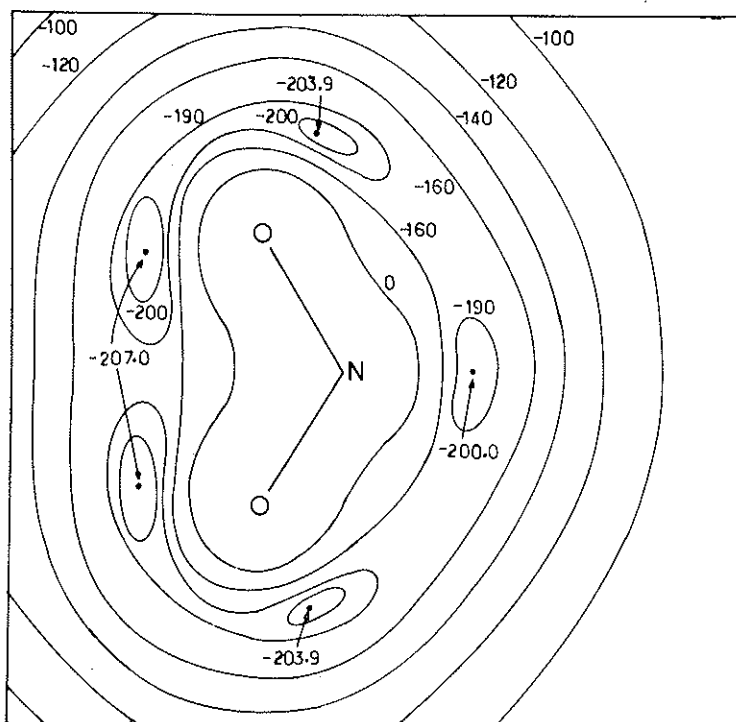


FIG. 6. The molecular electrostatic potential of  $\text{NO}_2^-$  in the plane of the ion (values in kcal/mole).

TABLE V - Best location and binding energy (kcal/mole) of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  on  $\text{NO}_2^-$ .

|                      | d (Å)   | $-\Delta E$ | $-\Delta H$ (d) |
|----------------------|---------|-------------|-----------------|
| $\text{H}_2\text{O}$ | 2.9 (a) | 15.4        | 15.2 $\pm$ 0.1  |
| $\text{CO}_2$        | 2.7 (b) | 8.2         | 9.3 $\pm$ 0.1   |
| $\text{SO}_2$        | 2.2 (c) | 26.1        | 25.9 $\pm$ 0.2  |

(a) O ... O distance; water bridging the two oxygens of the anion; coplanar arrangement.

(b) O ... C distance V; C on the bisectrix of ONO;  $\text{CO}_2$  perpendicular to the ONO plane.

(c) S ... O distance,  $\text{SO}_2$  perpendicular to ONO plane, NOS angle =  $110^\circ$  bisectrix of  $\text{SO}_2$  at  $50^\circ$  from O ... S direction.

(d) Keese *et al.*, 1980.

energy. Our least satisfactory agreement occurs for  $\text{CO}_2$ . It is possible that this is due to the relatively poor representation of the polarisability in our small basis set. This point is being explored by more refined calculations.

2) The pure electrostatic exploration indicates in all cases, in accord with the complete calculations, the most favorable orientation of the ligand to be in-plane for water, perpendicular to the plane for  $\text{CO}_2$  and for  $\text{SO}_2$ . Furthermore it points out that the most favorable positions at the periphery of  $\text{NO}_2^-$  should be on the internal bisectrix (position  $B_1$ ) for water and  $\text{CO}_2$ , the external bisectrix (position  $B_2$ ) being much less favored. It also indicates that a rather wide region of possible binding exists in the lateral region external to the  $\text{ONO}$  angle and in its symmetrical counterpart (position E). When the complete interaction energies are calculated, they show that, in agreement with these indications, the most stable positions of water are in the order  $B_1 > E > B_2$  (figure 7) with a large lability in the neighbourhood of the best E position. Very similar results are obtained for  $\text{CO}_2$  where the regions of most favorable binding are also those indicated by the pure electrostatic data (see Pullman and Berthod, 1981, for details).

The case of  $\text{SO}_2$  offers a more complex situation. As for the two other ligands the electrostatic results point to three areas of favorable interaction: the inner bisectrix region, the external bisectrix region and

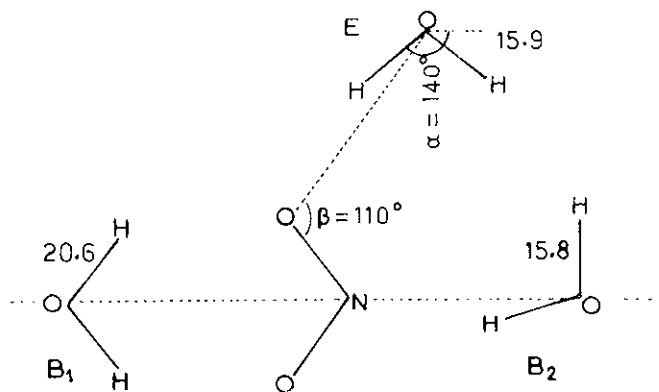


FIG. 7. Best positions and energies in the pure electrostatic search for the arrangement of water around  $\text{NO}_2^-$ .

an intermediate domain in the exterior of the ONO angle (fig. 8). The differences in the energy values are not very marked, however, an indication that other components of the binding energies can reverse the final order of the positions. Indeed the complete computation (Table V) indicates that the preferred position is external. Moreover it is followed by another angular position I internal to the ONO angle (see figure 9), nearly symmetrical from E with respect to the NO bond, then by the two bisecting positions, but with B<sub>2</sub> this time more favorable than B<sub>1</sub>.

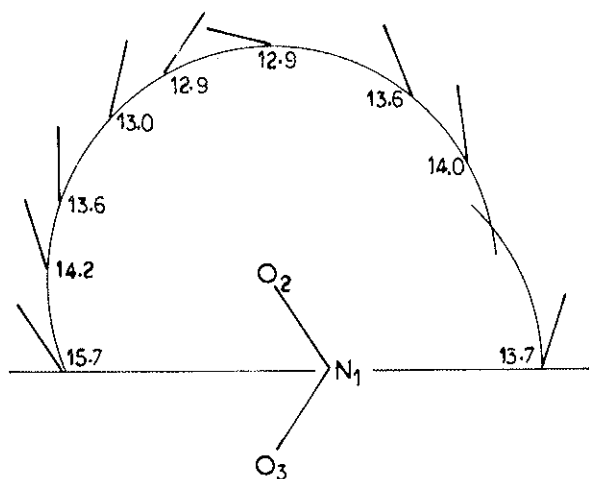
A further analysis of the data indicates that the element responsible for the difference in the order of the electrostatic and total energies is the charge transfer component of the binding energy: the amount of electron population transferred to SO<sub>2</sub> by the ion was computed as 0.331, 0.273, 0.211 and 0.169 e<sup>-</sup> for positions E, I, B<sub>2</sub> and B<sub>1</sub> respectively. (In the best CO<sub>2</sub> adduct it was only 0.048, and in the best water complex 0.008). This confirms the partial charge transfer character of the SO<sub>2</sub> adduct suspected by Keese *et al.* (1980) on the basis of the strong electron affinity of SO<sub>2</sub>. Interestingly our calculations have shown that the lowest empty molecular orbital of SO<sub>2</sub>, which is indeed very low, is a  $\pi$  orbital, thus perpendicular to the molecule. It is notable that the orientations favored by the electrostatic energy, are thus also those in which this empty orbital is oriented at best to receive the transfer from both O and N of NO<sub>2</sub><sup>-</sup>. The preference of B<sub>2</sub> over B<sub>1</sub> is also clearly related to the charge transfer effect which is favored on the nitrogen side.

The consequences of the partial charge transfer character in the SO<sub>2</sub> adduct may affect in an interesting fashion the binding of further molecules in the cluster. We are pursuing the explorations of these problems, as well as that of the CO<sub>2</sub> polarization and intend to utilize the experience acquired in this study for investigating clusters around more abundant atmospheric ions, particularly NO<sub>3</sub><sup>-</sup>.

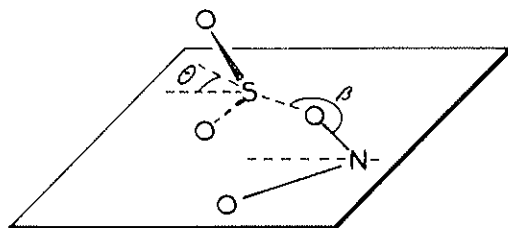
### III. AN EXCURSION IN SPACE

Although the object of the present Study Group is not the study of molecules in the interstellar space, I would like to mention briefly some contributions of quantum chemistry in this domain where neither the methodologies nor the molecular problems are fundamentally different from those occurring in atmospheric research.

There are three essential areas where quantum chemistry can provide



(a)



(b)

FIG. 8. a) The preferred orientation of the plane of  $\text{SO}_2$  in the mutual perpendicular arrangement when the S atom moves around the periphery of the nitrite ion (values of the electrostatic interaction as indicated, in kcal/mole;  $\text{O}_2 \dots \text{S}$  or  $\text{N} \dots \text{S} = 2.6 \text{ \AA}$ ). b) Angles defining the position of  $\text{SO}_2$  with its sulfur atom in the plane of the nitrite ion.  $\Theta$  is the angle of the bisectrix of  $\text{SO}_2$  with  $\text{N} \dots \text{S}$  for bisecting positions, with the direction of the bisectrix of  $\text{ONO}$  for the more general case.  $\beta$  is the  $\text{NOS}$  angle.



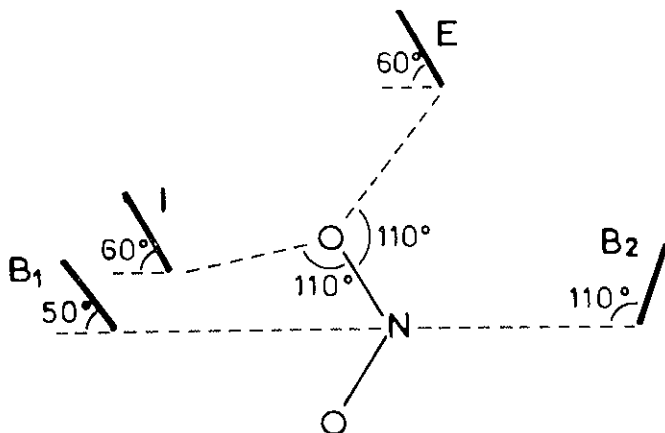


FIG. 9. Location of the minima of the energies of interaction ( $\text{SO}_2$  perpendicular to the plane with its bisectrix oriented as indicated).

useful informations in Astrochemistry: i) computation of molecular geometries and dipole moments, from which can be deduced the frequencies and intensities of rotation spectra, ii) calculation of energy balances for formation and destruction of species, very often ion-molecule reactions, iii) obtention of potential energy curves to be used in the theory of collisions between molecules, electrons and photons. Thus, when a rotation line is detected its attribution to a given species can be helped by a theoretical calculation in the absence of a laboratory spectrum. A well-known example of such a situation in the recent past was the attribution of the so-called X-ogen line to  $\text{HCO}^+$ . A more recent example concerns the identification of  $\text{HCS}^+$  by its computed rotation line. On the other hand the value of the dipole moment of a species (which determines the intensity of the lines) indicates whether its detection by radiotelescopes is likely. Finally the energy balances computed will indicate the probability of formation of a given species, taking into consideration the fact that in the interstellar conditions of low densities and low temperatures only exothermic reactions and transformations with low activation energies can occur.

Let us mention two very recent studies along these lines. After the identification of  $\text{HCS}^+$  as responsible of a rotation line observed at 85.387 GHz (Chekir *et al.*, 1983) and its near-simultaneous confirmation by a laboratory spectrum, the possibility of existence and detection of the sister

species  $\text{HSC}^+$  was considered (Berthier *et al.*, 1983). Table VI indicates the dipole moments computed for the known and unknown species as well as the energy balance for their formation in different possible reactions. Both the energetics of the reactions and the computed dipole moments of the two species led the authors to conclude a small probability of detecting  $\text{HSC}^+$ .

The second study concerns the silicium analogs of the  $\text{HCO}^+/\text{HOC}^+$  and  $\text{HCS}^+/\text{HSC}^+$  pairs (Berthier *et al.*, 1984). The essential results summarized would appear to be, by far, the most likely to exist (large exothermicity of production) but its dipole moment is so weak as to make its detection impossible, whereas its isomer, which could be detectable, appears difficult to form. The corresponding sulfur compounds present a much smaller difference in stability and may probably form. Furthermore they have sufficiently large dipole moments to be good candidates for detection. For the most stable one, the predicted rotation spectrum has been calculated.

#### IV. CONCLUSION

In this brief summary, I have attempted to give an idea of some of the areas in which quantum chemical calculations can be helpful to the experimentalist in atmospheric or space chemistry. Although the prediction of very accurate binding energies, reaction balances or rotation lines require the use of the most elaborate versions of theory and although they generally cannot be considered as substitutes for an experimental

TABLE VI - *Computed dipole moments (debye units) and energy balances for different forming reactions for  $\text{HCS}^+$  and  $\text{HSC}^+$ .*

|                                   | $\text{HCS}^+$ | $\text{HSC}^+$ |
|-----------------------------------|----------------|----------------|
| $\mu$ (D)                         | 2.2            | < 1.3          |
| $\text{CS}^+ + \text{H}_2$        | - 41 kcal/mole | + 31 kcal/mole |
| $\text{C}^+ + \text{H}_2\text{S}$ | - 136 »        | - 64 »         |
| $\text{CS} + \text{H}_3^+$        | - 90 »         | - 18 »         |
| $\text{CS} + \text{H}^+$          | - 196 »        | - 124 »        |
| $\text{CS}^+ + \text{H}$          | - 146 »        | - 74 »         |

TABLE VII - *Computed energy differences, dipole moments and energy balances in formation reactions for the Si analogs of HCO<sup>+</sup> and HCS<sup>+</sup>.*

|                               | HOSi       | HSiO       | HSSi      | (b)<br>HSiS |
|-------------------------------|------------|------------|-----------|-------------|
| Energy<br>(kcal/mole)         | - 65       | 0          | - 16      | 0           |
| $\mu$ (D)                     | 0.02       | 6.48       | 2.82      | 4.83        |
| (a)<br>Balance<br>(kcal/mole) | - 46/- 198 | + 19/- 133 | - 3/- 106 | + 13/- 90   |

(a) in reactions analogous to those of table VI.

(b) bent.

measurement, there are clearly areas where careful systematic studies may lead to predictions or rationalizations which can be used as a guide to further experimentation and better understanding. It is my hope that our encounter at this meeting will help establish contacts for a still more useful collaboration.

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## DISCUSSION

CHAMEIDES

How many ligands make up the first shells on  $\text{NO}_2$ ?

PULLMAN

It depends on the ligands; 3 or 4.  $\text{CO}_2$  has not been studied beyond 1 molecule, but for  $\text{SO}_2$  it is of the order of 3 to 4 — a small number.

CHAMEIDES

Is the definition of the second shell that the ligand of the second shell attaches to the ligand of the first shell? Is that by definition?

PULLMAN

Yes, that is my definition.

CHAMEIDES

I have another simple question. The difference between the bisecting binding and the direct binding of  $\text{NH}_4^+$  — this one that you showed, is that direct? It looks like it is bisecting to me. Could you explain the difference?

PULLMAN

In figure 2 is the correct drawing of  $\text{NH}_4^+$  and the definitions: direct approach to  $\text{NH}$ , bisecting in the plane (bisecting the angle of two  $\text{NH}$  bonds), axial in the prolongation of the  $\text{NH}$ , on the axis of the molecule in between the three other hydrogens on the other side.

ARNOLD

First of all, a brief comment on the first question or discussion about the definition of the first shell and the ammonia clusters. There is an additional piece of information from energy measurements by Kebarle and colleagues. They studied the mixed clusters containing both ammonia and water molecules and

they found that the mixed clusters contain only up to 4 ammonia molecules, and the rest of the ligands would be water molecules. Then another brief comment: you mentioned that the ammonium ion clusters may not be of importance; at least in the atmosphere they have not been measured. It seems from recent studies that they can be quite important, and it can also be found from the laboratory measurements at our institute that ammonia reacts with the other mixed clusters which have been observed in the lower parts of the atmosphere, namely those containing water and another molecule having large proton affinity, not as large as ammonium. It appears that ammonia also reacts with these cluster ions forming even more complex clusters containing several molecular species as ligands. And then a brief question: you mentioned that in future work you will focus also on calculations of a bit larger clusters — you mentioned second shell or more ligand molecules. How urgent would these calculations be? How are the prospects for those calculations? How accurate would these calculations be? We have seen from your discussion that you can calculate rather accurately the bond energy for smaller systems containing an ion and one ligand molecules, and we have seen that the calculations for the more complex systems were capable of giving an order of magnitude, a sequence and things like that but not necessarily very good absolute numbers for these  $\Delta H$  values.

#### PULLMAN

Yes, that is a very good remark, because you have to be extremely careful. As I said, for the ammonia problem it was very lucky that the very small basis set used at the beginning was able to go so far and that the results were confirmed upon improvement of the basis later without change in a qualitative sense. Generally this small, (very small) basis sets. STO 3G is a bit dangerous in these areas, and I would not nowadays (this was ten years ago) use it to start the calculations. However, the way to deal with this problem is the following: there are now a number of calculations of very accurate energies, particularly on the metal cations and on a few molecular ions. On the other hand there exist possible tests of these energies by measurements of enthalpies of binding in the gas phase. Thus, once you know that a very good theoretical calculation reproduces the experimental energy results you can try to tailor a smaller basis to reproduce all the characteristics (not only the energies) given by the best existing calculation. This is what we have done for the metal cations, lithium, sodium, and potassium, for instance. And we have found a basis set which is appropriate to reproduce the binding energy and the rest to a fair accuracy. It is not quite as good as the final values you have seen, but for most purposes it is

quite good. Of course there is always a possibility of an artefact which has not been detected. The best thing, if you can, is to take the best available method, of course, but it is not always possible. I do not think that for the second molecule of  $\text{SO}_2$  going on  $\text{NO}^-_2$ , it would be possible to go to the most accurate calculations. Thus one must try otherwise, and if possible perhaps do it by calculations of two different accuracies. But the philosophy is always: obtain as much as possible information with a very good calculation, try to find a basis set which reproduces it and then use this basis to go over to more complicated systems involving the same ligands.

CANUTO

Would you be kind enough to tell me how many free parameters do you have when you begin your computations? because I was struck by your statement at the end, something about the rotational energy not being as reliable as something else.

PULLMAN

You generally want a rotational energy to the second decimal place after the point. This is too much to ask at present except perhaps for very small systems.

CANUTO

The only experience I have in nuclear physics when you compute the rotational energy of the one for which you have an analogy is ask the easiest one to compute. Here it seems to be the other way around. But how about the free parameters? How many free parameters would you say you have at the beginning?

PULLMAN

In a computation of the kind of clustering reactions, between molecules you need the positions of the atoms for each ligand, that is the distances and the angles (and even that you can nowadays optimize if you wish). That is one input; the other input is the basis set, namely the linear combination of atomic orbitals in terms of which you decide to develop your molecular orbitals. Now this is not an empirical parameter, it is a choice: you decide that you are going to express your molecular orbitals as a linear combination of a certain set of

atomic orbitals. If you choose a small number (small basis set) you have a poor result, energy speaking; if you choose a very large basis set you have a much better energy. That's all — and you compute the wave function of all the electrons in the field of all the nuclei in each configuration of the system. There is no empirical parameter properly speaking.

CANUTO

Your variable D that you gave as a number — that was a variation parameter, was it not? When you showed the energy versus D and it was shallow...

PULLMAN

Yes. When you search for the equilibrium position of two ligands, you start with, say, your water molecule somewhere at a certain distance of the ion, compute the wave function of the whole system and its energy, then vary the distance, find the energy, etc. Doing so along an axis yields a minimum in the curve at some place. Generally you also rotate your molecule in all possible directions looking again for the minimum. Overall you make a very detailed span of the so-called "hypersurface of interaction". It has to be done in a detailed way, otherwise you may miss unexpected minima. For example the external position for  $\text{SO}_2$  and its angular position with respect to the  $\text{NO}_2$  molecule would be difficult to guess a priori. I may add one thing on this occasion, which concerns the slide I passed, which concerns the problem  $\text{H}_2\text{O}$  clustering on  $\text{NO}^+$ . It was posed to us by E.E. Ferguson who wanted to know the structure of tetrahydrate of  $\text{NO}^+$  in order to understand the production of nitric acid. To start this problem we searched first the structure of the monohydrate with a very large basis set; the detailed span of the surface has shown that the position of a first water molecule is neither direct to nitrogen nor direct to the oxygen, but is an external position, on the side of the ion, difficult to guess a priori.

ROWLAND

A comment about two calculations that had to do with the stratospheric chemistry. I would like to make a comment and ask for your comments on that. The first one had to do with where in the first place I think that quantum mechanics was brought in as an attempt to solve a problem that was very pressing at the time which was the question of the proto-absorption coefficients for the molecule  $\text{HOCl}$ , and the calculation that was done on  $\text{HOCl}$  said that there



should be very little absorption out beyond 300 nanometers — this was given some publicity in Chemical Engineering News as being a solution to a problem by quantum mechanics. However, the experimental measurements did not reproduce the theory and showed that there was substantial absorption, sufficiently that HOCl is photochemically quite active out beyond 300 nanometers. That is one comparison.

The other is a calculation that was done at Irving by the research group of Warren Hehre, with Michel le Fanson working on it. She was interested and did calculations on the possible isomers of chlorine nitrate, a question that has been of considerable interest in terms of the chemistry as to how the free radicals ClO and NO<sub>2</sub> might combine. The conclusions that she came to were two. One of them is that on an energetic basis the only isomer of chlorine nitrate that is feasible energetically is chlorine nitrate itself. The molecule ClO ONO is about one electron-volt higher. It does show a minimum in the potential but it is probably not going to be able to be formed under stratospheric conditions. She then tried to calculate the infrared spectrum of this molecule ClO ONO in order to know how one might look for it, that is just to confirm it experimentally. But she gave up on that because she found that with the heavier atom chlorine the calculation for chlorine nitrate itself did not reproduce satisfactorily the known infrared spectra there. So since it did not reproduce a known molecule then it was not going to be useful for a search for an unknown molecule.

Those are the two cases that I know of in the stratospheric chemistry where there have been attempts to apply quantum mechanics directly to the problems as they were being considered at the time. The question is: when do you think we will start being able to get quantum mechanical calculations that are competitive with experiments for solving some of these problems?

PULLMAN

I agree completely with you, and I mentioned it, I think, at the end of my talk. In the two problems you quoted, one faces the most difficult things to do, particularly when there is a "heavy" atom. When can we do this kind of computations? For smaller molecules it is more hopeful, and I mentioned briefly examples but as I said, calculations there give only an indication; for instance if it is worth looking for a laboratory spectrum. Very often, in space chemistry for instance there is an observation of a certain rotation line. One suspects two possible candidates to be responsible for it. There is no laboratory spectrum for either one. Which one are you going to try and handle first?

If a reasonably accurate calculation is possible I would suggest to undertake it, and this is what has been done for a few cases. But for a molecule like those you mentioned, accurate enough calculations are not yet feasible. When is it going to be possible? Well progress goes very fast. If you would tell me, when we did the  $\text{NH}_4^+$  calculations ten years ago, that I would be able to do it now to the bitter end, that is, to be able to reproduce a numerical value of the binding energy, I would be dubious. Ten years after, it is nearly standard calculation, although still very expensive. I told you that the rotation lines are one very difficult thing to compute precisely. So are also exact balances of energy in reactions or in comparing isomers. According to the refinement of the calculation you can make minima appear which had not been seen before especially when radicals are involved. Clustering reactions are easier to deal with. I have tried at least to tell you what can be done and what cannot (yet).

ARNOLD

A very brief comment: there is a famous example of the application of quantum chemistry, the one which you have briefly mentioned, namely the detection or the identification of the so-called X-ogen line in interstellar space, which was identified as  $\text{HCO}^+$  and this opened an entirely new avenue to interstellar chemistry and molecule formation, namely, it stimulated the discussion about the possibility of ion-molecule reactions being responsible for the formation of many of the molecular states.

PULLMAN

Yes, It is the same with  $\text{HCS}^+$ . In fact the calculation has been done and the laboratory measurements on the spectra have been done in parallel, and it was a convergent effort; and I think this is the way quantum chemistry should be used, not pick a calculation and say: it doesn't fit; theory is no good. First, theorists should work in close connection with experimentalists. And experimentalists, in particular in atmosphere chemistry should ask the questions which they would like to have answered from the quantum chemists. I think this might help sometimes.

ROWLAND

I would comment also that the calculations of the bond distances for chlorine nitrate are very close to the experimental values. It works very well for that.

# THE YOUNG SUN, THE EARLY EARTH AND THE PHOTOCHEMISTRY OF OXYGEN, OZONE AND FORMALDEHYDE IN THE EARLY ATMOSPHERE

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## 1. THE PRIMITIVE NEBULA

While cosmogony, i.e. the study of the origin of the solar system, has interested scientists for centuries, it is only in the seventeenth century that the first well posed model of the origin of the solar system was proposed. In 1644, R. Descartes proposed the "vortex theory" whereby the entire universe was made up of vortices which eventually ended up as planets. It must be noted that the idea of vortices evokes turbulence which, as we shall see, plays a basic role in the evolution of the solar nebula. In 1745, Buffon suggested that the solar system was formed out of the material torn away from the sun by a passing object. Having no way of calculating the probability of stellar encounters, there was no way to confirm or refute Buffon's suggestion. (Buffon's hypothesis must have certainly pleased those who believed in the uniqueness of our solar system, since a close encounter of two stars, or a star and a comet as Buffon suggested, must have been considered an infrequent event). Today we know that the probability for two stars to encounter during the entire age of the Universe is so small as to make Buffon's model unacceptable.

Ten years later, in 1755, I. Kant proposed a rather modern theory, that of a rotating gas cloud that flattened into a disc which then somehow

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broke into separate rings or planets. In 1796, P.S. Laplace first spoke of a "Solar Nebula, SN", a term now commonly used when referring to the origin of the solar system. One serious problem however remained: if things occurred this way, the sun should still be rotating at a near rotational breakup, i.e. its period should be

$$P = 0.02 \text{ days} \quad (1)$$

while the observed value is

$$P = 25.3 \text{ days} \quad (2)$$

How did the sun get rid of its spin angular momentum? The discovery of acceptable mechanisms for the transfer of angular momentum has been one of the major reasons why the Nebular Hypothesis has gained general acceptance. First is the realization that the sun is continually losing matter through a strong wind which, near the sun, is forced to flow along the magnetic field lines determined by the sun's magnetic field. This generates a strong magnetic torque that can remove angular momentum from the sun (Mestel, 1968 a,b). How efficiently this angular momentum can subsequently be redistributed to the entire nebula depends on physical processes linked to turbulence. Before reviewing recent work on the evolution of the solar nebula and the subsequent formation of planets, we shall discuss the stages of star formation believed to lead to a protosun and an accompanying solar nebula.

## 2. A FRAGMENTATION PROCESS. A DIFFICULTY

There is convincing observational evidence that the placental interstellar medium (ISM) from which the solar system originated was a dense molecular cloud (Wasserburg *et al.*, 1982; 1979). In fact, the recent evidence of the presence of short-lived nuclei in meteorites requires that the free-fall time scale for gravitational collapse ( $t_{\text{ff}}$ ) be less than or comparable to the mean lifetime of  $^{26}\text{Al}$  ( $\sim 10^6$  yrs), i.e.  $t_{\text{ff}} \leq 4 \cdot 10^7 / \sqrt{V_{\text{ff}}} < 10^6$  yrs, which requires  $n_{\text{H}} \geq 10^3/\text{cc}$ , a value typical of molecular clouds. Since molecular clouds are observed to be a major feature in our galaxy, they constitute a most reliable starting point for the processes that will eventually lead to the formation of stars and planetary systems (Falk and

Schramm, 1979). A detailed analysis of the events that take place in such clouds, after an external agent has caused them to become unstable, has been worked out for a large variety of initial conditions (Bodenheimer, 1978; 1981). Typically:  $M/M_{\odot} = 10^4$ ,  $\rho = 1.7 \cdot 10^{-23}$  g/cc,  $T = 75^{\circ}\text{K}$ ,  $R = 6.6 \cdot 10^{19}$  cm,  $\Omega = 10^{-15}$  rad/sec, and  $J/M = 1.75 \cdot 10^{24}$  cm<sup>2</sup> sec<sup>-1</sup>. Since T-Tauri stars have  $J/M = (10^{17} - 10^{18})$  cm<sup>2</sup> sec<sup>-1</sup>, a major effort has been dedicated to understand how to achieve a reduction of about 6 orders of magnitude in the value of  $J/M$ . The analysis indicates that the  $J/M$  reduction may be best achieved via a hierarchy of collapse and fragmentation and that the process yields binary fragments, a reassuring result in view of the preponderance of binary star systems. The most relevant result of these computations is that the fragments form with masses *larger* than the local Jean masses, ensuring their continuous collapse, thus placing, the hierarchical fragmentation model on firm foundations (Boss, 1982). Recent work by Boss (1983) has however indicated difficulties with the previous scenario. Study of the collapse of a dark cloud ( $M = 50 M_{\odot}$ ,  $T = 10^{\circ}\text{K}$ ,  $R = 2 \times 10^{18}$  cm,  $\Omega = 3 \times 10^{-14}$  rad sec<sup>-1</sup>,  $J/M = 4 \cdot 10^{22}$  cm<sup>2</sup> sec<sup>-1</sup>) indicates that a binary system is first formed with  $M/M_{\odot} = 8$ , each of the two fragments dividing further into a triple system with  $M/M_{\odot} = 2$ ,  $R = 2 \cdot 10^{15}$  cm,  $J/M = 10^{20}$  cm<sup>2</sup> sec<sup>-1</sup>. The dynamics of each triple system indicates (Agekyan and Anosova, 1968) that one object will be ejected in a time scale of  $t \approx 10^5$  yrs, thus isolating one of the three partners. A recent study by Boss (1983) of the fate of the  $2 M_{\odot}$  ejected body indicates that it will further fragment into a multiple system, a process that will stop only at  $M < .1 M_{\odot}$ . These results show that fragmentation is not a self-regulating mechanism until  $M \sim 10^{-2} M_{\odot}$ , in agreement with a result by Low and Lynden-Bell (1976) on opacity limited fragmentation. Boss's analysis casts serious doubts on whether the solar system actually originated through an inviscid fragmentation process. The difficulty remains unresolved.

### 3. MASS AND EVOLUTION OF THE SOLAR NEBULA. THE NEW CONVECTIVE MODEL

If one assumes that the solar nebula had a solar composition, then one can obtain a *lower limit* for its mass  $M_N$ . Following Hoyle's procedure (1962), we have

| Constituents                           | Jupiter<br>Saturn<br>H, He ( $\sim 1$ ) | Uranus<br>Neptune<br>C,N,O<br>(1.5%) | Terrestrial<br>Planets<br>Mg, Si, Fe<br>(0.25%) |
|--|---|--------------------------------------|---|
| Present Mass ( $10^{-5} M_{\odot}$ )   | 124                                     | 9.6                                  | .6  |
| Multiplier                             | 1                                       | 67                                   | 400   |
| Augmented Mass ( $10^{-5} M_{\odot}$ ) | 124                                     | 643                                  | 240   |

The result is therefore that the mass of the nebula  $M_N$  must have been larger than

$$M_N > 10^{-2} M_{\odot} \text{ or } M_N > 7.5 M_{NO} \quad (3)$$

where  $M_{NO} = 1.34 \cdot 10^{-3} M_{\odot} = 448 M_{\oplus}$  is the present mass.

Since the sun is located at the center of such nebula, one may expect that the nebular temperature  $T$  vs.  $R$ , the radial distance from the sun, would be determined roughly by

$$\frac{L}{4\pi R^2} \simeq \sigma T^4 \quad (4)$$

i.e. that

$$T \sim R^{-1/2} \quad (5)$$

This is however not the case. Through careful analysis of the temperature required for the condensation of various chemical elements, Lewis (1972, 1974) has derived the relation

$$T \sim R^{-1}, \quad (6)$$

leading one to conclude that the primary source of thermal energy in the nebula could not have been solar energy alone. Today it is generally believed that the primary source of energy was the release of gravitational energy of material that fell toward the protosun.

Consider in fact a disc in which the fluid elements follow Keplerian orbits, i.e., the fluid is in a state of differential rotation  $\Omega = \Omega(R)$ . This implies a non-zero rate of shearing  $R d\Omega/dR$ .

If there is *viscosity* present, its effect would be that of damping out the shearing motion, whose energy content will be dissipated into heat to

be then radiated away (Pringle, 1981). Thus, viscosity causes the fluid to lose energy. Since the only available energy is the gravitational binding energy, the material will spiral inward to lower energy and angular momentum levels. As a result, mass is transferred inward and angular momentum is transferred outward.

The equations governing the disc are given by Pringle (1981) as ( $v_\phi = \Omega R$ )

$$R \frac{\partial \Sigma}{\partial t} + \frac{\partial}{\partial R} (R \Sigma v_R) = 0, \quad (7)$$

$$R \frac{\partial}{\partial t} (\Sigma R^2 \Omega) + \frac{\partial}{\partial R} (\Sigma R^3 \Omega v_R) = \left( \frac{\partial}{\partial R} \right) \bar{\nu} \Sigma R^3 \frac{\partial \Omega}{\partial R}$$

representing conservation of mass and angular momentum respectively.  $\Sigma$  is the surface density at  $R$ ,  $\bar{\nu}$  is an average effective viscosity at  $R$ ,  $\Omega$  is the angular velocity and  $v_R$  is the radial velocity.

For the case of a Keplerian steady disc, eqs. (7) can be integrated and combined to yield

$$-2\pi R \Sigma v_R = 3\pi \bar{\nu} \Sigma = \dot{M} \quad (8)$$

where the constant of integration  $\dot{M}$  has the physical interpretation of a rate of mass accretion toward the central object.

The heat generated by viscosity must be transported away from the midplane to the surface layer of the nebula, in order for the nebula to attain thermal equilibrium. It follows that at any given distance  $R$  from the central sun, there must exist a flux  $F$  that carries away such heat, i.e. we must have

$$\frac{1}{\rho} \frac{dF}{dz} = \frac{9}{4} \bar{\nu} \frac{GM}{R^3}, \quad (9)$$

where in general

$$F = F_r + F_c$$

Here  $F_r$  is the radiative flux and  $F_c$  the convective flux,

$$F_r = \frac{4acT^3}{3k_{op}\rho} \left( -\frac{\partial T}{\partial z} \right) \equiv c_p \rho \chi_r \left( -\frac{\partial T}{\partial z} \right) \quad (10)$$

$$F_c = c_p \rho \chi_c \left[ -\frac{\partial T}{\partial z} + \left( \frac{\partial T}{\partial z} \right)_{ad} \right] \equiv c_p \rho \chi_c \beta \quad (11)$$

where  $k_{op}$  is the opacity of the material in the nebula,  $c_p$  is the specific heat, and  $\chi$  is the thermometric conductivity.

To complete the determination of the  $z$ -structure of the nebula, a further equation is needed, namely

$$\frac{dp}{dz} = - \left( g \frac{z}{R} \right) \rho, \quad g = \frac{GM}{R^2} \quad (12)$$

representing hydrostatic equilibrium in the  $z$ -direction, i.e. gravitational pull toward the midplane must be compensated by a pressure gradient which supports the gas above the midplane.

This completes the list of the needed equations. If one employs a theory (like the mixing length theory of convection) to compute  $\chi_c$ , as well as a model for the opacity  $k_{op}$ , then eqs. (9) and (12) determine the vertical structure of the nebula, i.e.  $T$ ,  $\rho$  and  $F$  vs.  $z$ , provided appropriate boundary conditions are imposed. These are usually taken to be

$$F(z=0) = 0, \quad F(z=H) = \sigma T_e^4, \quad p(z=H) = \frac{2}{3} \frac{g}{k_{op}} \frac{H}{R} \quad (13)$$

where  $T_e$  is the nebula effective surface temperature and  $H$  is the height of the nebula. Let us now discuss  $k_{op}$  and  $\chi_c$ . For  $k_{op}$  it is customary to follow De Campli and Cameron (1979), who proposed that

$$k_{op} = k(\text{ice}) + k(\text{SiO}_2) + k(\text{Fe}_2) \quad (14)$$

where the temperature dependence of each  $k$  is of the form

$$k = k_0 T^2 \quad (15)$$

For  $F$ , the situation is more complex. For many years it was assumed that the major contribution to  $F$  came from  $F_r$ . However, it has been



recently pointed out by Lin and Papaloizou (1980) that in parts of the nebula "convection" is most likely triggered by the opacity (14), so that  $F_c \neq 0$ . Lin and Papaloizou (1980), Lin (1981), and Lin and Bodenheimer (1982) have adopted the Mixing Length Theory (MLT) which provides expression for  $\bar{\nu}$  and  $\chi_c$ . In particular ( $a$  is an undetermined constant)

$$\chi_c = a \Lambda^2 (g^* \bar{\alpha} \beta)^{1/2} \quad (16)$$

where the mixing length  $\Lambda$ ,  $g^*$  and  $\bar{\alpha}$  are given by

$$\Lambda = \text{Min} \left( z, \frac{p}{g^* \rho} \right), \quad g^* = g \frac{z}{R}, \quad \bar{\alpha} = - \left( \frac{d \ln \rho}{dT} \right)_p \quad (17)$$

Equations (9) and (12) have been solved numerically by Lin and Papaloizou (1980) and some of their results are presented in Figures (1) and (2). Lin (1981) has also analyzed the inner region of the nebula,  $R < 10^{14}$  cm, where most of the protoplanets form. When the opacity is mainly contributed by ice-grain, Lin deduced the following results (cgs units):

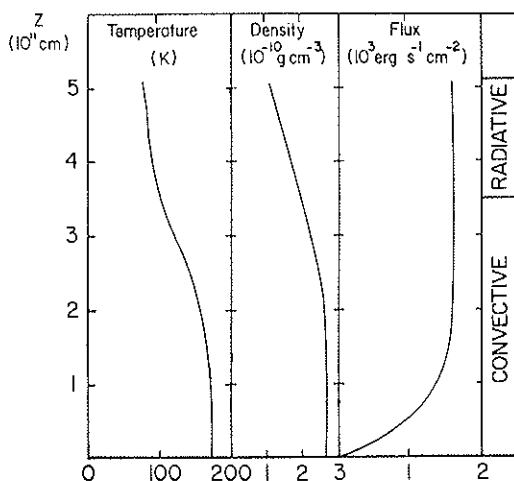


FIG. 1. The vertical structure of the nebula as from the work of Lin *et al.* (1980, 1981). Note that the convective region makes up to 2/3 of the entire  $z$ -structure. In the radiative region  $\nu = 0$ , and so  $F = \text{constant}$  because of eq. (9). (Reproduction with permission of Dr. D.N.C. Lin).

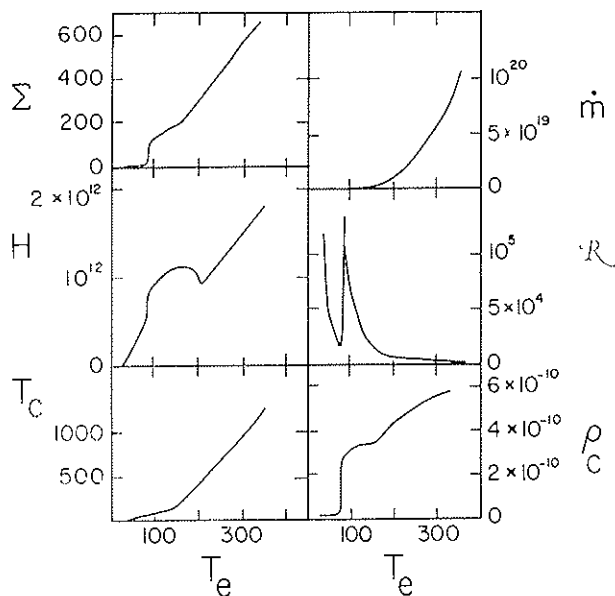


FIG. 2. Numerical solutions as a function of  $T_e$  (effective temperature) for  $R = 10^{13}$  cm. The units of  $\Sigma$  are  $\text{g cm}^{-2}$ , those of  $H$  are cm.  $T_e$  and  $\rho_c$  are the value of  $T$  and  $\rho$  at mid-plane,  $\dot{m}$  is the mass flux ( $\text{g sec}^{-1}$ ). The quantity  $R$  is the Reynolds number. (Reproduction with permission of Dr. D.N.C. Lin).

$$\begin{aligned}
 \Sigma &= 15 \dot{m}^{1/3} \alpha^{-2/3}, & R &= 7 \cdot 10^3 \dot{m}^{-2/3} r^{1/2} \alpha^{-2/3} \\
 H &= 10^{12} \dot{m}^{1/3} r^{3/4} \alpha^{-1/6}, & T_e &= 400 \dot{m}^{2/3} r^{-3/2} \alpha^{-1/3} \\
 \rho_c &= 2 \cdot 10^{-11} r^{-3/4} \alpha^{-1/2}, & \tau &= 300 \dot{m}^{5/3} r^{-3} \alpha^{-4/3},
 \end{aligned} \tag{18}$$

where  $\dot{m}$  ( $= \dot{M}/10^{18} \text{ g sec}^{-1}$ ) and  $r = R/10^{13} \text{ cm}$ ;  $\alpha$  is related to the coefficient  $a$  of eq. (16) by  $\alpha = 2\sqrt{8} a$ . (For simplicity we have assumed a molecular weight of unity,  $m = 1$  and Lin's  $\beta$  also unity). When the opacity is determined mostly by  $\text{SiO}_2$ , like in the region near the sun, the functional forms (18) remain unchanged but the numerical coefficients vary. For example, the value 400 in  $T_e$  becomes 200.

With the knowledge of these quantities, one can evaluate the mass of the nebula  $M_N$ , as well as the time scale for its evolution. The results are

$$\begin{aligned}
 M_N &= 10^{28} (\dot{m}^{1/3} \alpha^{-2/3} r^2 + 5 \dot{m}^{11/9} \alpha^{-10/9}) \text{ g} \\
 t_N &= M_N/\dot{M} = 3 \cdot 10^2 (\dot{m}^{-2/3} \alpha^{-2/3} r^2 + 6.7 \dot{m}^{2/9} \alpha^{-10/9}) \text{ yr}
 \end{aligned} \tag{19}$$

All the quantities given above depend on  $\dot{m}$  and  $\alpha$ , which cannot be evaluated a priori. In order to fix them, Lin proceeded to impose the following constraints:

(a) In order for Jupiter to be able to grow to its present mass, the Reynolds number must be less than  $M_{\odot}/M_J$ . From eq. (18), one obtains

$$\dot{m} > 1.6 \cdot 10^3 r_J^{3/4} \alpha^{-1}$$

where  $r_J$  is the initial orbital radius of Jupiter.

(b) Grains play the dual role of triggering convection and at the same time of forming the seed for planetary accretion. Since most grains condense at  $1000\text{K} < T < 2000\text{K}$ , the nebular temperature must have been less than 2000K at the orbit of Mercury. This implies

$$\dot{m} < 10 \delta_M^{9/4} \alpha^{1/2}$$

where  $\delta_M = r_M/r_{M_0}$ ,  $r_{M_0}$  being the present semimajor axis of Mercury.

(c) At large distances from the protosun, the nebular material becomes transparent. Such distance must be greater than the initial orbit of Neptune  $r_N$ . From (18), one finds that the nebula remains convective if

$$\dot{m} > 30 \delta_N^{9/5} \alpha^{4/5}.$$

Putting together these constraints, Lin's best fitting values for  $\alpha$  and  $\dot{m}$  were found to be

$$10 < \dot{m} < 20, \quad \alpha = 2$$

which implies that

$$\dot{M} = (1.2) \cdot 10^{19} \text{ g sec}^{-1} = (1.5-3) \cdot 10^{-7} M_{\odot}/\text{yr} \quad (20)$$

An immediate consequence of (20) is that such mass flux could not have lasted for more than a few million years, otherwise the sun would end up with a mass greater than  $1 M_{\odot}$ . This time scale can also be compared with information derived from isotopic data. One of the most interesting discoveries in the past few years concerns the excess of  $\text{Mg}^{26}$  found in the Allende Meteorite (Lee *et al.*, 1976). This is interpreted in terms of  $\text{Al}^{26}$  which can only be produced by a nearby supernova explosion.

What is relevant is that since its lifetime is short,  $\tau \approx .5 \cdot 10^6$  yrs,  $A\ell^{26}$  must have been condensed well within this time in order for it to be still present today. This period of time is consistent with the previous estimates based on eq. (20).

With the values of  $\bar{m}$  and  $\alpha$ , one can then proceed to determine other quantities of interest. For example:

1) *Mass of the solar nebula  $M_N$ .* One obtains

$$10 < M_N/M_{N0} < 20 \quad (21)$$

where  $M_{N0}$  is the present mass of the planetary system,  $= 1.34 \cdot 10^{-3} M_\odot = 448 M_\oplus$ . (The quantity  $r_0$  was taken to be Neptune's distance. The upper and lower limits correspond to the case of low and high opacities respectively).

Since the value of  $M_N$  is significantly lower than required for gravitational instability to set in (Toomre, 1964; Goldreich and Lynden-Bell, 1965; Goldreich and Ward, 1973), the nebula is found to be gravitationally stable.

2) *Mass of the nebula within Jupiter's radius  $M_J$ .* One obtains

$$.6 < M_J/M_{N0} < 1.1 \quad (22)$$

Assuming that the nebula had a solar abundance ( $Z = 0.015$ ), one finds that the total mass of heavy elements contained in the solar nebula within the distance of Jupiter is

$$M_Z = (.6 - 1.1) M_{N0} Z = (4 - 7.4) M_\oplus \quad (23)$$

to be compared with the total mass of the terrestrial planets

$$M_{TP} = 2 M_\oplus \quad (24)$$

The closeness of  $M_Z$  and  $M_{TP}$  is considered a "dilemma" for it implies a very high efficiency in collecting the heavy elements into proto-planets. Lin therefore proposed that the formation of the terrestrial planets must have occurred prior to the formation of Jupiter when the mass of the nebula was larger and the requirements on the efficiency less stringent.

3) *Time scale for the Solar Nebula.* Using for  $r_0$  the orbital radius of Neptune, one obtains

$$t_N \cong 10^5 \text{ yrs} , \quad (25)$$

as the time available for the protoplanets to grow. By this time, most of the gas has been used up and one must conclude that the Jovian planets, being gas rich, had to be formed. For the terrestrial planets the situation is not so clear cut because all that is actually needed is that by this time a sufficient amount of heavy elements be converted into planetesimals that may at later times form planets.

The details of how they accreted the remaining mass and the corresponding time scale remain to be worked out. It seems however reasonable to expect that the end product will be a planet with a thin atmosphere since most of the gas had already been used up early on. This conclusion may be relevant to the recent suggestion by Hayashi and collaborators (1981, 1982) that the young earth may have ended up shrouded in a thick atmosphere. In Section 5, we shall discuss the work done in the field of formation of the earth and indicate that even in that case there are reasons to believe that no thick atmosphere actually formed.

The reason why we prefer to present the "standard scenario" in a separate Section is because we feel it is premature to engage in a full comparison of the two approaches since all the details are as yet not available.

One comparison however can be made. Lin's approach implies time scales *shorter* by a factor of about ten with respect to the ones discussed in Section 5. This in turn implies that the relevance of the UV radiation from the Sun may have been even greater than the one we shall discuss in Section 8.

#### 4. *Conclusions*

While the work of Lin *et al.* is interesting in that it tries to model convective turbulence from first principles, it still contains arbitrary parameters (four) and approximations that cast doubts on the reliability of the results. Specifically, the height of the nebula  $H$  had to be chosen arbitrarily since the model as constructed by Lin *et al.* gives rise to a degenerate set of solutions for  $H$ . The arbitrariness in the choice of  $H$

reflects on the value of the surface density ( $\Sigma$ ), which in turn affects the value of the nebula's mass ( $M$ ).

#### 4. AN IMPROVED MODEL FOR CONVECTIVE TURBULENCE

Having pointed out that viscosity is the key quantity for the overall behavior and structure of the nebula, we must ask ourselves what is its origin. The first possibility is evidently particle viscosity. It can however be seen that in that case, the timescale for mass redistribution would be much longer than the age of the solar system itself. Lin (1981) has also pointed out that density perturbations could not grow into protoplanets because they could not accrete material beyond their immediate vicinity.

The next phenomenon that comes to mind because of its efficiency is *turbulence*, which can be generated in a large variety of ways. Until Lin and Papaloizou's work (1980), it was generally believed that turbulence may originate from meridional currents (Mestel, 1965), infall of material onto the nebula (Cameron, 1976) and magnetic dragging of ionized nebular material (Hoyle, 1960; Hayashi, 1982). While these are physically reasonable mechanisms to boost-up the poor efficiency of particle viscosity, their actual effectiveness depends on ad hoc assumptions. Progress was achieved when Cameron (1978) suggested that turbulent *convection* is the most natural mechanism to contribute to the viscosity  $\bar{\nu}$ . As noted in Section 3, Lin and his collaborators (1980, 1981) adopted the Mixing Length Theory, which however cannot fix the parameter  $\alpha$  entering in eq. (16). As discussed, Lin and his collaborators had to use other constraints to make the model fully predictable. Recently Canuto *et al.* (1984, 1985) have tried to improve on the situation by proposing a model for convective turbulence that allows  $\alpha$  to be determined and which also offers a natural way to incorporate important physical parameters like rotation. We shall sketch here the main points of this new approach.

A complete theory of convective turbulence, if it existed, would provide an expression for the turbulent viscosity  $\nu_t$ . Lacking such theory one usually writes, on dimensional grounds,

$$\nu_t = \xi \ell_t v_t \quad (26)$$

where  $\ell_t$  and  $v_t$  are typical lengths and velocities of the turbulent medium and  $\xi$  is an unknown numerical parameter.

Following the standard description of turbulence (Landau and Lifshitz,

1959), one divides the spectrum of eddy sizes into three regions: (1) *Large* eddies  $k \sim k_0$ ,  $\ell_i \sim L$ , where  $L \sim k^{-1}$ , is the size of the system itself. In the case of a disc,  $L$  is the width of the disc. This part of the spectrum contains most of the energy. (2) *Small* eddies,  $k \sim k_1$ ,  $\ell_i \sim \lambda = L/\text{Re}^{3/4}$ , where  $\text{Re}$  is the Reynolds number. In region (2), energy is dissipated into heat via molecular viscosity. Finally, (3) there is the so-called inertial region,  $k_0 < k < k_1$ , where energy is not dissipated but simply transferred from region (1) to region (2). This region is characterized by eddies of almost all sizes, the largest ones being of the order  $L$  and the smallest ones being almost of the order  $\lambda$  respectively, i.e.  $\lambda < \ell_i < L$ . The properties of the turbulent region can be described once one knows the "energy spectrum function"  $E(k)$  (Batchelor, 1970)

$$v_i^2(k) = \int_k^\infty E(k) dk. \quad (27)$$

The determination of  $E(k)$  from first principles is the main goal of any theory of turbulence. Using dimensional arguments (Landau and Lifshitz, 1959) or a form  $E(k) \sim k^{-n}$ , one derives ( $2r = n - 1$ ,  $r = 1/3$  corresponds to Kolmogoroff)

$$v_i = v_L \left( \frac{\ell_i}{L} \right)^r, \quad v_i = \xi v_L L \left( \frac{\ell_i}{L} \right)^{r+1} \quad (28)$$

In all practical applications to problems in astrophysics, eq. (28) is actually written as

$$v_i = \alpha c_s H \quad (29)$$

where  $c_s$  is the speed of sound and  $H$  some characteristic scale height. It is clear that eq. (29) is consistent with (28), *only if*  $\ell_i/L$  is considered a constant of order unity because we limit ourselves to the largest eddies.

Adopting eq. (29), one is then faced with the problem of evaluating the parameter  $\alpha$ . The model used by Canuto *et al.* (1985) is based on the equation

$$\epsilon_{\text{gain}} = \epsilon_{\text{loss}} + \epsilon_{\text{transfer}} \quad (30)$$

Here  $\epsilon_{\text{gain}}$  represents the rate (per unit mass) of energy gain from buoyancy forces and radiation mechanisms;  $\epsilon_{\text{loss}}$  represents the losses due to heat conduction and molecular viscosity and finally  $\epsilon_{\text{transfer}}$  is the energy trans-

ferred by the nonlinear interactions from large eddies to small ones. Since  $E(k)dk$  represents the energy in the interval between  $k$  and  $k + dk$ , one writes, in analogy with the molecular viscosity (Batchelor, 1970)

$$\epsilon_{\text{transfer}} = 2 \nu_t(k) \int_{k_0}^k E(k) k^2 dk \quad (31)$$

Let us now consider the growth rate of the unstable modes  $n(k)$  derived from the linear analysis. The net rate of energy gain from these modes is obtained by multiplying the average energy of the mode by  $2n(k)$ , i.e.

$$\epsilon_{\text{gain}} - \epsilon_{\text{loss}} = 2 \int_{k_0}^k n(k) E(k) dk \quad (32)$$

(Ledoux *et al.*, 1961). The value of  $\nu_t$  at  $k = k_0$  is then easily obtained by combining (31) and (32) with (30). The result is

$$\nu_t = \frac{n(k_0)}{k_0^2} \quad (33)$$

For simplicity, let us approximate the actual geometry of the disc by a plane parallel model with the  $z$ -component of  $k$ ,  $k_z$  satisfying the boundary conditions  $k_z L = n\pi$  ( $n = 1, 2, \dots$ ), where  $0 \leq z \leq L$ . We have  $k_0 L = \pi \sqrt{1+x}$ ,  $x = (k_x^2 + k_y^2)/k_z^2$ . Using (29) and (33), we then derive

$$\alpha = \frac{1}{\pi^2 (1+x)} \left( \frac{H}{c_s} \right) n(k_0) \left( \frac{L}{H} \right)^2 \quad (34)$$

Eq. (34), providing an expression for  $\alpha$  in terms of the ratio between the growth rate  $n(k_0)$  and the hydrostatic rate  $c_s/H$ , is of general validity regardless of the specific mechanism generating instability.

#### a) *Convective Turbulence*

In the absence of rotation, the form of  $n(k)$  for a plane-parallel geometry is given by (Chandrasekhar, 1961)



$$2n(k) = \left\{ (\chi - \nu)^2 k^4 + \frac{4\chi\nu}{L^4} \mathcal{R} \frac{x}{1+x} \right\}^{1/2} - (\chi + \nu) k^2 \quad (35)$$

Here,  $\chi$  is the thermometric conductivity,  $\nu$  is the kinematic viscosity,  $\mathcal{R}$  is the Raleigh number  $= g_* \bar{\alpha} \beta L^4 / \chi \nu$ ;  $\bar{\alpha}$  is the coefficient of thermal expansion and  $\beta$  is the temperature gradient excess over the adiabatic gradient eq. (11); finally,  $g_*$  is the  $z$  component of gravity ( $g_x = g_y = 0$ ). In the presence of rotation  $\vec{\Omega}$  parallel to  $\vec{g}$ , the function  $n(k)$  is given by the solution of the cubic equation (Chandrasekhar, 1961)

$$\frac{L^4}{\nu\chi} (n + \chi k^2) (n + \nu k^2) = \frac{\mathcal{R} x}{1+x} \left[ 1 - \frac{\sigma T^*}{\mathcal{R} x} \frac{n + \chi k^2}{n + \nu k^2} \right] \quad (36)$$

where  $T^* = L^4 \Omega^2 / \nu^2$  is the Taylor number and  $\sigma = \nu / \chi$  is the Prandtl number. For  $T^* = 0$ , eq. (36) has the solution (35). The last term in eq. (36) represents the effect of Coriolis forces on the perturbations in the velocity and temperature fields.

### b) Application to the Rotating Solar Nebula

As we have already stated, the horizontal disc is usually taken to be Keplerian, i.e. the gravitational acceleration in the plane of the disc is balanced by the centrifugal force. The only component of gravity that acts on velocity and temperature perturbations is the vertical component  $g_*$ , and so the following relations hold

$$g_* = z g / R, \quad dp = -g_* \rho dz, \quad \sigma T^* / \mathcal{R} = \frac{\Omega^2}{g_* \bar{\alpha} \beta} = \frac{1}{\bar{\alpha} \beta z} \quad (37)$$

Eq. (34) can now be written as

$$\alpha = \frac{1}{\pi^2} (\bar{\alpha} \beta z)^{1/2} \left( \frac{L}{H} \right)^2 \frac{N}{(1+x)} \left( \frac{H}{c_s} \sqrt{\frac{\bar{g}}{R}} \right) \quad (38)$$

where we have found it convenient to introduce the dimensionless variable

$$N \equiv \frac{n(k_0)}{(g_* \bar{\alpha} \beta)^{1/2}} \quad (39)$$

to be chosen as the real, positive part of the solutions of eq. (36), which for  $k = k_0$  becomes

$$(N + N_0)(N + \sigma N_0) = \frac{x}{1+x} \left[ 1 - \frac{\sigma T^*}{\mathcal{R}_x} \frac{N + N_0}{N + \sigma N_0} \right], \quad N_0 \equiv \frac{(1+x) \pi^2}{(\mathcal{R}\sigma)^{1/2}} \quad (40)$$

The evaluation of  $\alpha$  is complete once the quantity  $\mathcal{R}\sigma$  is expressed in terms of the physical variables of the problem. Since in the case of radiative conduction

$$\mathcal{R}\sigma = \frac{g_* \bar{\alpha}\beta L^4}{\chi^2}, \quad \chi \equiv \chi_r \equiv \frac{4acT^3}{3 k_{op} c_p \rho^2} \quad (41)$$

where  $k_{op}$  is the opacity, we derive (in c.g.s. units)

$$\mathcal{R}\sigma = 1.45 \cdot 10^{33} \left( \frac{M}{M_\odot} \right) (\bar{\alpha}\beta z) \frac{(\rho L)^4}{(RT^2)^3} c_p^2 k_{op}^2 \quad (42)$$

Equations (38), (40) and (42) provide the full determination of  $\alpha$ , i.e. of  $\nu$  to be used in eq. (9),  $\nu = \nu_i$ .

Next, we must determine  $F_c$  the convective flux, eq. (11),

$$F_c = c_p \rho \chi_c \beta \quad (43)$$

To that end, we shall adopt a model first proposed by Spiegel (1963) and worked out by Gough (1976), in which the basic ingredient is the growth rate  $n(k)$  which, as we have seen, can easily incorporate rotation, eq. (40). Following Gough, with the changes suggested in a later paper, Gough (1978), we derive

$$\chi_c = \frac{A}{1+x} \frac{L^2 n^3(k_0)}{g_* \bar{\alpha}\beta} = \frac{A}{1+x} (\mathcal{R}\sigma)^{1/2} N^3 \chi_r \quad (44)$$

where we have estimated  $A = .65$  and  $\chi_r$  is given by eq. (41).

Eqs. (38) and (44) should be now inserted in eqs. (9) and (11); together with (12), one could then determine the disc structure and then compare the results with those of Lin and his collaborators. The

advantage of such a procedure is that one has fewer free parameters and the possibility of including rotation. This last point may be an important one. In fact, the original Mixing Length Theory was devised for slow rotators like the sun. On the other hand, in the solar nebula the rotation, being Keplerian, is at its maximum and it may therefore play a significant role. The standard MLT can be extended to include rotation at the expense of introducing extra parameters that are then difficult to evaluate. Since the present formalism obviates such difficulties it is important to study the disc structure on this basis (Cabot *et al.*, 1986). It seems clear that the presence of rotation will decrease the value of  $\alpha$ , i.e. of  $\nu_i$ , since from (40) for  $\sigma \rightarrow 0$  and  $\mathcal{R}\sigma \gg 1$

$$N \sim 1 - \frac{\sigma T^*}{\mathcal{R}_x} \quad (45)$$

A smaller  $\nu_i$  implies a smaller  $\dot{M}$ , eq. (8), and therefore a longer evolutionary time for the nebula (for a constant  $\Sigma$ ).

## 5. THE FORMATION OF THE EARTH - STANDARD SCENARIO

The accretion process that led to the formation of the earth from grains, dust and gas has been studied by several authors (Safronov, 1972; Weidenshilling, 1974, 1976, 1980). For a detailed review, see Wetherill (1980). While early estimates by Schmidt resulted in an accretion time  $t_A \approx 250$  m.yrs., recent analyses yield considerably lower values, i.e.  $23 \leq t_A \leq 88$  m.yr. These results assume that accretion occurred in the absence of gas. In the presence of gas (Mizuno *et al.*, 1982; Nakagawa *et al.*, 1981),  $t_A$  decreases to about 10 m.yr., and a massive atmosphere ( $\sim 10^4$  times the present one or the one corresponding to the gas-free situation) results. Since the two models lead to very different conclusions for the earth's atmosphere, it is important to analyze their basic ingredients. A critical role is played by  $t_N$ , the dissipation time of the solar nebula, whose value depends, in most models considered thus far, on the turbulent viscosity  $\nu_i = \xi \ell_i \nu_i$  (where  $\ell_i$  and  $\nu_i$  are typical lengths and velocities of the turbulent motion). A detailed analysis (Elmegreen, 1978; 1979) leads to the following dependence of  $t_N$  on  $\xi$

$$t_N = \frac{A}{4\xi} \text{ m.yrs.} \quad (46)$$

where

$$A = (M_N/10^{-1} M_\odot)^{1.37} (X/50 \text{ AU})^{-1.37} (V_w \dot{M}_w/2 \cdot 10^{26})^{-1.33} \quad (47)$$

Here,  $M_N$  is the mass of the solar nebula,  $X$  its extension,  $V_w$  the solar wind, and  $\dot{M}_w$  the rate of mass loss. The parameter  $\xi$  satisfies the following inequalities

$$10^{-3} \leq \xi \leq 1/3, \quad (48)$$

a result arrived at in the following way. As stated earlier, in a turbulent fluid one envisages three regions characterized by different sizes of the eddies there contained. In the first region, the eddies sizes  $\ell$  are comparable with  $L$ , the size of the system itself. In this case one writes  $\nu = \xi_L \nu \ell$ , where  $\xi_L$  is the inverse of the Reynolds number  $Re$  which, for turbulence to set in, must be  $> 10^3$ , and so  $\xi_L < 10^{-3}$ , yielding the lower limit in (48). At the other end of the spectrum, the eddies are sufficiently small for molecular forces to dominate, and so  $\nu = \xi_m \nu \ell$ , where  $\xi_m = 1/3$ , thus yielding the upper unit in (48). Because of the large indeterminacy of (48) Canuto *et al.* (1984) have attempted to calculate  $\xi$  from first principles.

One begins by using the Heisenberg-Weizsacker's theory of turbulence (Batchelor, 1970). One has

$$\nu_t(k) = \gamma \int_k^\infty \left( \frac{E(k)}{k^3} \right)^{1/2} dk, \quad \nu_t^2 = \int_k^\infty E(k) dk, \quad \ell_t = \pi/k \quad (49)$$

Here  $E(k)$  is the spectral energy distribution function solution of the dynamical equations governing turbulence. Several forms were employed:

1) Kolmogoroff spectrum,  $E(k) \sim k^{-5/3}$ . In this case

$$\xi = \frac{\gamma}{\pi} \sqrt{\frac{3}{8}} = .06, \quad \gamma = 1/3 \quad (50)$$

2) The Stewart-Townsend (1951) "experimental" spectrum  $E(k) \sim k^{-\alpha_2 \ln k}$ . The result is ( $\Psi(x)$  is the error function)

$$\xi = \frac{\gamma q}{\pi} \sqrt{\frac{2}{\alpha}} \frac{1 - \Phi(x)}{\{1 - \Phi(y)\}^{1/2}} \quad (51)$$

where  $x\sqrt{2} = \alpha \ln q + .5 \alpha^{-1}$ ,  $y = \alpha \ln q - .5 \alpha^{-1}$ ,  $q = k/k_0 = L/\ell$ . For a wide range of parameters, the resulting values of  $\xi$  are

$$.03 \leq \xi < .08 \quad (52)$$

3) In the case of convective turbulence (Ledoux *et al.*, 1961)  $E(k)$  cannot be given in closed analytic form. The evaluation of  $\xi$  was therefore done numerically. For the range  $10^{-7} < \delta < 10^{-1}$  of  $\delta = 8\pi^4/\mathcal{R}$ , the result is

$$\mathcal{R}\sigma \ll 1 \quad .03 < \xi < .07 \quad (53)$$

4) The previous theory was extended to the case  $\mathcal{R}\sigma \gg 1$ . The result is

$$\mathcal{R}\sigma \gg 1 \quad .06 \leq \xi \leq .07 \quad (54)$$

Using these results, as well as those of Nakano *et al.* (1979),  $\xi = .05$ , it was concluded that (Canuto *et al.*, 1984).

$$t_N = (2.5-8.3) 10^6 \text{ A yrs} \quad (55)$$

It is interesting to note that for  $A = 1$  the upper limit of  $t_N$  closely corresponds to the point where the T-Tauri phase (vertical part of the  $1 M_\odot$  track, Fig. 4) ends. Furthermore, since either value of  $t_N$  is smaller than the values of  $t_A$ , (Wetherill, 1980) it seems unlikely that gas might have influenced accretion to the point of producing a massive  $H_2$  atmosphere. Since the quoted values of  $t_A$ , ranging from 10 m.yrs. to (23-88) m.yrs. correspond to extreme assumptions as far as the gas is concerned, our result suggesting a gradual dispersion of the gas while the earth was accreting, would in principle require a new evaluation of  $t_A$  with a time decreasing gas density. However, for the present purposes, it is sufficient to take an average of the previous values. If we take  $t_A = 50$  m.yrs., we would conclude that the SN gas was present only for 10% of  $t_A$ , and that most of the accretion occurred while the sun was moving along the radiative track stage of Fig. 4, at which point the UV flux was  $10^2$  times larger than its present value.

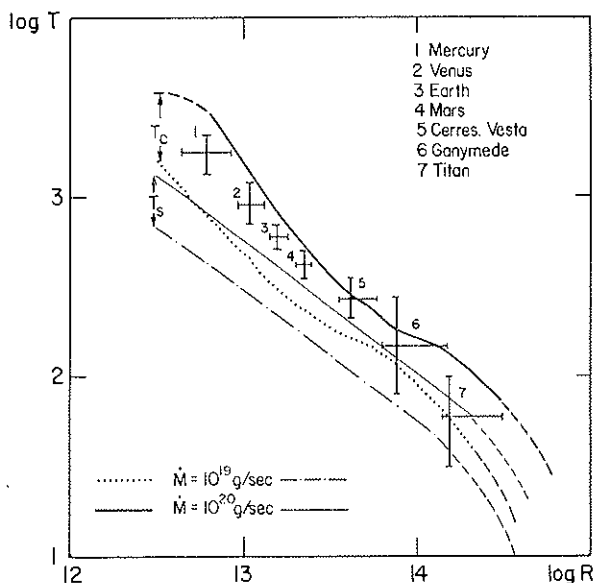


FIG. 3. A comparison of the  $T$  vs.  $R$  function as deduced from the solutions of Lin and collaborators with those from the work of Lewis. The best fit is achieved for  $\dot{M} \approx 10^{-6} M_{\odot}/\text{yr} = 10^{20} \text{ g sec}^{-1}$ . (Reproduction with permission of Dr. D.N.C. Lin).

As we have stated at the end of Section 3, while this "standard scenario" implies time scales of the order of

$$(10-50) 10^6 \text{ yrs}, \quad (56)$$

Lin's analysis implies time scales shorter by at least a factor of *ten*, thus implying that the Solar UV flux was  $10^4$  larger than today, as one can see from Figure 4. (For the photochemical implications of high UV fluxes see Section 8).

## 6. THE ORIGIN OF THE ATMOSPHERE

Since the SN was unlikely the major contributor to the earth's atmosphere, one may consider the following contributors: (1) collision with comets, (2) volatilization of impacting material and (3) outgassing. One may distinguish two periods of outgassing. While the accretion energy due to impact was in principle sufficient to melt the entire Earth, this

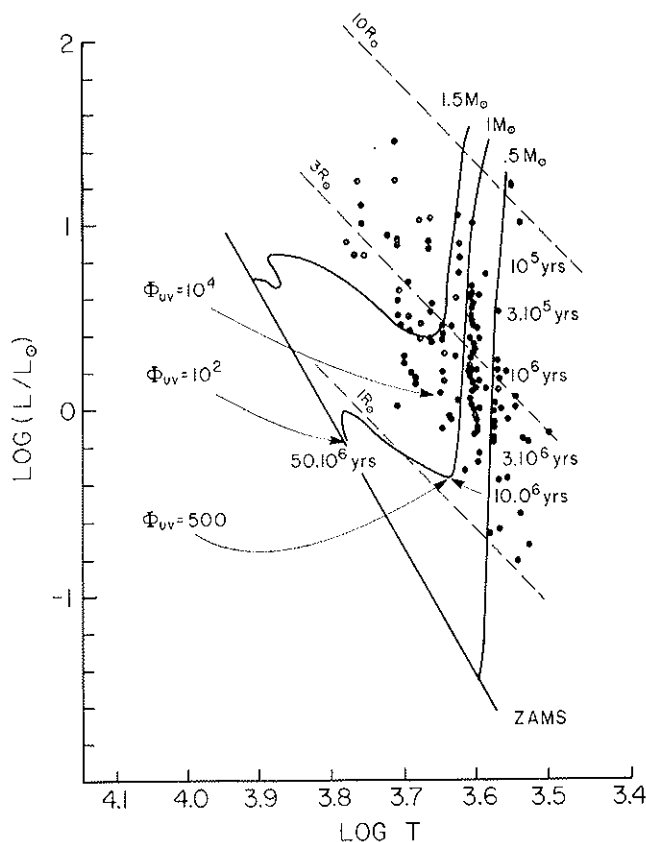


Fig. 4. The pre-main sequence evolution of 0.5 to 1.5 solar mass stars in the Hertzsprung-Russell diagram. The lines represent theoretical evolutionary tracks, while the dots represent observational data for T Tauri stars (Cohen and Kuhn, 1979). The corresponding ages and ratios of UV flux to present solar UV flux are indicated for a solar-mass star.

may not have occurred, since a fully melted Earth would have expelled all volatiles, whilst it is known that  $\text{He}^3$  is still degassed today. Accretional heating may have produced partial melting including Fe alloys that migrated toward the center forming ultimately the Earth's core. The time scales for the core formation discussed in the past ( $\approx 10^9$  yrs) have been shown to be too long. The conclusion is that the core formed *contemporaneously* with the accretion of the earth itself in  $\approx 10^7$  yrs (Stevenson, 1981, 1983). During this period, *two sources of volatiles* therefore acted simultaneously, the outgassing caused by the impacting material that stirred the mantle and

the impacting meteorites. Since volatiles are bound in these meteorites, the energy retained as heat upon impact would be sufficient to vaporize the volatile species releasing them so as to form an atmosphere. As stated by Benlow and Meadows (1977) this conclusion seems unavoidable: the formation *only* of a solid body with the subsequent outgassing seems an artificial division of events which more naturally should be thought of as having occurred simultaneously. As the embryonic Earth continued to grow, the impact velocities increased until vaporization of the impacting material occurred. Non-volatile solids so vaporized cooled and condensed onto the surface. Volatiles like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , the noble gases, etc., probably remained in the atmosphere. Calculations by Jakosky and Abrens (1979) indicate that this process occurs for impact velocities greater than 5 km/sec, which in the case of the Earth were achieved (Wetherill, 1976) when the radius was 50% of its present value, i.e. before  $\sim 10^6$  yrs.

The chemical composition of this atmosphere depends critically on complex chemical reactions between the infalling vaporized gas, the outgassed volatiles and other elements, particularly Fe (Wetherill, private communication). In the specific impact originated atmosphere studied by Jakosky and Ahrens (1979), the partial pressure of water was estimated to be  $p(\text{H}_2\text{O}) \approx .01$  bar. The fate of atmospheric  $\text{CO}_2$  is difficult to quantify and ongoing experiments by Ahrens and collaborators (Stevenson, private communication, 1983) are expected to shed light on this point, since carbonate growth may have removed a great deal of  $\text{CO}_2$  during the time scale of the Earth's accretion. The first phase of outgassing, together with an impact-originated atmosphere, lasted a period of time not greatly different from the accretion time itself, at the end of which the Earth entered a period in which accretion is over, the mantle is solid and the core fully formed (Stevenson, 1983). Such a period is characterized by a large "mass flux" which transports large masses of the mantle to the surface region, thus making them available for the second period of outgassing. Since the length of this period is difficult to estimate, the following argument can be made (Thomsen, 1980).

The abundance of  $^{129}\text{Xe}/^{130}\text{Xe}$  in the atmosphere is smaller than that in the solid Earth, the latter being due to enrichment caused by the decay of  $^{129}\text{I}$  to  $^{129}\text{Xe}$ . If the outgassing took much longer than a few lifetimes of  $^{129}\text{I}$  ( $17 \cdot 10^6$  yrs), at the end of it there would have been no  $^{129}\text{I}$  left and both the atmospheric and the terrestrial  $^{129}\text{Xe}$  would have been equally abundant. Since this is not the case, the separation of the  $^{129}\text{Xe}$  from the Earth (outgassing), must have occurred while  $^{129}\text{I}$  was still present, i.e.



within a few  $^{129}\text{I}$  lifetimes, say  $50 \cdot 10^6$  yrs. (It must however be pointed out that, as Wetherill has noted, the argument is also consistent with no outgassing of the Earth at all, all the atmospheric  $^{129}\text{Xe}$  having perhaps been deposited in the atmosphere by impact).

We therefore conclude that the entire set of phenomena, (1) collapse of the nebula, (2) accretion of the Earth, (3) dissipation of the nebular remnant, (4) formation of the Earth's core, (5) formation of an atmosphere by impact volatiles plus outgassing and finally (6) contribution to the atmosphere by the second outgassing period, may have occurred within  $50\text{-}100 \cdot 10^6$  yrs, corresponding to the time when the sun entered the main sequence, (Fig. 4).

For our photochemical calculations, Section 8, we have assumed a background composition of the paleoatmosphere consistent with both the impact and outgassing scenarios.

## 7. PROTOSTARS AND THE ULTRAVIOLET FLUX

For a protostar evolving to the main sequence, theoretical models can be used to predict a few observational quantities such as surface temperature and luminosity. However, the models are not sufficient to predict accurately the ultraviolet flux emitted by a pre-main sequence star. Thus we employ ultraviolet observations of young solar-like stars as the best estimate of the UV flux emitted by the young sun.

Observations of pre-main sequence stars indicate that the stars pass through three identifiable stages. During the first stage, the star is still accreting material from its gaseous, dusty environment. The cocoon of dust largely shrouds the star, which is detectable only at infrared and radio wavelengths. Models indicate that a solar-like protostar passes through this stage in about 100 Kyr years (Stahler *et al.*, 1980).

The second stage, which is the best studied, begins as the star becomes visible at visual wavelengths. Several hundred such stars, known as the T Tauri stars, have been identified. The stars still possess an envelope or disk of gas and dust, but it has become thin enough for the stellar surface to be studied. The protostar has become truly "stellar" in structure, possessing a convective interior, a photosphere, and a bright chromosphere. The T Tauri phase is largely defined by the characteristic bright line and continuous emission spectrum, originating primarily in a dense, active chromosphere.

The end of the T Tauri stage can be estimated from the ages of the stars. Ages of 3 to 5 Myr are indicated by the association of the T Tauri

stars with other stars of known ages or from stability arguments (Herbig, 1962; 1970). It has been suggested that the T Tauri phase corresponds to the stage when the protostar's interior is completely convective (Jones and Herbig, 1979). If this is the case, then the theoretical models for stars of various masses may be used to indicate the endpoints of the T Tauri phase. For a solar-mass protostar, the phase would last 10 Myr. More massive stars evolve more quickly; a 2 solar-mass star passes through the phase in 2 Myr. Conversely, a less massive star of 0.7 solar masses passes through the convective phase in 40 Myr. The theoretical predictions of the evolution of a solar-like protostar in the Hertzsprung-Russell diagram are given in Figure 4. Evolutionary tracks for stars of 1.5, 1.0, and 0.5 solar masses are given for comparison. In addition, the time scale for the solar-mass star is indicated. The convective phase of the pre-main sequence evolution corresponds to the vertical portion of the tracks; i.e. the luminosity is decreasing but little change in surface temperature is seen. The change in luminosity is thus largely due to the decreasing radius of the star as it contracts. Superimposed on these evolutionary tracks are observational data for T Tauri stars found in the Taurus-Auriga dark clouds and in the Orion complex (data are from Cohen and Kuhl, 1979). If one compares the observational data and the theoretical tracks, then ages of 100 Kyr to 10 Myr are derived. The overall agreement of all these determinations is good, despite the expected problems of comparing observations of "real stars" to theoretical models. We can conclude, then, that a solar-mass star begins the T Tauri phase of evolution at an age of about 100 Kyr and continues until it is about 6 to 12 Myr of age.

The portion of the star's pre-main sequence evolution following the T Tauri phase comprises about 80% of the time required to reach the main-sequence. Theoretical models indicate that the star's interior develops a radiative core within its convective envelope. During this phase the protostar loses the bright emission and spectral features which make the T Tauri phase so identifiable. As a consequence, these stars, which have been called the post-T Tauri stars, have been found less frequently and are not as well studied. Herbig (1973) originally postulated the probable observational characteristics of the post-T Tauri stars. A handful of these stars have been unexpectedly discovered in recent years by observers using the Einstein X-ray satellite (Feigelson and Kriss, 1981; Walter and Kuhl, 1981). So far the ages of these stars do not appear greatly different from those of the T Tauri stars (Mundt *et al.*, 1983). Therefore clear, observed examples of solar-mass stars with ages of 10 to 50 Myr are lacking.

The sun is a relatively normal star of intermediate mass, temperature and luminosity. It is therefore very reasonable to assume that it once passed through the same three phases of protostellar evolution observed for other stars. This assumption allows us to draw upon ultraviolet observations of young stars to represent the probable ultraviolet spectrum of the young sun.

The brighter T Tauri stars have been observed by various investigators using the International Ultraviolet Explorer (IUE) satellite (Appenzeller *et al.*, 1980; Gahm *et al.*, 1979; Giampapa *et al.*, 1981; Imhoff and Giampapa, 1980; Brown *et al.*, 1981). It is thus possible to derive a reasonable ultraviolet spectrum which is typical of a solar-like star with an age of a few Myr. No IUE observations have been made of the first, infrared stage of a protostar's life. The surrounding dust shell is expected to absorb any ultraviolet radiation emitted by the star. A few observations have been made of the post-T Tauri stars. However, since the evolutionary status of the stars is uncertain and the IUE observations are few, we omit them from further discussion.

We have assembled IUE spectra of three well-observed T Tauri stars to represent a probable ultraviolet spectrum for the very young sun. The three stars, T Tauri, SU Aurigae, and RW Aurigae, represent a range of observational characteristics and thus should provide a reasonable sample of T Tauri ultraviolet spectra. We have reduced fourteen low-resolution IUE spectra of the three stars and formed an average ultraviolet spectrum from about 1225 to 3200 Angstroms. The very important hydrogen Lyman- $\alpha$  emission line is masked in our spectra by geocoronal hydrogen emission. However, a weak stellar feature can be discerned in one of our spectra of RW Aur, superimposed with the geocoronal emission. A rough estimate indicates that the observed stellar Lyman- $\alpha$  emission is about 1/10 the flux of the Balmer- $\alpha$  emission observed in the visible for this star (Kuhi, 1974). If one assumes that the same ratio applies to the other stars, then one would expect much lower Lyman- $\alpha$  fluxes for T Tau and SU Aur. This assumption is consistent with the non-detections of Lyman- $\alpha$  for two of these stars; therefore we adopt this estimate, that the Lyman- $\alpha$  flux is 0.1 times the Balmer- $\alpha$  flux for these stars. We have used published visual fluxes for the stars to complete the wavelength coverage required for the photochemical models (Kuhi, 1974). Small gaps in the ultraviolet and visual data occur where no strong emission lines are expected; therefore simple interpolations were performed for these wavelengths. The average spectrum for the entire range of wavelengths from the ultraviolet

through the visual was formed, corrected for 0.5 magnitudes of visual extinction, and reduced to a distance of 1 AU. The choice of visual extinction was made as a conservative estimate, expected to err on the side of somewhat smaller ultraviolet fluxes, compared to derived values for T Tau, SU Aur, and RW Aur (about 1.4, 0.9, and 0.2 mag respectively).

Figure 5 compares our typical T Tauri spectrum to those of the present sun from 1200 to 7200 Å. The sun, during its T Tauri phase, was more luminous at all wavelengths than it is now. The strong chromospheric lines of hydrogen Lyman- $\alpha$  (1215 Å), the doublet of ionized magnesium (2800 Å), and hydrogen Balmer- $\alpha$  (6563 Å) are clearly seen in the T Tauri-phase spectrum. In Figure 6 we have converted the T Tauri-phase and present solar fluxes to units of photons per bin, as used in our photochemical code. The discontinuity at 6500 Å reflects a change in the bin size. Figure 7 shows the ratio of the T Tauri-phase fluxes to the present solar fluxes, using a logarithmic scale. The enhancement of the ultraviolet fluxes, which are very important in many photochemical processes, becomes obvious in this figure. The far-ultraviolet fluxes during the T Tauri phase were up to 10,000 times those currently observed for the sun. This result agrees with the rougher estimate given in our previous paper (Canuto *et al.*, 1982).

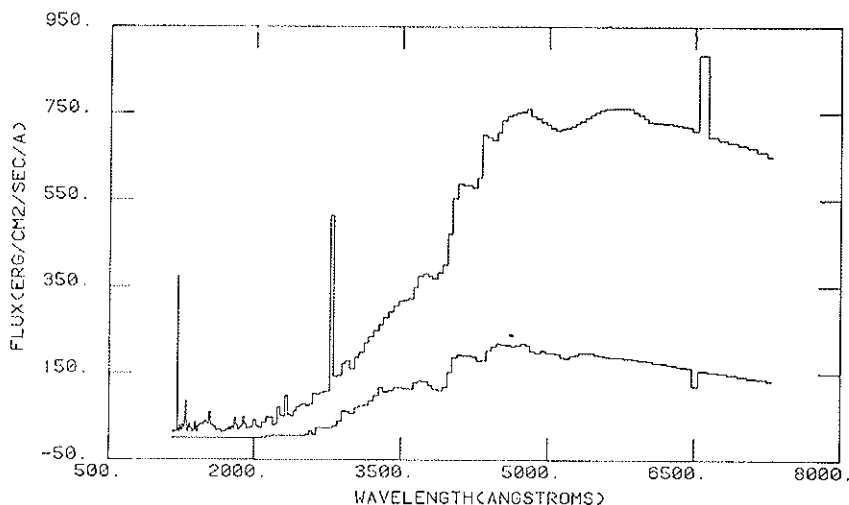


FIG. 5. The T Tauri-phase fluxes (top) compared to present solar fluxes (Ackermann, 1971) for ultraviolet and visual wavelengths. The strong emission lines of Lyman- $\alpha$  (1215 Å), MgII (2800 Å) and Balmer- $\alpha$  (6563 Å) can be seen in the T Tauri spectrum. Fluxes have been reduced to those intercepted at a distance of 1 AU from the star.

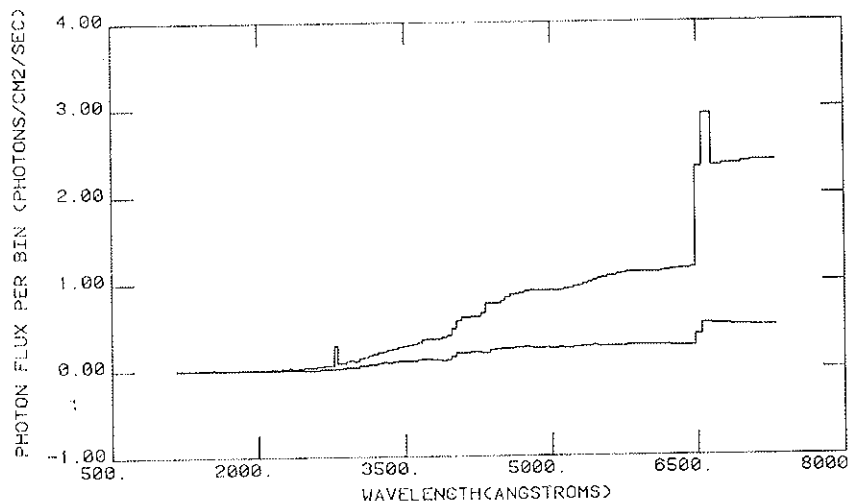


FIG. 6. T Tauri-phase and present solar fluxes converted to photons per bin, as required by the photochemical code. The discontinuity near 6500 Å represents a change in the bin size.

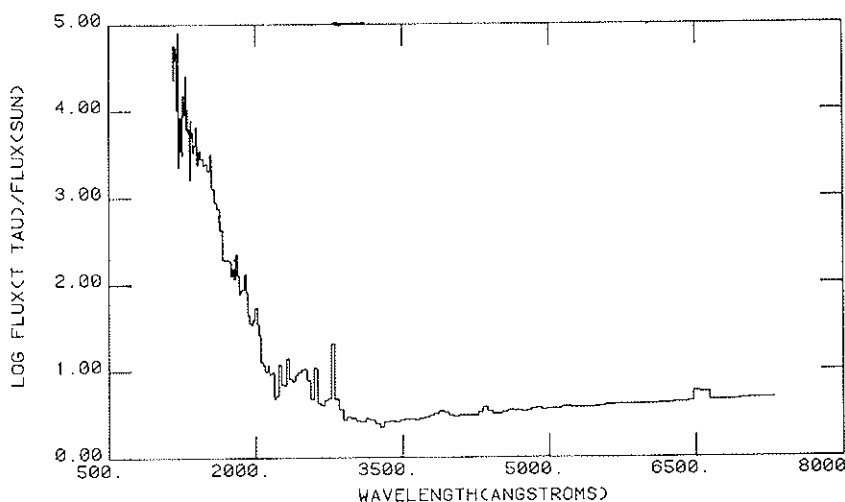


FIG. 7. The ratio of T Tauri-phase fluxes to the present solar fluxes, using a logarithmic scale. Although the enhancement of the T Tauri over the solar fluxes is seen at all wavelengths, it is the most dramatic in the far-ultraviolet.

The enhancement of the T Tauri-phase ultraviolet flux over the present sun's fluxes is clearly very wavelength-dependent (see also Table 1). Thus use of this average T Tauri spectrum should represent a significant improvement to our wavelength-independent treatment used previously as input for the photochemical models (Canuto *et al.*, 1982).

The T Tauri phase represents a very early stage in the evolution of a solar-like protostar. Is it possible to estimate what changes occur to the ultraviolet spectrum during the 80% of the protostar's life after the T Tauri phase? A study of the variation of the ultraviolet emission lines with age has been performed for young main-sequence stars (Boesgaard and Simon, 1982). They find that the emission line fluxes decrease as  $t^{-1/2}$  (although some of the higher temperature lines may fall off more rapidly). If this is the case for stars which have not yet reached the main sequence, then we can estimate the overall decrease in the ultraviolet fluxes with time after the T Tauri phase (see Table 2 in Canuto *et al.*, 1982). We find that the far-ultraviolet luminosity of the sun when it reached the main sequence was 100 times its present value. Thus with some small caveats the results obtained here for the T Tauri stars may be applied to the later stages of the sun's pre-main sequence evolution.

#### 8. THE PHOTOCHEMISTRY OF OXYGEN, OZONE, AND FORMALDEHYDE IN THE EARLY ATMOSPHERE

In the prebiological early atmosphere, the photolysis of water vapor ( $H_2O$ ) and carbon dioxide ( $CO_2$ ) led to the photochemical production of

TABLE 1 - Solar energy flux averaged over the Earth during T-Tauri phase (Values in parentheses correspond to today).

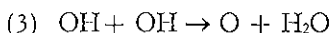
| Source          | Energy (cal cm <sup>-2</sup> yr <sup>-1</sup> ) |
|-----------------|---|
| Total Radiation | 4.6 10 <sup>6</sup> (.26 10 <sup>6</sup> )      |
| UV light        |   |
| < 3000 Å        | 2.4 10 <sup>4</sup> (.34 10 <sup>4</sup> )      |
| < 2500 Å        | 9.9 10 <sup>3</sup> (.56 10 <sup>3</sup> )      |
| < 2000 Å        | 5.0 10 <sup>3</sup> (40)                        |
| < 1500 Å        | 2.2 10 <sup>3</sup> (1.7)                       |

three biologically-significant species: molecular oxygen ( $O_2$ ), ozone ( $O_3$ ), and formaldehyde ( $H_2CO$ ). Oxygen is important due to its detrimental effects on the origin and evolution of life; i.e., laboratory chemical evolution experiments cannot proceed to the synthesis of complex organic molecules in the presence of free oxygen above trace levels. Ozone, a photochemical product of oxygen, absorbs solar ultraviolet (UV) radiation between 200 and 300 nm and eventually shielded the Earth's surface from this biologically lethal radiation. Formaldehyde was a key molecule in the process of chemical evolution — that is the formation of complex organic molecules. In the present atmosphere,  $H_2CO$  is a trace species photochemically produced via the methane ( $CH_4$ ) oxidation chain (for example, see Levine and Allario, 1982) with the precursor  $CH_4$  being produced via biogenic activity. However, because the lifetime of  $CH_4$  in the prebiological atmosphere was extremely short due to photochemical destruction, if it was present at all (Levine *et al.*, 1982), the question then arises as to how to produce  $H_2CO$  in the absence of  $CH_4$ . A prebiological photochemical source for  $H_2CO$  initiated by the photolysis of  $H_2O$  and  $CO_2$  has been suggested by Pinto *et al.* (1980). The photochemical and chemical processes leading to the production of  $O_2$ ,  $O_3$ , and  $H_2CO$  in the prebiological atmosphere will be summarized and then theoretical calculations obtained with a one-dimensional photochemical of the prebiological paleo-atmosphere will be discussed.

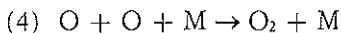
The photochemical production of  $O_2$ ,  $O_3$ , and  $H_2CO$  is initiated by the photolysis of  $H_2O$  and  $CO_2$ :

- (1)  $H_2O + h\nu \rightarrow OH + H$  ( $\lambda \leq 240$  nm), and  
(OH = hydroxyl radical; H = atomic hydrogen)
- (2)  $CO_2 + h\nu \rightarrow CO + O$  ( $\lambda < 230$  nm)  
(CO = carbon monoxide; O = atomic oxygen)

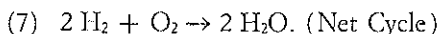
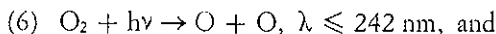
Reaction (1) leads to the production of oxygen atoms (O) through:



The oxygen atoms formed in reactions (2) and (3) form molecular oxygen ( $O_2$ ) through the following reactions:



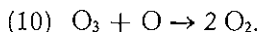
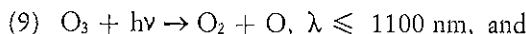
The destruction of  $O_2$  is controlled by its photolysis (6) and its chemical reaction with  $H_2$



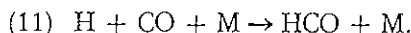
Closely coupled to the origin and evolution of  $O_2$  is the origin and evolution of  $O_3$ .  $O_3$  is photochemically produced through the reaction:



$O_3$  is photochemically destroyed through direct photolysis (9), reaction with  $O$  (10), and through a series of catalytic cycles involving the oxides of nitrogen, hydrogen, and chlorine:



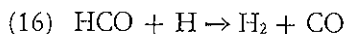
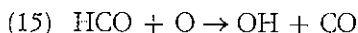
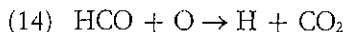
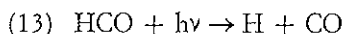
The photochemical production of  $H_2CO$  proceeds with reaction  $H$  and  $CO$  formed in (1) and (2), leading to the formation of the formyl radical ( $HCO$ ):



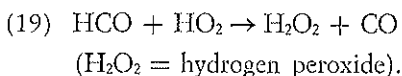
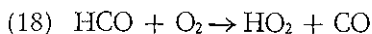
The reaction between two  $HCO$  radicals forms  $H_2CO$ :



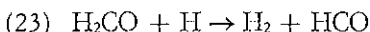
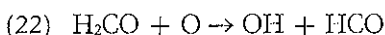
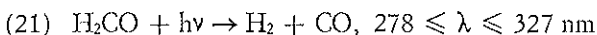
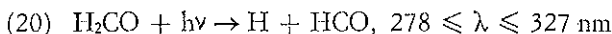
The radical is photochemically destroyed by direct photolysis (13) and by reactions with  $O$ ,  $H$ ,  $OH$ ,  $O_2$ , and  $HO_2$  (hydroperoxyl radical) (14) through (19):







$\text{H}_2\text{CO}$  is photochemically destroyed through direct photolysis (20) and (21) and by reactions with O, H, and OH:



Once photochemically formed in the early atmosphere via reactions (1), (2), (11), and (12),  $\text{H}_2\text{CO}$ , being very water soluble, rained out of the atmosphere. In the early oceans,  $\text{H}_2\text{CO}$  accumulated and eventually underwent aqueous solution polymerization reactions leading to the abiotic synthesis of organic molecules of increasing complexity (Pinto *et al.*, 1980).

We have calculated the vertical distributions of  $\text{O}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{CO}$  as well as O, CO, H, OH,  $\text{HO}_2$ , and  $\text{H}_2\text{O}_2$  by simultaneous solution of reactions (1) to (24), along with other reactions that govern the chemical transformations of the hydrogen species (H, OH,  $\text{HO}_2$ , and  $\text{H}_2\text{O}_2$ ). The total reaction scheme includes nine photochemical processes, 37 chemical processes, and the rainout loss of the water-soluble species ( $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}_2$ ). These photochemical, chemical, and rainout processes and their reaction rates are summarized in Table 2. In our calculations, we have assumed that molecular nitrogen ( $\text{N}_2$ ), at a partial pressure of 0.8 bar, is the major atmospheric constituent.  $\text{N}_2$  is a chemically-inert gas that participates in chemical reactions only as a third body (M). The  $\text{H}_2\text{O}$  vapor mixing ratio is specified in the troposphere (surface to 14.5 km) and varies from  $1.2 \times 10^{-2}$  at the surface to  $4.6 \times 10^{-7}$  at 14.5 km (the tropopause in the model). Above the tropopause, the distribution of  $\text{H}_2\text{O}$  vapor is calculated as a chemically-active species using a continuity/transport equation for  $\text{H}_2\text{O}$ . Because of the lack of information concerning the level of  $\text{CO}_2$  in the prebiological paleoatmosphere, we have performed theoretical calculations for two different values: the pre-industrial level of

TABLE 2 - Photochemical and Chemical Reactions.

| Reaction Number | Reaction                               | Rate Constant*  |                       |
|-----------------|--|---|-----------------------|
|                 |  | (sec <sup>-1</sup> , cm <sup>3</sup> sec <sup>-1</sup> or cm <sup>6</sup> sec <sup>-1</sup> ) |                       |
| J1:             | $O_2 + h\nu \rightarrow O + O$         | $4.7 \times 10^{-10}$   | $6.3 \times 10^{-9}$  |
| J2:             | $O_3 + h\nu \rightarrow O + O_2$       | $2.2 \times 10^{-4}$  | $8.5 \times 10^{-4}$  |
| J3:             | $O_3 + h\nu \rightarrow O(^1D) + O_2$  | $4.4 \times 10^{-3}$  | $2.8 \times 10^{-2}$  |
| J4:             | $H_2O + h\nu \rightarrow OH + H$       | $1.1 \times 10^{-14}$   | $5.1 \times 10^{-13}$ |
| J5:             | $H_2O_2 + h\nu \rightarrow OH + OH$    | $5.3 \times 10^{-5}$  | $4.4 \times 10^{-4}$  |
| J6:             | $H_2CO + h\nu \rightarrow H + HCO$     | $4.8 \times 10^{-5}$  | $1.6 \times 10^{-4}$  |
| J7:             | $H_2CO + h\nu \rightarrow H_2 + CO$    | $4.9 \times 10^{-5}$  | $1.4 \times 10^{-4}$  |
| J8:             | $CO_2 + h\nu \rightarrow CO + O$       | $1.3 \times 10^{-12}$   | $6.3 \times 10^{-11}$ |
| J9:             | $HCO + h\nu \rightarrow H + CO$        | $1.3 \times 10^{-2}$  | $5.8 \times 10^{-2}$  |
| 1               | $O + O_2 + M \rightarrow O_3 + M$      | $1.1 \times 10^{-34}$   | exp (510/T)           |
| 2               | $O + O_3 \rightarrow 2O_2$             | $1.5 \times 10^{-11}$   | exp(-2218/T)          |
| 3               | $O(^1D) + O_2 \rightarrow O + O_2$     | $3.2 \times 10^{-11}$   | exp (67/T)            |
| 4               | $O(^1D) + N_2 \rightarrow O + N_2$     | $2.0 \times 10^{-11}$   | exp (107/T)           |
| 5               | $H_2O + O(^1D) \rightarrow 2OH$        | $2.3 \times 10^{-10}$   |                       |
| 6               | $H + O_2 + M \rightarrow HO_2 + M$     | $2.1 \times 10^{-32}$   | exp (290/T)           |
| 7               | $H + O_3 \rightarrow OH + O_2$         | $1.4 \times 10^{-10}$   | exp (-470/T)          |
| 8               | $OH + O \rightarrow H + O_2$           | $4.0 \times 10^{-11}$   |                       |
| 9               | $OH + O_3 \rightarrow HO_2 + O_2$      | $1.6 \times 10^{-12}$   | exp (-940/T)          |
| 10              | $OH + OH \rightarrow H_2O + O$         | $1.0 \times 10^{-12}$   | exp (-500/T)          |
| 11              | $HO_2 + O \rightarrow OH + O_2$        | $3.5 \times 10^{-11}$   |                       |
| 12              | $HO_2 + O_3 \rightarrow OH + 2O_2$     | $1.1 \times 10^{-14}$   | exp (-580/T)          |
| 13              | $HO_2 + OH \rightarrow H_2O + O_2$     | $4.0 \times 10^{-11}$   |                       |
| 14              | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $2.5 \times 10^{-12}$   |                       |
| 15              | $H_2O_2 + OH \rightarrow HO_2 + H_2O$  | $1.0 \times 10^{-11}$   | exp (-750/T)          |
| 16              | $O(^1D) + H_2 \rightarrow OH + H$      | $9.9 \times 10^{-11}$   |                       |
| 17              | $OH + OH + M \rightarrow H_2O_2 + M$   | See JPL Publication 82-57 (1982)  |                       |
| 18              | $H_2O_2 + O \rightarrow OH + HO_2$     | $2.8 \times 10^{-12}$   | exp(-2125/T)          |
| 19              | $H_2 + OH \rightarrow H_2O + H$        | $1.2 \times 10^{-11}$   | exp(-2200/T)          |
| 20              | $H_2CO + OH \rightarrow HCO + H_2O$    | $1.7 \times 10^{-11}$   | exp(-100/T)           |
| 21              | $H_2CO + O \rightarrow OH + HCO$       | $2.8 \times 10^{-11}$   | exp(-1540/T)          |
| 22              | $HCO + O_2 \rightarrow CO + HO_2$      | $5.0 \times 10^{-12}$   |                       |
| 23              | $CO + OH \rightarrow H + CO_2$         | See JPL Publication 82-57 (1981)  |                       |

\* Photolysis rates (sec<sup>-1</sup>) for H<sub>2</sub> = 17 ppmv are given for UV = 1 (first value) and UV = T-Tauri phase.

TABLE 2 - (Continued).

| Reaction Number | Reaction  | Rate Constant<br>( $\text{sec}^{-1}$ , $\text{cm}^3 \text{sec}^{-1}$ or $\text{cm}^6 \text{sec}^{-1}$ ) |
|-----------------|---|---|
| 24              | $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$      | $2.8 \times 10^{-34} \exp(710/T)$   |
| 25              | $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$      | $8.3 \times 10^{-33}$   |
| 26              | $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$                | $3.0 \times 10^{-14} \exp(-4480/T)$   |
| 27              | $\text{H} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2$            | $4.7 \times 10^{-11} (\times 0.29)$   |
| 28              | $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$      | $4.7 \times 10^{-11} (\times 0.02)$   |
| 29              | $\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$              | $4.7 \times 10^{-11} (\times 0.69)$   |
| 30              | $\text{H} + \text{CO} + \text{M} \rightarrow \text{HCO} + \text{M}$     | $2.0 \times 10^{-33} \exp(-850/T)$  |
| 31              | $\text{H} + \text{HCO} \rightarrow \text{H}_2 + \text{CO}$              | $3.0 \times 10^{-10}$   |
| 32              | $\text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$   | $6.3 \times 10^{-11}$   |
| 33              | $\text{OH} + \text{HCO} \rightarrow \text{H}_2\text{O} + \text{CO}$     | $5.0 \times 10^{-11}$   |
| 34              | $\text{O} + \text{HCO} \rightarrow \text{H} + \text{CO}_2$              | $1.0 \times 10^{-10}$   |
| 35              | $\text{O} + \text{HCO} \rightarrow \text{OH} + \text{CO}$               | $1.0 \times 10^{-10}$   |
| 36              | $\text{HO}_2 + \text{HCO} \rightarrow \text{H}_2\text{O}_2 + \text{CO}$ | $1.0 \times 10^{-11}$   |
| 37              | $\text{H}_2\text{CO} + \text{H} \rightarrow \text{H}_2 + \text{HCO}$    | $2.8 \times 10^{-11} \exp(-1540/T)$   |
| 38              | $\text{H}_2\text{CO}$ and $\text{H}_2\text{O}_2$ rainout                | $1.0 \times 10^{-6} \text{ s}^{-1}$   |

280 ppmv ( $\text{CO}_2 = 1$ ) and for 100 times this value ( $\text{CO}_2 = 100$ ). We have also added trace volcanic gases — molecular hydrogen ( $\text{H}_2$ ) and carbon monoxide ( $\text{CO}$ ) — in our model. Calculations were performed for two values of  $\text{H}_2$  surface mixing ratio: 17 ppmv (Kasting and Walker, 1981) and  $10^{-3}$  (Pinto *et al.*, 1980). The surface volcanic flux of  $\text{CO}$  was taken to be  $2 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$  (Kasting and Walker, 1981). Methane and ammonia were not included as constituents of the prebiological paleo-atmosphere for reasons discussed in Levine (1982) and Levine *et al.* (1982). The U.S. Standard Atmosphere Mid-Latitude Spring/Autumn temperature profile is specified in the troposphere. An early atmosphere temperature profile for the  $\text{O}_3$ -deficient stratosphere that decreases linearly from the tropopause to the mesopause is used. This profile is based on coupled photochemical-radiative equilibrium temperature calculations (Levine and Boughner, 1979). Photodissociation rates are diurnally averaged for a latitude of  $30^\circ$  and solar declination of  $0^\circ$  (Rundel, 1977). The model includes the solar spectrum from 110 to 735 nm (Ackermann, 1971). We have performed calculations for the present ultraviolet flux ( $\text{UV} = 1$ )

(Ackermann, 1971) and for two additional values: 300 times the present value and for the wavelength-dependent ultraviolet flux emitted by early sun-like stars (T-Tauri) as observed with the International Ultraviolet Explorer (IUE) satellite (Canuto *et al.*, 1982, and Canuto *et al.*, 1983). The model extends from the surface to 53.5 km with 1 kilometer spatial resolution between the surface and 10 km, and 1.5 kilometers spatial resolution between 10 and 53.5 km. Further details about the model are given in Levine *et al.* (1981) and Levine *et al.* (1982).

### a) Results

The effects of  $H_2$  on the calculated vertical distribution of  $O_2$  for preindustrial levels of  $CO_2$  (280 ppmv) for three different values of solar ultraviolet radiation (UV): 1,300, and the T-Tauri flux, are shown in Figure 8 (for  $H_2 = 17$  ppmv) and Figure 9 (for  $H_2 = 10^{-3}$ ). We found higher  $O_2$  levels for lower values of  $H_2$ . This is not surprising since higher values of  $H_2$  result in the more rapid loss of  $O_2$  due to the reformation of  $H_2O$  (reaction (7)). For  $H_2 = 17$  ppmv, the surface  $O_2$  mixing ratio increased from  $10^{-14}$  to  $10^{-11}$  as the solar UV flux was increased. For  $H_2 = 10^{-3}$ , the surface  $O_2$  mixing ratio increased from  $10^{-17}$  to almost  $10^{-13}$  for the same increase in the UV flux.

The effects of  $H_2$  on the calculated vertical distribution of  $O_2$  for enhanced levels of  $CO_2$  (100 times the pre-industrial level, corresponding

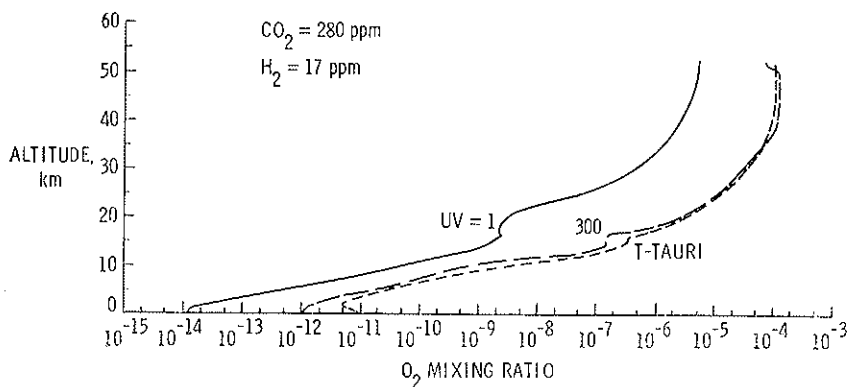


FIG. 8. Vertical distribution of molecular oxygen ( $O_2$ ) mixing ratio in prebiological paleo-atmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 17 ppmv, carbon dioxide ( $CO_2$ ) = 280 ppmv, and three different solar ultraviolet fluxes.

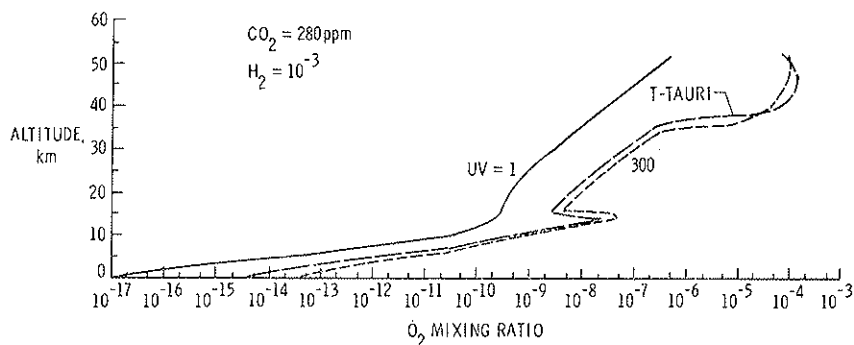


FIG. 9. Vertical distribution of molecular oxygen ( $O_2$ ) mixing ratio in prebiological paleo-atmosphere. Calculations for molecular hydrogen ( $H_2$ ) =  $10^{-3}$ , carbon dioxide ( $CO_2$ ) = 280 ppmv, and three different solar ultraviolet fluxes.

to a mixing ratio of  $2.8 \times 10^{-2}$  or 0.028 or 2.8 percent by volume) for three different values of solar UV flux are shown in Figure 10 ( $H_2$  = 17 ppmv) and Figure 11 ( $H_2$  =  $10^{-3}$ ). For  $H_2$  = 17 ppmv, the surface  $O_2$  mixing ratio increased from less than  $10^{-10}$  to more than  $10^{-9}$  (several parts per billion by volume) as the UV flux was increased. The calculations

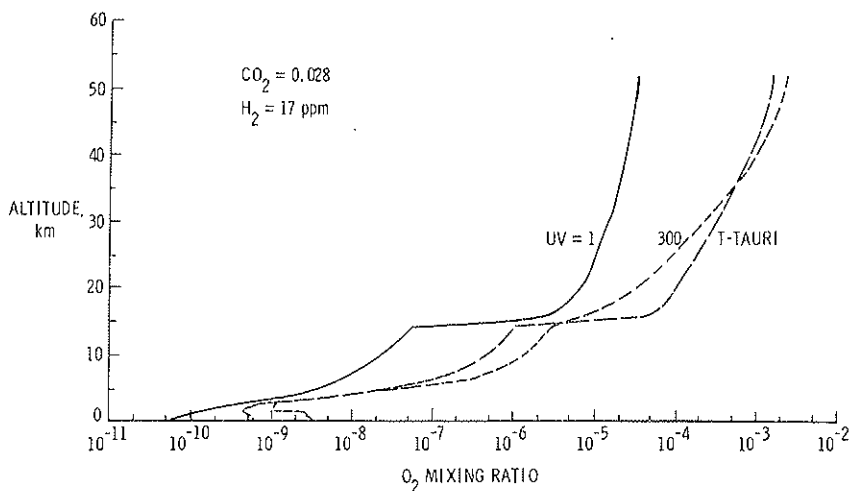


FIG. 10. Vertical distribution of molecular oxygen ( $O_2$ ) mixing ratio in prebiological paleo-atmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 17 ppmv, carbon dioxide ( $CO_2$ ) = 0.028, and three different solar ultraviolet fluxes.

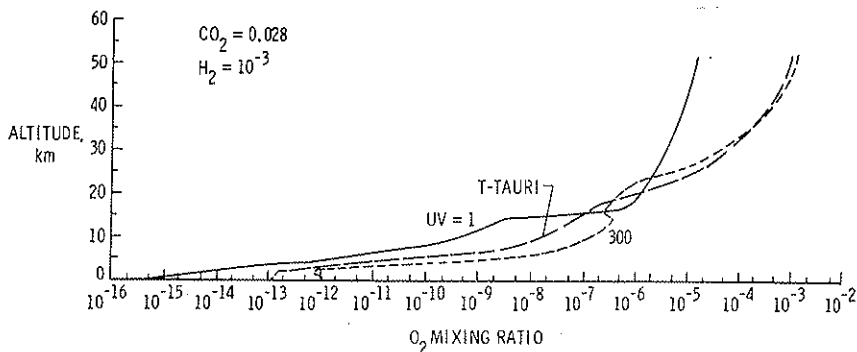


FIG. 11. Vertical distribution of molecular oxygen ( $O_2$ ) mixing ratio in prebiological paleo-atmosphere. Calculations for molecular hydrogen ( $H_2$ ) =  $10^{-3}$ , carbon dioxide ( $CO_2$ ) = 0.028, and three different solar ultraviolet fluxes.

shown in this figure represent our maximum calculated levels of  $O_2$ . For  $H_2 = 10^{-3}$ , the surface  $O_2$  mixing ratio increased from  $10^{-15}$  to  $10^{-12}$  (parts per trillion by volume) as the UV flux was increased.

Surface concentrations of  $O_2$ , as well as  $O_3$ ,  $H_2CO$ ,  $O$ ,  $OH$ ,  $CO$ ,  $H$ , and  $HCO$  as a function of  $H_2$ ,  $CO$ , and solar UV levels, are summarized in Table 3.

The effects of  $H_2$ ,  $CO_2$ , and UV levels on the calculated distribution of  $O_3$  corresponding to the previous four  $O_2$  calculation figures are shown in Figures 12-15. Figures 12 and 13 are for the pre-industrial level of  $CO_2$ . For  $H_2 = 17$  ppmv (Figure 12), the surface number density of  $O_3$  increased from less than  $10$  to more than  $10^3$  molecules  $cm^{-3}$  as the solar UV was increased. For  $H_2 = 10^{-3}$  (Figure 13), the surface number density of  $O_3$  increased from less than  $10^{-4}$  to more than  $10^{-1}$  molecules  $cm^{-3}$  as the solar UV was increased. Figures 14 and 15 are for enhanced levels of  $CO_2$  ( $CO_2 = 0.028$ ). For  $H_2 = 17$  ppmv (Figure 14), the surface number density of  $O_3$  increased from  $10^5$  to  $10^7$  molecules  $cm^{-3}$  as the solar UV was increased. For  $H_2 = 10^{-3}$  (Figure 15), the surface number density of  $O_3$  increased from  $10^{-1}$  to  $10^2$  molecules  $cm^{-3}$  as the solar UV was increased.

For  $O_3$  shielding considerations, the total atmospheric burden or column density of  $O_3$  (molecules  $cm^{-2}$ ) above the surface is a more relevant quantity. The column density represents the integral over the  $O_3$  profiles given in Figures 12-15. The  $O_3$  column density as a function of  $H_2$ ,  $CO_2$ , and solar UV levels is summarized in Table 4. Even though certain com-

TABLE 3 - Surface concentration of several species ( $\text{cm}^{-3}$ ) as a function of UV flux and  $\text{CO}_2$  and  $\text{H}_2$  level.

| I. $\text{H}_2 = 17 \text{ ppm}$ |                   |                     |                    |                     |
|----------------------------------|-------------------|---------------------|--------------------|---------------------|
| Species                          | UV = 1            |                     | UV = T-Tauri phase |                     |
|                                  | $\text{CO}_2 = 1$ | $\text{CO}_2 = 100$ | $\text{CO}_2 = 1$  | $\text{CO}_2 = 100$ |
| O                                | 8.95 (6)          | 4.47 (7)            | 4.92 (8)           | 1.96 (9)            |
| $\text{O}_2$                     | 2.72 (5)          | 1.36 (9)            | 2.33 (7)           | 1.29 (10)           |
| $\text{O}_3$                     | 5.66              | 1.69 (5)            | 2.20 (3)           | 1.46 (7)            |
| OH                               | 4.13 (3)          | 1.51 (4)            | 2.28 (5)           | 6.66 (5)            |
| CO                               | 5.09 (11)         | 7.86 (13)           | 1.10 (11)          | 5.16 (13)           |
| H                                | 3.24 (7)          | 4.09 (6)            | 1.36 (9)           | 1.28 (8)            |
| HCO                              | 1.39 (6)          | 2.06 (7)            | 5.58 (5)           | 2.50 (7)            |
| $\text{H}_2\text{CO}$            | 1.62 (6)          | 2.65 (8)            | 3.38 (4)           | 7.17 (7)            |
| $\text{CO}/\text{CO}_2$          | 9.02 (-5)         | 1.39 (-4)           | 1.95 (-5)          | 9.15 (-5)           |
| II. $\text{H}_2 = 10^{-3}$       |                   |                     |                    |                     |
| O                                | 2.10 (5)          | 6.57 (6)            | 9.49 (6)           | 1.44 (8)            |
| $\text{O}_2$                     | 1.87 (2)          | 1.20 (4)            | 6.12 (4)           | 1.99 (6)            |
| $\text{O}_3$                     | 1.07 (-4)         | 2.21 (-1)           | 2.18 (-1)          | 1.15 (2)            |
| OH                               | 7.64 (1)          | 2.60 (2)            | 3.67 (3)           | 1.45 (4)            |
| CO                               | 3.09 (13)         | 3.63 (15)           | 2.66 (13)          | 2.37 (15)           |
| H                                | 3.46 (6)          | 2.32 (5)            | 4.34 (7)           | 8.60 (6)            |
| HCO                              | 1.50 (7)          | 7.95 (7)            | 3.26 (7)           | 3.55 (8)            |
| $\text{H}_2\text{CO}$            | 4.14 (8)          | 4.12 (9)            | 3.79 (8)           | 2.43 (10)           |
| $\text{CO}/\text{CO}_2$          | 5.48 (-3)         | 6.44 (-3)           | 4.72 (-3)          | 4.20 (-3)           |

binations of  $\text{H}_2$ ,  $\text{CO}_2$ , and solar UV flux result in  $\text{O}_3$  column densities as high as  $10^{16}$  molecules  $\text{cm}^{-2}$ , this is still significantly below the value needed for shielding of the surface from solar ultraviolet radiation of about  $6 \times 10^{18}$  molecules  $\text{cm}^{-2}$ . The present  $\text{O}_3$  column density, which varies with latitude and season, is about  $1 \times 10^{19}$  molecules  $\text{cm}^{-3}$ . Therefore, we conclude that prebiological levels of  $\text{O}_3$  offered no shielding of the surface from biologically lethal solar ultraviolet radiation (200-300 nm). The problem of shielding is further complicated by the enhanced levels of ultraviolet radiation that the early sun may have emitted (Canuto *et al.*, 1982; Canuto *et al.*, 1983).

The effects of  $\text{H}_2$ ,  $\text{CO}_2$ , and solar UV flux on the vertical distribution of  $\text{H}_2\text{CO}$  are summarized in Figure 16 ( $\text{H}_2 = 17 \text{ ppmv}$ ) and Figure 17

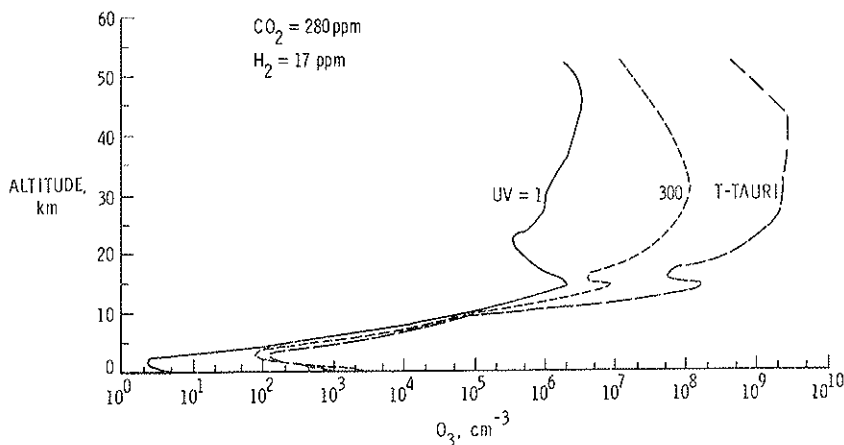


Fig. 12. Vertical distribution of ozone ( $\text{O}_3$ ) concentration (molecules  $\text{cm}^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $\text{H}_2$ ) = 17 ppmv, carbon dioxide ( $\text{CO}_2$ ) = 280 ppmv, and three different solar ultraviolet fluxes.

( $\text{H}_2 = 10^{-3}$ ). For  $\text{H}_2 = 17$  ppmv, the  $\text{H}_2\text{CO}$  profiles exhibited a range of surface concentrations from  $10^4$  to  $10^8$  molecules  $\text{cm}^{-3}$  as the  $\text{CO}_2$  and solar UV flux were increased. For  $\text{H}_2 = 10^{-3}$ , the profiles exhibited a more constant value of between  $10^9$  and  $10^{10}$  molecules  $\text{cm}^{-3}$  as the  $\text{CO}_2$  and solar UV flux were increased. Maximum surface  $\text{H}_2\text{CO}$  number densities corresponded to the high  $\text{H}_2$  cases ( $10^{-3}$ ).

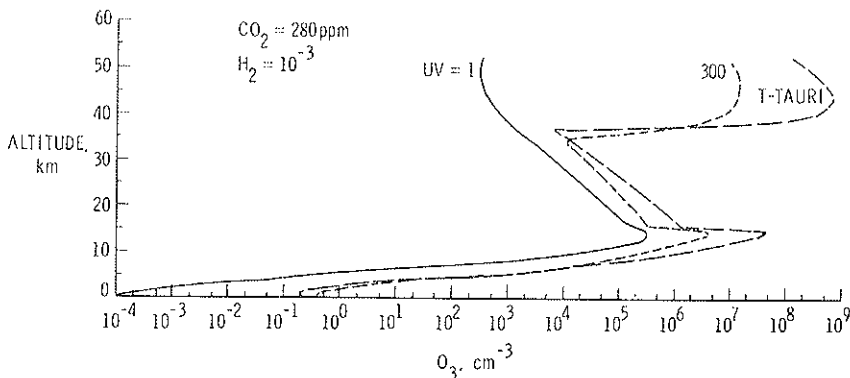


Fig. 13. Vertical distribution of ozone ( $\text{O}_3$ ) concentration (molecules  $\text{cm}^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $\text{H}_2$ ) =  $10^{-3}$ , carbon dioxide ( $\text{CO}_2$ ) = 280 ppmv, and three different solar ultraviolet fluxes.



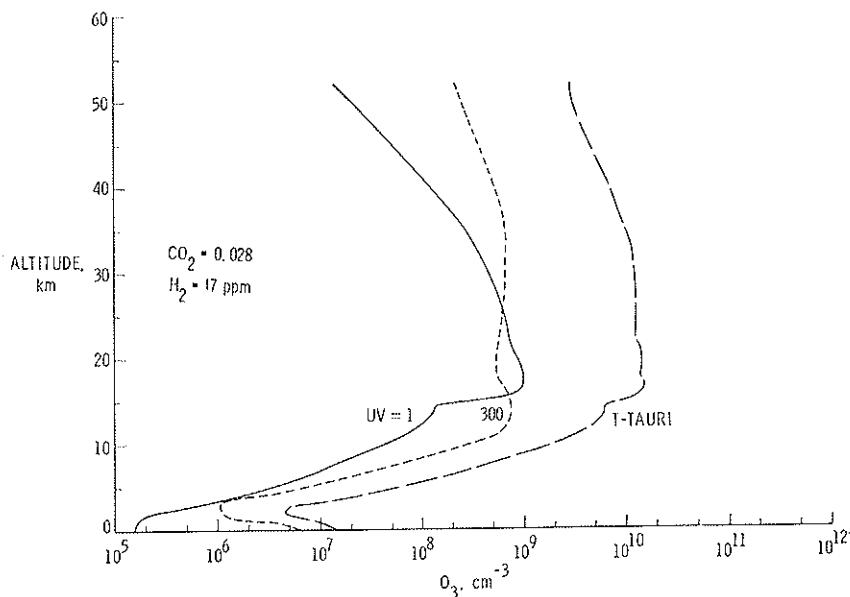


FIG. 14. Vertical distributions of ozone ( $O_3$ ) concentration (molecules  $cm^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 17 ppmv, carbon dioxide ( $CO_2$ ) = 0.028, and three different solar ultraviolet fluxes.

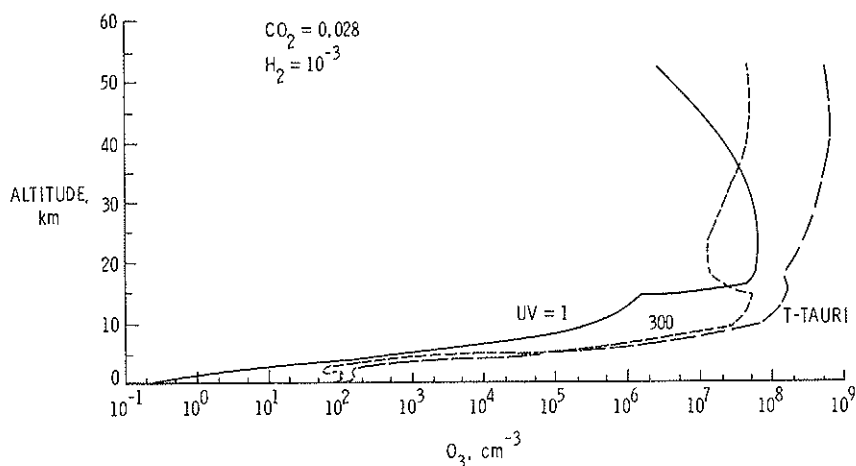


FIG. 15. Vertical distribution of ozone ( $O_3$ ) concentration (molecules  $cm^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $H_2$ ) =  $10^{-3}$ , carbon dioxide ( $CO_2$ ) = 0.028, and three different solar ultraviolet fluxes.

TABLE 4 - Column Densities of  $O_3$  and  $H_2CO$  (molecules  $cm^{-2}$ ).

|                 | $O_3$      |              |                    |              |
|-----------------|------------|--------------|--------------------|--------------|
|                 | UV = 1     |              | UV = T-Tauri phase |              |
|                 | $CO_2 = 1$ | $CO_2 = 100$ | $CO_2 = 1$         | $CO_2 = 100$ |
| $H_2 = 17$ ppmv | 3.3(12)    | 1.5 (15)     | 7.4(15)            | 4.05(16)     |
| $H_2 = 10^{-3}$ | 2.1(11)    | 1.3 (14)     | 6.5(14)            | 2.01(15)     |
| $H_2CO$         |            |              |                    |              |
| $H_2 = 17$ ppmv | 5.4(11)    | 7.34(13)     | 5.9(9)             | 5.45(13)     |
| $H_2 = 10^{-3}$ | 8.6(14)    | 2.02(15)     | 3.7(14)            | 1.1 (16)     |

To calculate the rainout rate of  $H_2CO$ , the total atmospheric burden or column density (molecules  $cm^{-2}$ ) must be known. The  $H_2CO$  column density as a function of  $H_2$ ,  $CO_2$ , and solar UV flux levels is summarized in Table 4. The surface production and loss rates, including the loss due to rainout of  $H_2CO$  as a function of  $H_2$ ,  $CO_2$ , and solar UV levels, are summarized in Table 5. The last entries in this table summarize the rainout fluxes of  $H_2CO$  (molecules  $cm^{-2} sec^{-1}$ ). The rainout flux is the product

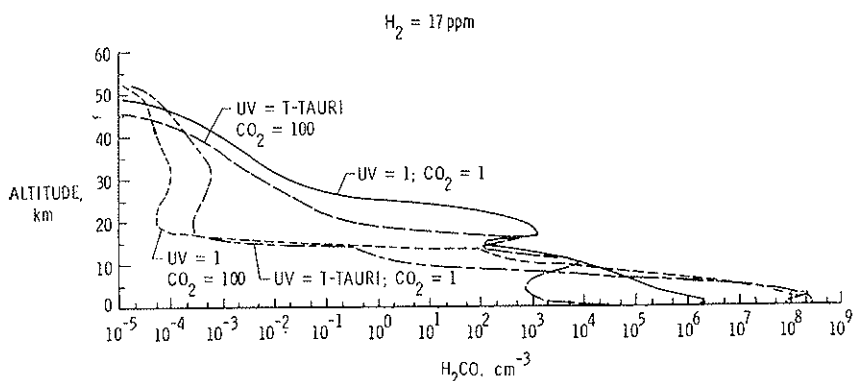


FIG. 16. Vertical distribution of formaldehyde ( $H_2CO$ ) concentration (molecules  $cm^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 17 ppmv and four different combinations of carbon dioxide ( $CO_2 = 1$  and 100) and solar ultraviolet radiation (UV = 1 and T-Tauri).

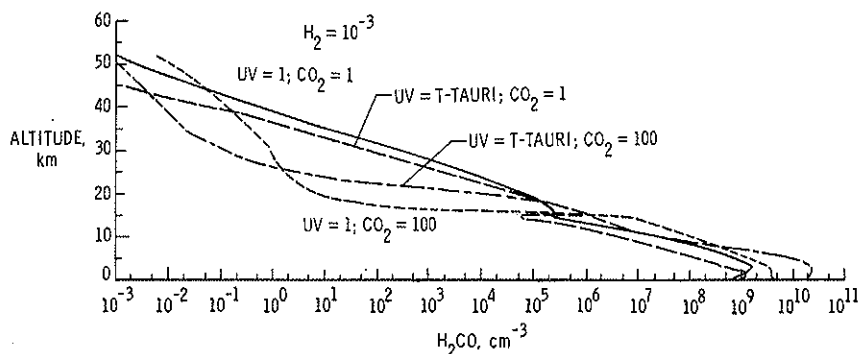


FIG. 17. Vertical distribution of formaldehyde ( $\text{H}_2\text{CO}$ ) concentration (molecules  $\text{cm}^{-3}$ ) in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $\text{H}_2 = 10^{-3}$ ) and for four different combinations of carbon dioxide ( $\text{CO}_2 = 1$  and 100) and solar ultraviolet radiation ( $\text{UV} = 1$  and T-Tauri).

TABLE 5 - Surface Production and Loss Rates for  $\text{H}_2\text{CO}$  as a function of UV flux and  $\text{CO}_2$  level ( $\text{H}_2 = 17$  ppmv).

| Reaction  | Reaction Rate (molecules $\text{cm}^{-3} \text{ s}^{-1}$ ) |                   |                 |                   |
|---|--|-------------------|-----------------|-------------------|
|   | UV = 1   |                   | UV = T-Tauri    |                   |
|   | $\text{CO}_2=1$  | $\text{CO}_2=100$ | $\text{CO}_2=1$ | $\text{CO}_2=100$ |
| 1. Production   |  |                   |                 |                   |
| (4) $\text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$     | 1.22 (2)   | 2.67 (4)          | 1.97 (1)        | 3.93 (4)          |
| 2. Loss due to photochemistry/chemistry                                       |  |                   |                 |                   |
| $\text{H}_2\text{CO} + h\nu \rightarrow \text{H} + \text{HCO}$                | 7.75 (1)   | 1.26 (4)          | 5.35 (0)        | 1.05 (4)          |
| $\text{H}_2\text{CO} + h\nu \rightarrow \text{H}_2 + \text{CO}$               | 7.97 (1)   | 1.30 (4)          | 4.84 (0)        | 9.86 (3)          |
| $\text{H}_2\text{CO} + \text{H} \rightarrow \text{H}_2 + \text{HCO}$          | 7.03 (0)   | 1.45 (2)          | 6.16 (0)        | 1.22 (3)          |
| $\text{H}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$ | 8.04 (-2)  | 4.81 (1)          | 9.26 (-2)       | 5.74 (2)          |
| $\text{H}_2\text{CO} + \text{O} \rightarrow \text{OH} + \text{HCO}$           | 1.94 (0)   | 1.58 (3)          | 2.22 (0)        | 1.88 (4)          |
| Total:  | 1.66 (2)   | 2.74 (4)          | 1.87 (1)        | 4.10 (4)          |
| 3. Loss due to rainout ( $\text{cm}^{-3} \text{ sec}^{-1}$ )                  | 1.62   | 2.65 (2)          | 3.38 (-2)       | 7.17 (1)          |
| 4. Rain-out rate ( $\text{cm}^{-2} \text{ sec}^{-1}$ )                        |  |                   |                 |                   |
| $\text{H}_2 = 17$ ppmv  | 5.5 (5)  | 7.34 (7)          | 5.98 (3)        | 5.45 (7)          |
| $\text{H}_2 = 10^{-3}$  | 8.6 (8)  | 2.02 (9)          | 3.7 (8)         | 1.07 (10)         |

of the column density of  $\text{H}_2\text{CO}$ , summarized in Table 4, and the rainout loss coefficient, which has a value of  $10^{-6} \text{ sec}^{-1}$  (11.6 days).

The effects of  $\text{H}_2$ ,  $\text{CO}_2$ , and solar UV on the vertical distribution of the ratio of  $\text{CO}/\text{CO}_2$  are shown in Figures 18 ( $\text{H}_2 = 17 \text{ ppmv}$ ) and 19 ( $\text{H}_2 = 10^{-3}$ ). The value of the ratio of  $\text{CO}/\text{CO}_2$  has recently been identified as a key parameter in laboratory experiments dealing with the abiotic synthesis of complex organic molecules in mildly reducing early atmospheric mixtures of  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$  (Bar-Nun and Chang, 1983). The calculated ratio of  $\text{CO}/\text{CO}_2$  in the lower atmosphere exhibited a strong dependence on the level of  $\text{H}_2$ . For  $\text{H}_2 = 17 \text{ ppmv}$ , this ratio was about  $10^{-4}$  for various combinations of  $\text{CO}_2$  and solar UV flux, while for  $\text{H}_2 = 10^{-3}$ , this ratio was considerably more — about  $10^{-2}$  for the same combination of  $\text{CO}_2$  and solar UV flux. However, for either value of  $\text{H}_2$ , a ratio of  $\text{CO}/\text{CO}_2$  of unity or greater was reached above about 40 km. The surface ratio of  $\text{CO}/\text{CO}_2$  as a function of  $\text{H}_2$ ,  $\text{CO}_2$ , and UV levels is summarized in Table 3.

#### b) *Summary of the photochemical results*

1. Calculated concentrations of  $\text{O}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{CO}$ , and the ratio of  $\text{CO}/\text{CO}_2$  in the prebiological paleoatmosphere are very sensitive to atmospheric levels of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and to the flux of incident solar ultraviolet. At least two of these parameters ( $\text{CO}_2$  and solar UV) may have varied significantly over geological time.

2. For high levels of  $\text{CO}_2$  (100 times the pre-industrial level of 280 ppmv) and solar UV, surface levels of  $\text{O}_2$  may have approached the parts per billion ( $10^{-9}$ ) level in the prebiological paleoatmosphere.

3. Prebiological levels of  $\text{O}_3$  offered no shielding of the surface to incoming solar ultraviolet radiation (200-300 nm).

4. Enhanced levels of  $\text{H}_2\text{CO}$  could have been photochemically produced in the atmosphere for high levels of  $\text{CO}_2$  and solar ultraviolet flux. On the order of 10 percent or more of the total production of  $\text{H}_2\text{CO}$  may have been rained out of the atmosphere into the early oceans where they could have been synthesized into more complex organic molecules by polymerization reactions.

5. Values of  $\text{CO}/\text{CO}_2$  of greater than unity were possible for enhanced levels of solar UV flux. Values of this ratio greater than unity

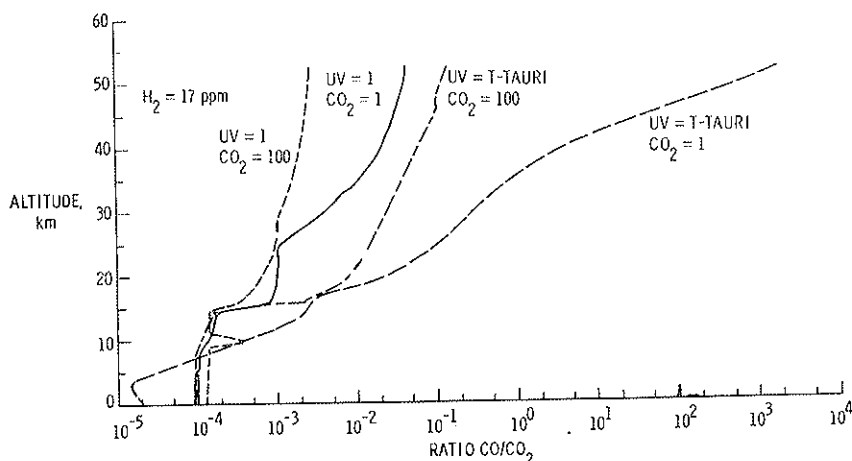


FIG. 18. Vertical distribution of the ratio of CO/CO<sub>2</sub> in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 17 ppmv and for four different combinations of carbon dioxide ( $CO_2$  = 1 and 100) and solar ultraviolet radiation (UV = 1 and T-Tauri).

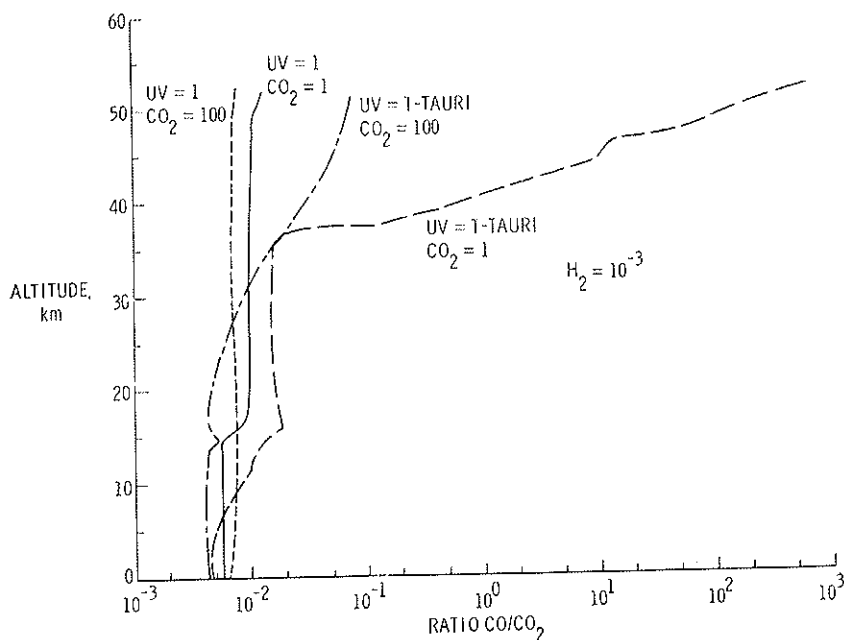


FIG. 19. Vertical distribution of the ratio of CO/CO<sub>2</sub> in prebiological paleoatmosphere. Calculations for molecular hydrogen ( $H_2$ ) = 10<sup>-3</sup> and for four different combinations of carbon dioxide ( $CO_2$  = 1 and 100) and solar ultraviolet radiation (UV = 1 and T-Tauri).

are required for the abiotic production of organic molecules in mildly reducing atmospheric mixtures of  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$  according to recent laboratory experiments of Bar-Nun and Chang (1983).

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## DISCUSSION

REVELLE

How you consider in your model the  $\text{CO}_2$ ?

It is a problem for those who suggest that much  $\text{CO}_2$  was present. In other words, they must solve this problem if they want to solve the dim sun paradox entirely. They put up so much  $\text{CO}_2$  that they must also propose a way to remove it — which is what you are saying. They need not only an ocean, but also an efficient mechanism for removal of the  $\text{CO}_2$ . That is why I do not know whether that is the solution or not. We are using an abundance of  $\text{CO}_2$  as usually discussed in the literature.

FIOCCO

I think I gathered from one of the slides that you kept the temperature equal to the standard atmosphere.

CANUTO

I discussed this problem with my colleagues at Langley, i.e., how to hook up this computation to a radiative transfer. Yes, this is one of the things we thought we should do. For the time being, we wanted to see the changes brought about by changes in one parameter, the UV flux. In the beginning we simply boosted up the UV flux independently of the wave-length dependent, up to 300 times more. Then we did a more refined computation with a wave-length UV flux. This is very important because the absorption cross sections are very wave-length dependent.

CHAMEIDES

The idea is that you are looking at variations  $\text{CO}_2$  not over a thousand years time scale but over millions of years, and the amount of  $\text{CO}_2$  present in the oceans and the atmosphere together is controlled by the larger cycle of continental uplift and weathering of rocks and so on and so forth; and the idea is that there is some sort of feedback between temperature and the rate at which the  $\text{CO}_2$  is put into the atmosphere and oceans together.

In fact, according to the models you can enhance the  $\text{CO}_2$  by factors of 100 or 1000 over long geological time scales, not over a thousand years.

CANUTO

Yes, but I don't think that was the gist of his question. Actually if I understood right, I think that one must have oceans in order to start the process that you are discussing. So that his question is: how soon do you have the oceans?

REVELLE

I don't believe that you can in fact have a high  $\text{CO}_2$  content in the atmosphere, probably only in the ocean.

CHAMEIDES

I agree that the total amount of carbon dioxide in the ocean and in the atmosphere together is controlled by a larger cycle which goes over millions of years, and the concept is that that can be upped several orders of magnitude. Apparently you could put together a consistent geochemical model for this system and argue in fact consistently, but you can argue that the model might be wrong; apparently you could consistently put together a scheme for increasing  $\text{CO}_2$  in the atmosphere-ocean system over millions of years and a geologic time scale of factors of 100 to 1000.

ROWLAND

I am sure that the modelers who are doing a one-dimensional model in which the rate of transport is the rate of transport that is calculated to fit species in the current atmosphere, when they start applying this to a remote atmosphere, a very different circumstance, it is not at all clear that the transport rate ought to be even similar to the one that one has now. What I wonder if you have done is to take the composition of the existing atmosphere rather than a hypothetical pre-biotic atmosphere, and put in 300 times or  $10^4$  times ultraviolet, see what it does to the existing atmosphere and whether the then radiation transfer characteristics of that atmosphere would be appreciably different from the present atmosphere. Then you already have the parameter; you are changing the atmosphere but you are assuming that the transport characteristics are exactly the same as this atmosphere.

CANUTO

There are several comments on that. First of all, there is a path that somehow you have to follow in order to compare your results with existing ones. We only meant to change one parameter, the one that astrophysics was telling us we should change. As for your second remark: a hypothetical atmosphere, well, it is hypothetical to a certain extent. There are in fact new data available for Jupiter and Titan. The composition used may be regarded as having been suggested by Titan.

As for your last point of taking today's atmosphere and today's composition and trying just to test those kinds of things, I had not thought of it, but it is certainly feasible, and could be done. I do not know if my collaborators want to spend extra money to do it, but it is a worthwhile kind of computation. There are other problems too. For instance, the UV absorption cross-section for OH. We used a 1949 reference, like everybody else. Recently I realized that the cross-section for OH has been reworked by people at Harvard. Their results are substantially different from the ones that were available in the literature. So we have a lot of cleaning up to do, even at the level of basic things like cross sections. What we have done is a test of how sensitive is this photochemical set of reactions to an increase of one of the external parameters, the UV flux. If you judge that the response is sufficiently interesting, then you have to do all these other things.

CRUTZEN

The nitrogen chemistry would be very interesting. Did you just not yet have the time to consider that, or did you leave it out because it is unimportant?

CANUTO

I am glad you asked that question. We have published two papers on this subject. In the results I have shown today, the nitrogen chemistry was not present. However, in our previous calculations we had included it and the results are available.

ROWLAND

I think I would dispute only a little bit with you. It seems to me that when you say that everyone, everyone else that has a one-dimensional photochemical model has done this; but some of the inferences about the early

atmosphere are not dependent upon photochemical models, so that if one looks at the geological record as to when we switch from reducing to an oxidizing atmosphere or something of this sort, the kind of question that I would phrase from this is: is there anything detectable at the surface of the earth that would reflect such a change in ultraviolet flux; that is, trying to eliminate the photochemical model.

#### CANUTO

I wish I could give a full answer. That is the same question I asked myself several times: what does all this mean? Is there any way to check the consequences? If one takes the point of view that one believes in the new UV data — and I think we have to — then the question is: have we chosen the right photochemical reactions in order to trace the consequences? And that is why we included formaldehyde, a useful, perhaps indispensable molecule for future polymerization processes. An increased UV increases the yield of such molecule, which is a good sign. Moreover, laboratory simulation experiments tell you that you need a ratio of CO to CO<sub>2</sub> which the standard model does not provide. The present model does. So I would say that higher UV helps at least in two cases. Clearly this is a compatibility argument, not a proof.

# ATMOSPHERIC IONS

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## ABSTRACT

Considerable progress has been made during recent years in exploring the ionized component of the denser regions of the earth's atmosphere, the stratosphere, and troposphere. It has been found that in these regions the plasma is composed mostly of large positive and negative cluster ions formed via a complex network of ion-molecule reactions starting from simple atomic and molecular primary ions. Various neutral trace gases involved as reactants in these ion transformations can be detected by measuring the ion composition. During recent years, this analytical application of in situ ion composition measurements became a powerful tool for trace gas detection and perhaps represents the most important aspect of current atmospheric ion research. The present paper reviews our present understanding of atmospheric ions with an emphasis on recent progress in stratospheric and tropospheric ion research. Interest will also be focussed on analytical applications and ion-induced aerosol formation.

## INTRODUCTION

Atmospheric gaseous ions not only control the electrical properties of the atmospheric medium but also have an interesting role in atmospheric chemistry. They have the potential to stimulate the formation of aerosols by ion-induced nucleation [1, 4] and to form or destroy trace gases by ion-molecule or ion-catalyzed reactions. Apart from these active roles ions also have an interesting passive role in serving as powerful probes

for trace gases and aerosols coexisting with the ions in the atmospheric medium [1]. This analytical application, which was introduced only during recent years, perhaps represents the most important aspect of current atmospheric ion research. It has already provided a wealth of interesting and new information on various atmospheric trace gases [1] also including species which could not be detected previously by other means than for example sulfuric acid vapour [2-10] which is of considerable importance since this trace gas has a key role in atmospheric aerosol formation. The ultimate physical cause of the importance of atmospheric ions lies in their very efficient interaction with atmospheric atoms, molecules, ions, and electrons. This interaction, of course, is due to long-range charge-dipole and Coulomb attraction forces which give rise to large collision cross sections, increase chemical reactivity, and promote the formation of molecular clusters by electrostatic bonding.

Our current understanding of the chemical nature of atmospheric ions and their role in atmospheric aerosol and trace gas processes derives primarily from in situ ion composition measurements using rocket-, balloon-, and aircraft-borne mass spectrometers [11, 12] as well as from laboratory studies of ion-molecule reactions and ion nucleation [13, 14].

Atmospheric plasma research was originally stimulated by the interest in radio wave propagation and therefore was focussed on the ionosphere. Thus, the early in situ ion composition measurements were made in the ionosphere at altitudes above about 100 km using rocket-borne spectrometers [15, 16, 17]. Below 100 km, the atmospheric gas pressure becomes so large that mass spectrometers have to be pumped which represents a major barrier for extending in situ ion composition measurements downwards into the mesosphere. Such measurements became technically feasible only with the advent of compact high speed cryopumps which could be used on rockets.

The first positive ion composition measurements reaching the mesosphere were made by Narcisi and colleagues [18]. Later on, several research groups contributed to the exploration of the mesospheric plasma, the so called ionospheric D-region. The first negative ion composition measurements in the atmosphere were performed in 1970 independently by Arnold *et al.* [19] and Narcisi *et al.* [20].

Further extension of in situ ion composition measurements into the even denser stratospheric layer required greatly improved mass spectrometric techniques and became feasible only in 1977 using balloon-borne mass spectrometers. The first negative ion composition measurements in

the stratosphere were made in 1975 by Arnold and Henschen [21] and positive ions were measured by Arnold *et al.* [22] and Arijs *et al.* [23].

Using balloon-borne mass spectrometers the groups of Arnold and Arijs during the following years explored the region mostly between about 20 and 33 km altitude. Only few measurements extended to heights above 33 km with a maximum height of 45 km [22, 24, 25, 26] and only a few measurements extended to heights below 20 km with a lowermost height around 12 km.

Thus, the balloon work covers the altitude range between about 12 and 45 km but by far most data were obtained only between about 20 and 33 km.

A further extension of ion composition measurements downwards in altitude into the troposphere became feasible only very recently using aircraft-borne mass spectrometers [12, 28, 29, 30]. These measurements which were made by our group at the MPI-K so far cover the altitude range between about 7 and 12 km.

Most recently, in 1984, detailed ion composition measurements could for the first time be performed in the stratopause region by our group [31], using a newly designed parachute-borne dropsonde mass spectrometer payload, which is carried by a rocket up to 60 km altitude and subsequently separated from the rocket motor. Positive and negative ion composition data could be obtained between about 30 and 60 km altitude. Thus, the gap between the regions covered by conventional rocket (above about 60 km) and balloon measurements (below 45-40 km) could be closed.

The purpose of the present paper is to review our current understanding of atmospheric ion chemistry with an emphasis on recent progress in the area of in situ ion composition measurements. Interest will be focussed also on analytical applications and ion-induced aerosol formation.

## SOURCES AND SINKS OF STRATOSPHERIC IONS

The only important source of ionization in the stratosphere, under most conditions, is galactic cosmic rays [32]. These are mostly energetic protons having average kinetic energies of about 100-1000 MeV corresponding to an atmospheric penetration depth of about 10-15 km. Thus, the galactic cosmic ray ionization rate,  $Q$ , reaches a maximum of about  $10\text{--}100\text{ cm}^{-3}\text{ s}^{-1}$  around this altitude.

Since the galactic cosmic rays are partially shielded by the interplanetary



and earth's magnetic fields,  $Q$  undergoes temporal and spatial variations. It decreases as solar activity increases, and it increases with increasing geomagnetic latitude.

Primary charged species formed by galactic cosmic ray ionization are  $N^+_{+2}$ ,  $O^+_{+2}$ ,  $O^+$ ,  $N^+$ , and free electrons. The latter are rapidly attached to gas molecules, giving rise to simple negative ions, mostly  $O^-_{-2}$ . Subsequent ion molecule reactions of primary positive and negative ions lead to complex positive and negative cluster ions. Ultimately these are removed by ion-ion recombination involving either a binary or a ternary mechanism [33].

Considerable experimental [33] and theoretical [34] progress has recently been made in determining stratospheric ion-ion recombination coefficients. In particular, it was found that binary ion-ion recombination can be enhanced as the gas pressure increases ("pressure enhanced binary ion-ion recombination") [33].

Taking recent effective ion-ion recombination coefficients  $\alpha$  and measured  $Q$ -values, the total ion concentration,  $n$ , can be calculated from the simple steady-state continuity equation  $n = (Q/\alpha)^{1/2}$ . Resulting  $n$ -values range between about  $10^3 - 10^4 \text{ cm}^{-3}$  and are in reasonable agreement with measured  $n$ -values recently obtained from improved Gerdien-condenser experiments [35] (Fig. 1).

Ion-recombination lifetimes  $t_R = (\alpha n)^{-1}$  range between about  $10^2 - 10^4 \text{ s}$  (Fig. 2). When compared with ion lifetimes  $t_A$  against collision with aerosols [36] (also shown in Fig. 2),  $t_R$  is much smaller throughout the stratosphere.

Consequently, ion attachment to aerosols should not be an efficient loss process for stratospheric ions.

## COLLISION PROCESSES OF STRATOSPHERIC IONS

Due to the very large abundance ratio of neutral molecules to ions (about  $10^{13} - 10^{14}$  in the middle stratosphere), ion interactions are dominated by ion-molecule collisions. These have cross sections being about 100 times larger than those for molecule-molecule collisions due to relatively long-ranging charge-dipole attraction forces.

Another consequence of these forces is that reactive ion-molecule collisions ("ion-molecule reactions"), in contrast to neutral gas reactions, in many cases do not possess activation energy barriers and thus proceed at the collision rate [37].

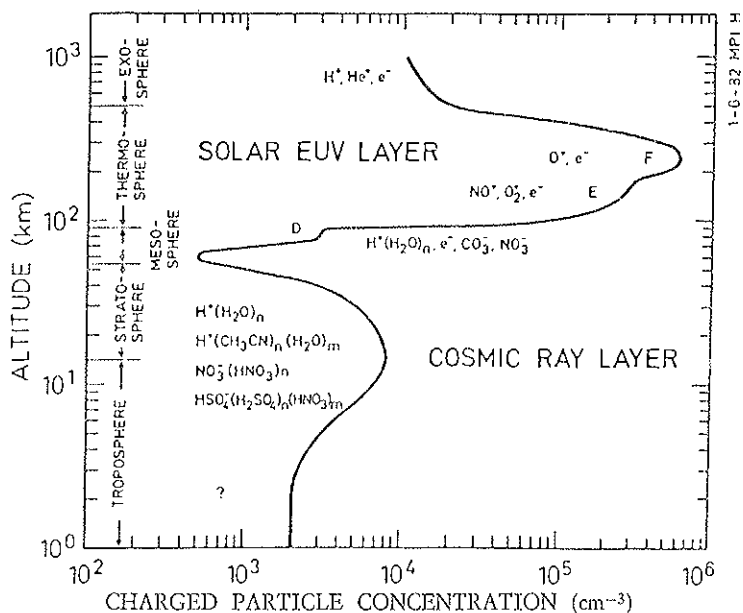


FIG. 1. Schematic representation of atmospheric ionization layers. [After Arnold, Ref. 1].

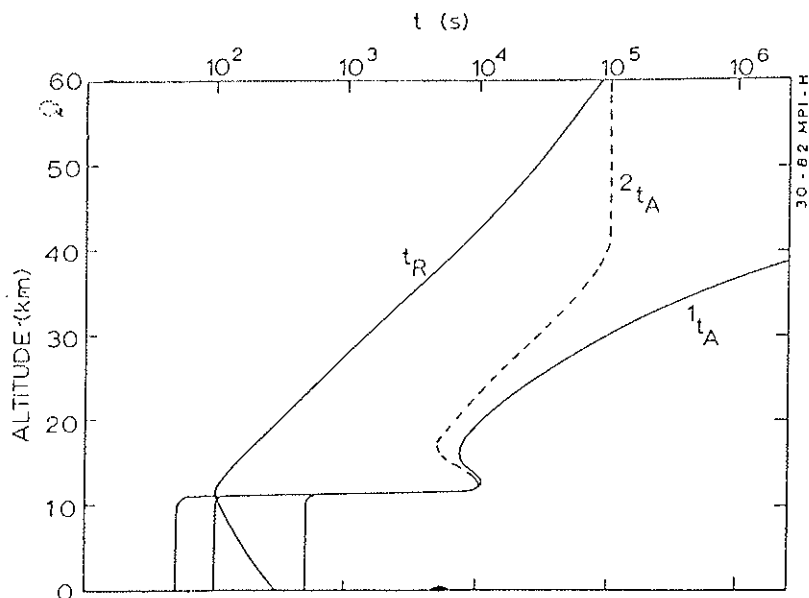


FIG. 2. Typical ion-recombination lifetimes ( $t_R$ ) compared with free-ion lifetimes against attachment to aerosols ( $1_{tA}$ ,  $2_{tA}$  "meteor smoke particles" added). [After Arnold, Ref. 1].

Finally, charge-dipole attraction also gives rise to clustering of molecules to ions [38], leading to large cluster ions which ultimately may become condensation nuclei [39]. Interestingly, even cluster ions which contain only a relatively small number of molecules, e.g., 5-10, develop properties similar to those of macroscopic liquid droplets [39].

Under stratospheric conditions, ion clustering proceeds via a ternary mechanism,



where M is a collision partner. If there is no kinetic limitation, a thermodynamic equilibrium between processes such as Eq. 1 and thermal dissociation (reverse of Eq. 1) determines the size distribution of  $A^+(B)_n$  cluster ions.

A new class of ion-molecule reactions, so-called ion-catalyzed reactions which were only recently [40] studied in the laboratory, may occur in the stratosphere. They involve the reaction of a molecule which is clustered to an ion with a gas-phase atom or molecule. Thus "ion-catalyzed reactions" involving larger cluster ions are somewhat similar to surface catalysis. The reactant molecule may be regarded as being adsorbed on the "surface" of the cluster ion.

When compared with its homogeneous gas-phase analog, an ion-catalyzed reaction may have a rate coefficient which is larger by orders of magnitude. The reactions [40]



and



e.g., have rate coefficients of  $1.3 \cdot 10^{-14}$  –  $2.1 \cdot 10^{-17}$  cm<sup>3</sup> s<sup>-1</sup> (depending on temperature) and  $6.5 \cdot 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, respectively.

Besides interacting with molecules, stratospheric ions preferably interact with oppositely-charged ions due to very long-ranging Coulomb-attraction forces.

Besides giving rise to free ion removal, ion-ion recombination may also lead to the formation of stable ion pairs [42] which by ion attachment may grow to polyions [43]. The polyions are still hypothetical as they have

neither been detected in the laboratory nor in the atmosphere. If existent, they may play a role as precondensation nuclei [42].

Thus, ions may promote aerosol formation in two ways, by conventional ion nucleation involving ion clustering and by polyion nucleation.

## ION CHEMISTRY

### *Positive Ions*

The most abundant stratospheric positive ions are  $\text{H}^+(\text{H}_2\text{O})_n$  and  $\text{H}^+(\text{CH}_3\text{CN})_l(\text{H}_2\text{O})_m$  cluster ions with the former dominating above about 35 km and the latter becoming most prominent below this altitude (Fig. 3).

Besides these major ions, various minor ion species were detected

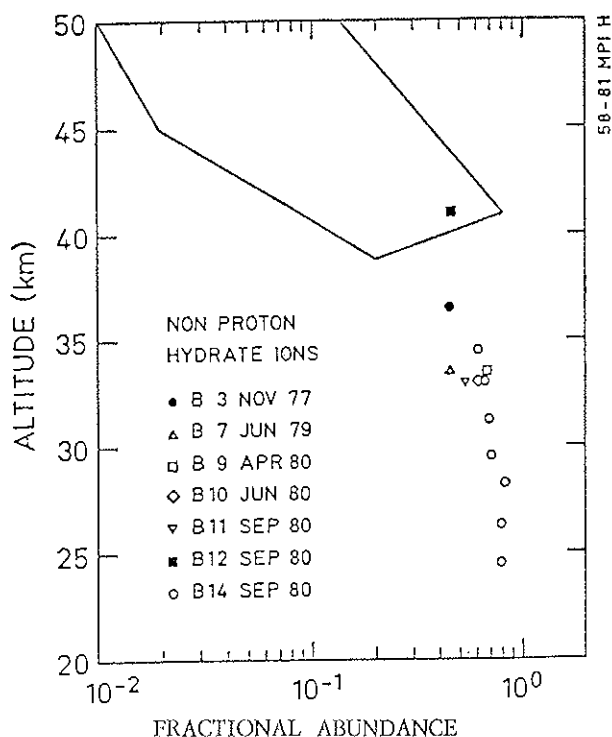


FIG. 3 - Fractional abundance of positive ions not belonging to the  $\text{H}^+(\text{H}_2\text{O})_n$  family [after Henschen and Arnold; Ref. 43, and Schlager and Arnold, unpublished material].

(Table 1), possibly also containing molecules such as  $\text{CH}_3\text{OH}$ . In addition, very massive positive ions (upt to about 320 atomic mass units) were detected but could as yet not be identified.

The chemical evolution of stratospheric positive ions may be viewed as proceeding in three stages. The first stage involves reactions of primary positive ions ( $\text{N}^+$ ,  $\text{O}^+_{2,3}$ ,  $\text{O}^+$ ,  $\text{N}^+$ ) with major gases ( $\text{N}_2$ ,  $\text{O}_2$ ) leading to  $\text{O}^+_{4,5}$  and  $\text{NO}^+$  (Fig. 4). The fractional rates of formation for these ions are about 90% and 10%. The time scale for stage one is only on the order of  $10^{-5}$  s in the middle stratosphere (if not otherwise indicated, time scales given hereafter refer to an altitude of 35 km).

Stage two involves reactions of major trace gases, mostly  $\text{H}_2\text{O}$  leading to  $\text{H}^+(\text{H}_2\text{O})_n$  cluster ions. It is essentially the large proton affinity of the water molecule and the strong bonding of  $\text{H}_2\text{O}$ -molecules to the hydro-

TABLE 1 - *Stratospheric positive ion species detected by balloon-borne mass spectrometers* (Schlager and Arnold, submitted for publication).

| Ion   | Mass       | Ion  | Mass        |
|---|------------|--|-------------|
| $\text{H}_3\text{O}^+$                                    | 19         | $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_2$     | $104 \pm 1$ |
| $\text{Na}^+$   | $23 \pm 1$ | $\text{H}^+(\text{H}_2\text{O})_6$                         | 109         |
| $\text{H}^+\text{HCN}$                                    | $29 \pm 2$ | $\text{H}^+\text{CH}_3\text{OH}(\text{H}_2\text{O})_2$     | $110 \pm 1$ |
| $\text{H}^+(\text{H}_2\text{O})_2$                        | 37         | $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_4$     | $114 \pm 1$ |
| $\text{H}^+\text{CH}_3\text{CN}$                          | 42         |  | $117 \pm 1$ |
| $\text{H}^+\text{HCN} \cdot \text{H}_2\text{O}$           | $45 \pm 1$ | $\text{H}^+(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2$ | 119         |
| $\text{H}^+\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ | $49 \pm 1$ |  | $121 \pm 1$ |
| $\text{H}^+(\text{H}_2\text{O})_3$                        | 55         |  | $125 \pm 1$ |
| $\text{Na}^+(\text{H}_2\text{O})_2$                       | $58 \pm 1$ |  | $128 \pm 1$ |
| $\text{H}^+\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ | 60         |  | $134 \pm 2$ |
| $\text{H}^+\text{HCN}(\text{H}_2\text{O})_2$              | $63 \pm 1$ |  | $139 \pm 2$ |
| $\text{H}^+\text{CH}_3\text{OH}(\text{H}_2\text{O})_2$    | $67 \pm 1$ | $\text{H}^+\text{H}_2\text{O}(\text{CH}_3\text{CN})_3$     | $142 \pm 1$ |
| $\text{H}^+(\text{H}_2\text{O})_4$                        | 73         |  | $151 \pm 2$ |
| $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_2$    | 78         |  | $158 \pm 3$ |
| $\text{H}^+\text{HCN}(\text{H}_2\text{O})_3$              | $81 \pm 1$ |  | $168 \pm 3$ |
| $\text{H}^+(\text{CH}_3\text{CN})_2$                      | 83         |  | $179 \pm 3$ |
| $\text{H}^+\text{CH}_3\text{OH}(\text{H}_2\text{O})_3$    | $86 \pm 1$ |  | $182 \pm 3$ |
| $\text{H}^+(\text{H}_2\text{O})_5$                        | 91         |  | $186 \pm 3$ |
| $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_3$    | 96         |  | $190 \pm 3$ |
| $\text{H}^+(\text{CH}_3\text{CN})_2\text{H}_2\text{O}$    | 101        |  | $202 \pm 3$ |

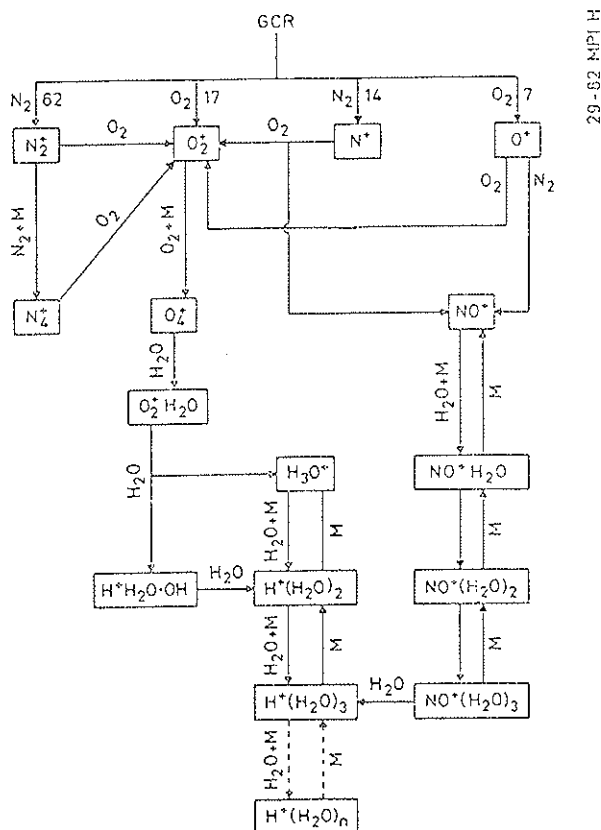


Fig. 4. Stratospheric positive ion reaction scheme (stages one and two) [after Ref.'s 13, 14].

mium ion,  $H_3O^+$ , which drive the formation of  $H^+(H_2O)_n$  ions. Due to the relatively large abundance of water vapor a quasi-equilibrium size distribution of  $H^+(H_2O)_n$  is rapidly established. Usually, the distribution peaks around  $n = 4$  or 5 in the middle stratosphere, depending somewhat on temperature. The time scale for stage two is only on the order of  $10^{-3}$  s, which is much smaller than the ion-recombination lifetime,  $t_R$  (see Fig. 2).

Stage three (Fig. 5) involves reactions of very low abundance trace gases having time scales which are on the order of  $t_R$  or even larger. Consequently, the abundance ratio for product ions and precursor ions never becomes very much larger than one.

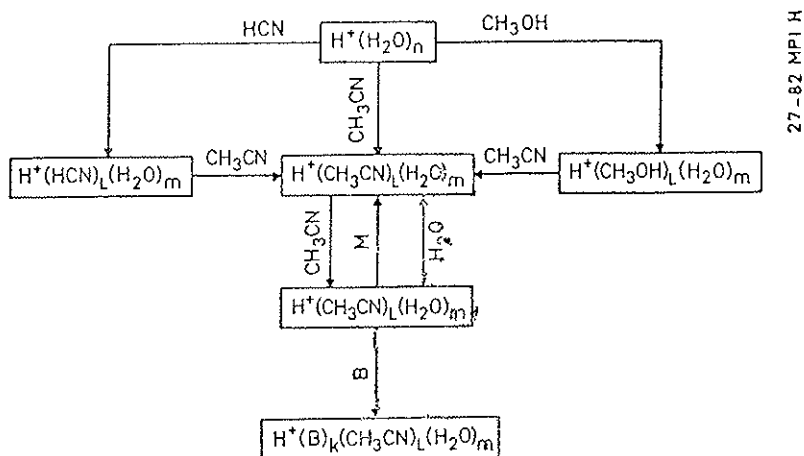
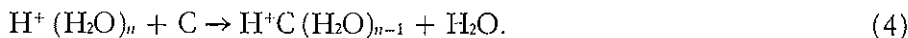


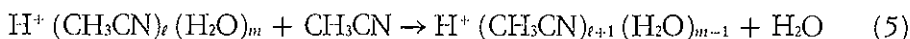
FIG. 5. Stratospheric positive ion reaction scheme (stage three).

These trace gases all have proton affinities substantially larger than that of  $\text{H}_2\text{O}$  ( $170 \text{ kcal mole}^{-1}$ ) and thus can react with  $\text{H}^+(\text{H}_2\text{O})_n$  ions via



Equation 4 is not a simple proton-transfer reaction but rather involves displacement of an  $\text{H}_2\text{O}$  molecule contained in an  $\text{H}^+(\text{H}_2\text{O})_n$  cluster ion by a molecule C. Usually, C must have a substantially larger proton affinity than  $\text{H}_2\text{O}$  ( $170 \text{ kcal mole}^{-1}$ ) in order to make Eq. 4 exothermic [13, 14]. This is true because  $\text{H}_2\text{O}$ -molecules mostly bond more strongly to  $\text{H}_3\text{O}^+$  than to  $\text{H}^+\text{C}$ .

Among the reactant molecules, C acetonitrile,  $\text{CH}_3\text{CN}$ , which has a proton affinity  $\text{PA}(\text{CH}_3\text{CN}) = 186 \text{ kcal mole}^{-1}$  seems to be the most important [22, 41]. Reactions such as Eq. 4 involving  $\text{CH}_3\text{CN}$  lead to  $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_m$  mixed cluster ions. Subsequent displacement of  $\text{H}_2\text{O}$ -ligands by  $\text{CH}_3\text{CN}$  via

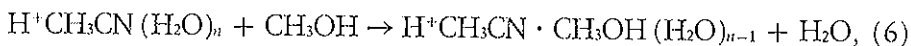


may occur. According to in situ observations and laboratory studies [33, 41, 47], however, it seems that the exothermicity of Eq. 5 decreases as  $\ell$  increases.

Under stratospheric conditions  $\ell$  is usually not larger than two to three. The total number of molecules attached to  $\text{H}^+\text{CH}_3\text{CN}$  is about the same as the number of  $\text{H}_2\text{O}$ -ligands attached to  $\text{H}_3\text{O}^+$ -cores.

It was also found from laboratory studies [41], that  $\text{H}^+(\text{CH}_3\text{CN})_3\text{H}_2\text{O}$  is a particularly stable cluster. This is probably due to a symmetric structure with an  $\text{H}_3\text{O}^+$ -core having a delocalized positive charge shared by its three hydrogen atoms to each of which a  $\text{CH}_3\text{CN}$  molecule is attached.

Mixed cluster ions of the type  $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_n$  react also with other large proton affinity molecules such as  $\text{CH}_3\text{OH}$  via



leading to even more complex heteromolecular cluster ions.

Generally, the competitive gas-phase solvation of the proton seems to favor  $\text{H}_2\text{O}$  in the outer "shell" of the cluster. This is probably due to the strong hydrogen bonding of  $\text{H}_2\text{O}$ , which is also responsible for the large heat of vaporization of bulk water.

If present in the stratosphere,  $\text{NH}_3$ , due to its very large proton affinity, should efficiently react with  $\text{H}^+(\text{CH}_3\text{CN})_\ell(\text{H}_2\text{O})_m$  ions. Recent laboratory studies [44] indicate large rate coefficients for these processes.

Other molecules with a high proton affinity which have been discussed [44, 13, 45] as potential reactants for stratospheric positive cluster ions are metal compounds such as  $\text{NaOH}$  or  $\text{NaCl}$ . It is thought that these are formed in the mesosphere from meteor ablation material which is mixed downwards into the stratosphere.

According to laboratory studies [46],  $\text{NaOH}$  and  $\text{NaCl}$  both react with  $\text{H}^+(\text{H}_2\text{O})_n$  ions, leading to  $\text{Na}^+(\text{H}_2\text{O})_n$  cluster ions.

From the failure to detect the latter ion species in the middle stratosphere, it was concluded [47, 48] that  $\text{NaOH}$  and  $\text{NaCl}$  are not present in gaseous form but probably are converted to some kind of aerosols before they reach the middle stratosphere.

An alternative possibility is that strongly polar compounds such as  $\text{NaCl}$  form dimers or higher polymers which by reaction with  $\text{H}^+(\text{H}_2\text{O})_n$  ions do not lead to simple  $\text{Na}^+(\text{H}_2\text{O})_n$  cluster ions but to more complex clusters containing two or more metal atoms.

Acetonitrile, the most important reactant molecule involved in stage three of the positive ion evolution, seems to originate from the troposphere (see section on Analytical and Diagnostic Applications of In Situ Ion Composition Measurements) as discussed by Henschen and Arnold [43].



Recently, this view received strong support from laboratory studies suggesting that  $\text{CH}_3\text{CN}$  hardly reacts with  $\text{OH}$  [43, 49] and is not photodissociated by UV-radiation reaching the middle stratosphere [50]. Thus, if formed in the troposphere,  $\text{CH}_3\text{CN}$  should be capable of reaching the middle stratosphere. However, the possibility exists that  $\text{CH}_3\text{CN}$ , due to its relatively large solubility in water, may efficiently be rained or washed out in the troposphere [49].

The tropospheric source of  $\text{CH}_3\text{CN}$  as yet has not been identified with certainty. Biomass burning has been discussed [50] as a potential  $\text{CH}_3\text{CN}$  source.

Kinetic and thermodynamic data on ion reactions involved in stages one and two are to a large extent available [51]. By contrast, only few data are available for stage three processes.

In summary, it seems that our understanding of the stratospheric positive ion chemistry is far from satisfactory because independent information on both underlying processes and reactant trace gases is largely lacking.

### *Negative Ions*

The most abundant negative ion species observed in the stratosphere can be grouped [21] in two main families,  $\text{NO}_3^-(\text{HNO}_3)_n$  and  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_l(\text{HNO}_3)_m$ , with the latter being dominant above about 25-30 km (Fig. 6). Besides these major ions various minor negative ion species [52, 53] were detected (Table 2). These are mostly cluster ions containing high electron affinity core molecules such as  $\text{CN}$  and  $\text{CO}_3$  and high gas phase acidity ligand molecules such as  $\text{HCl}$ ,  $\text{HNO}_2$ ,  $\text{HOCl}$ , and  $\text{HSO}_3$ . Water molecules are also present as ligands.

Usually, the  $\text{NO}_3^-(\text{HNO}_3)_n$  ions contain about two to three  $\text{HNO}_3$ -ligands. Major  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_l(\text{HNO}_3)_m$  ions may contain up to three  $\text{H}_2\text{SO}_4$  ligands.

Recently [53] it was found that larger  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  ions are markedly hydrated, suggesting an increase of the  $\text{H}_2$ -bond energy for increasing  $n$ .

The chemical evolution of stratospheric negative ions, like that of positive ions, may be viewed as proceeding in three stages.

Stage one (Fig. 7) involves reactions of the major gas,  $\text{O}_2$ , leading to  $\text{O}_4^-$  (time scale:  $10^{-3}$  s). Stage two (Fig. 7) involves reactions of relatively abundant trace gases such as  $\text{CO}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}$ , leading mostly to  $\text{CO}_3^-$  ions and its hydrates (time scale  $\leq 10^{-3}$  s). Since the latter time scale is

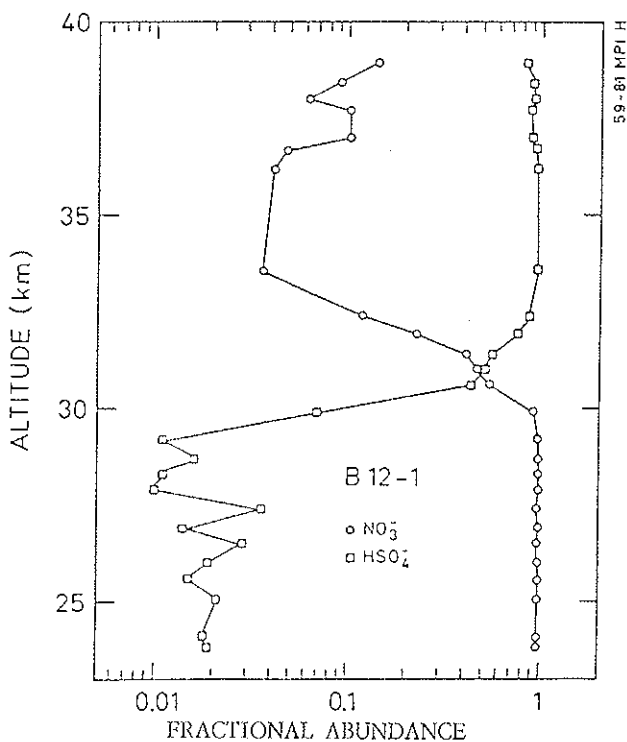


Fig. 6. Fractional abundance of major negative cluster ion families containing  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  cores [54].

TABLE 2 - Stratospheric negative ion species detected by balloon-borne mass spectrometers [52, 53].

| Mass        | Ion  | Mass        | Ion  |
|-------------|--|-------------|--|
| $26 \pm 2$  | $\text{CN}^-$  | $223 \pm 1$ | $\text{HSO}_4^- (\text{HNO}_3)_2$  |
| $43 \pm 2$  | $\text{CN}^- \text{H}_2\text{O}$                                     | $241 \pm 1$ | $\text{HSO}_4^- (\text{HNO}_3)_2 \text{H}_2\text{O}$                       |
| $61 \pm 1$  | $\text{CO}_3^- \text{NO}_3^-$  | $251 \pm 1$ | $\text{NO}_3^- (\text{HNO}_3)_3$   |
| $80 \pm 2$  | $\text{CO}_3^- \text{H}_2\text{O}, \text{NO}_3^- \text{H}_2\text{O}$ | $258 \pm 1$ | $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3$            |
| $97 \pm 1$  | $\text{HSO}_4^-$   | $274 \pm 1$ | $\text{HSO}_4^- (\text{HNO}_3)_2 \text{HClO}$                              |
| $109 \pm 2$ | $\text{NO}_3^- \text{HNO}_2$   |             | $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HSO}_3$            |
| 125         | $\text{NO}_3^- \text{HNO}_3$   | $286 \pm 1$ | $\text{HSO}_4^- (\text{HNO}_3)_3$  |
| $133 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{O})_2$                              | $293 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_2$                                 |
|             | $\text{HSO}_4^- \text{HCl}$  | $374 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_2 \text{HSO}_3$                    |
| $143 \pm 1$ | $\text{NO}_3^- \text{HNO}_3 \text{H}_2\text{O}$                      | $391 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3$                                 |
| $148 \pm 2$ | $\text{HSO}_4^- \text{HOCl}$   | $409 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 \text{H}_2\text{O}$              |
| 160         | $\text{HSO}_4^- \text{HNO}_3$  | $427 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 (\text{H}_2\text{O})_2$          |
| $174 \pm 1$ | $\text{NO}_3^- \text{HNO}_3 \text{HNO}_2$                            | $454 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 \text{HNO}_3$                    |
| 188         | $\text{NO}_3^- (\text{HNO}_3)_2$                                     | $472 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 \text{HSO}_3$                    |
| 195         | $\text{HSO}_4^- \text{H}_2\text{SO}_4$                               | $489 \pm 1$ | $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_3 \text{HSO}_3 \text{H}_2\text{O}$ |
| $206 \pm 1$ | $\text{NO}_3^- (\text{HNO}_3)_2 \text{H}_2\text{O}$                  |             |  |

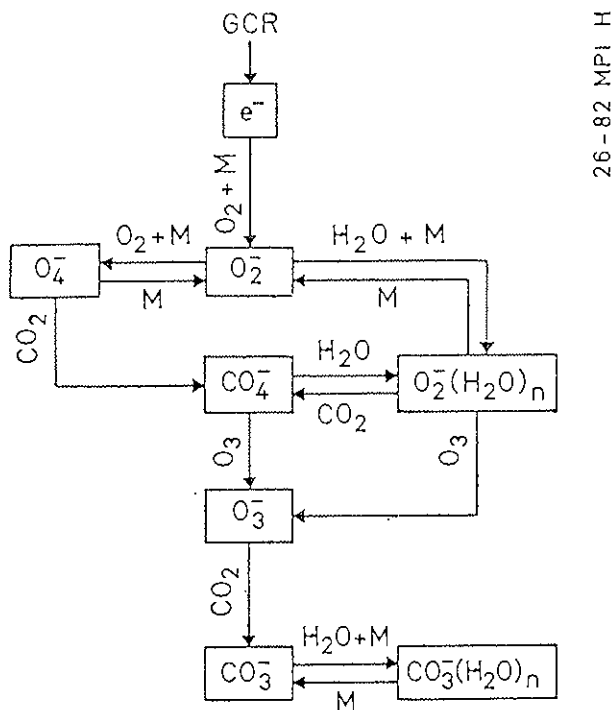


Fig. 7. Stratospheric negative ion reaction scheme (stages one and two) [after Ref. 13].

usually much smaller than the ion recombination lifetime,  $t_R$ ,  $\text{CO}_3^-$  and its hydrates are further converted by reactions with less abundant trace gases, mostly  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ). This leads to the formation of  $\text{NO}_3^- (\text{HNO}_3)_n$  cluster ions (stage three, Fig. 8).

Since the  $\text{HNO}_3$ -vapor concentration is sufficiently large in the stratosphere, a quasi-equilibrium size distribution of  $\text{NO}_3^- (\text{HNO}_3)_n$  is established, peaking around  $n = 2$  or 3.

The second part of stage three involves reactions with sulfur-bearing gases, mostly  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3$ , leading to  $\text{HSO}_4^-$ -cores. Subsequently,  $\text{H}_2\text{SO}_4$  displaces  $\text{HNO}_3$ -ligands, leading to  $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_\ell (\text{HNO}_3)_m$  mixed cluster ions. As  $\ell$  becomes larger than about two, these cluster ions are markedly hydrated. This probably reflects strong cooperative bonding effects between  $\text{H}_2\text{SO}_4$ - and  $\text{H}_2\text{O}$ -ligands. In this respect, the cluster ion

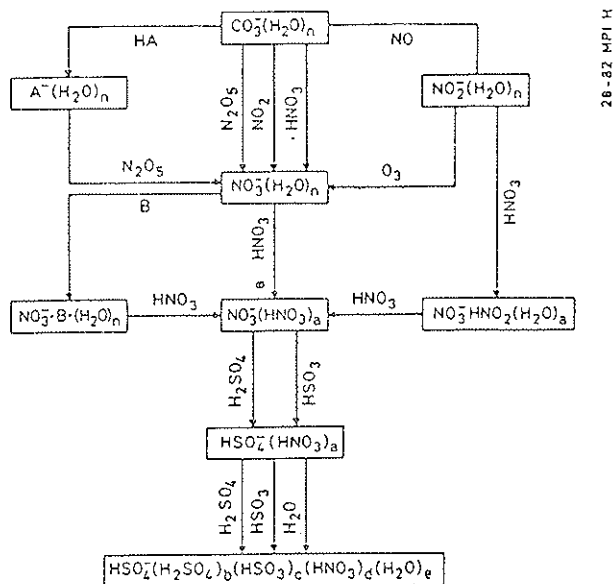


FIG. 8. Stratospheric negative ion reaction scheme (stage three).

already resembles a small solution droplet composed of an  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  mixture which has a large heat of mixing.

The  $\text{NO}_x$ -reactant gases leading to  $\text{NO}_3^-(\text{HNO}_3)_n$  ions are formed in the stratosphere by photochemical processes mostly from the precursor gas  $\text{N}_2\text{O}$  which is of tropospheric origin. The sulfur-bearing reactant molecules  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3$  are also formed in the stratosphere by photochemical and/or heterogeneous processes. Here, the most important precursor gas seems to be  $\text{OCS}$  which is also of tropospheric origin [55]. During volcanically very active periods  $\text{SO}_2$  may also become an important precursor gas.

Kinetic and thermodynamic data for negative ion reactions involved in stages one and two are to a large extent available from laboratory studies [51]. Stage three data are mostly lacking.

Thus, our understanding of stratospheric ion chemistry, like that of positive ion chemistry, is far from satisfactory due to the lack of independent information on reactant trace gases and laboratory data.

## POTENTIAL ROLE OF IONS IN STRATOSPHERIC TRACE GAS AND AEROSOL PROCESSES

Trace gases can be formed, destroyed, or removed from the gas phase by ion processes including ion-molecule reactions, ion-ion recombination, and ion nucleation.

Trace gas destruction is limited by the relatively small total ion concentration,  $n$ . Taking an upper limit of  $k = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  as the rate coefficient for an ion-molecule collision, a lower limit of about one day is obtained for the lifetime of a molecule against destruction or removal by ion processes. For noncatalytic ion processes the lifetime can be much larger.

Trace gas formation by noncatalytic ion processes is limited by the total ionization rate,  $Q$ , being on the order of  $10\text{-}100 \text{ cm}^{-3} \text{ s}^{-1}$ . For catalytic processes the upper limit to the rate of trace gas molecule formation is  $k n [\text{B}]$ , or about  $10^{-5} [\text{B}]$ , where  $[\text{B}]$  is the concentration of the reactant molecule.

Ions may also promote aerosol formation via ion nucleation. Basically two processes, conventional ion nucleation, IN [39, 42], and polyion nucleation, PIN [42] have been discussed (see also section on COLLISION PROCESSES OF STRATOSPHERIC IONS). IN, although suffering from severe kinetic limitations, may represent a potential source for stratospheric condensation nuclei [39]. IN rates may become particularly large around 30-35 km altitude during sudden winter coolings following major stratospheric warmings. Under these conditions, due to large  $[\text{H}_2\text{SO}_4]$  values, kinetic limitations of IN may be markedly reduced.

Thus, a seed layer of condensation nuclei may be formed around 30-35 km altitude. Even under conditions of a condensation-evaporation equilibrium, IN may be sufficiently efficient to maintain the stratospheric aerosol layer [39] (Fig. 9).

If ions were, in fact, involved in stratospheric aerosol formation, a physical link between solar activity and the stratospheric aerosol layer may exist [39].

## ANALYTICAL AND DIAGNOSTIC APPLICATIONS OF IN SITU ION COMPOSITION MEASUREMENTS

Atmospheric ions react selectively with certain neutral trace gases leading to characteristic product ion species. By measuring reactant and

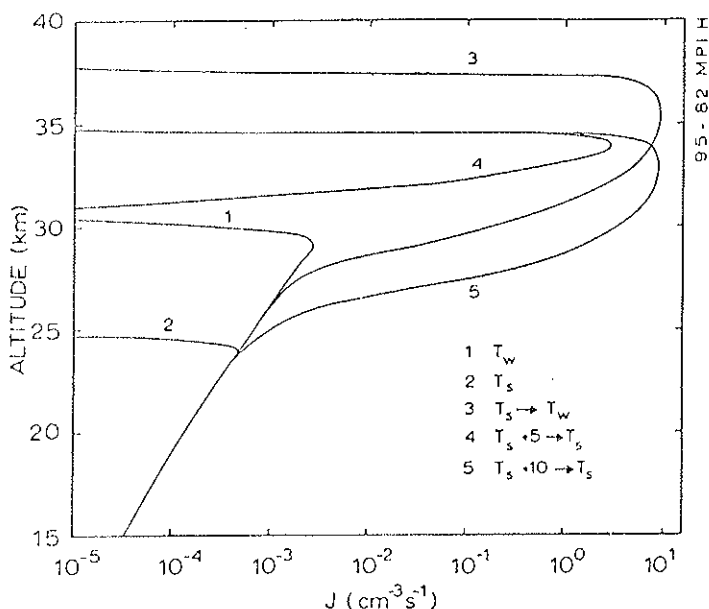


FIG. 9. Ion-nucleation rates as calculated by Arnold (see [39]) for winter [1], summer [2], and stratospheric winter warming-cooling events [3, 4, 5].

product ions in situ, the number densities of the reactant trace gases can be inferred with great sensitivity. This indirect method for atmospheric trace gas detection was termed PACIMS (passive chemical ionization mass spectrometry) [56].

The extremely large sensitivity of PACIMS is due to both the relatively large ion-recombination lifetime,  $t_R$ , and the large rate coefficients,  $k$ , for ion-molecule reactions. Assuming that an ion,  $C^+$ , is formed by



and lost preferably by ion-ion recombination, a steady-state treatment yields

$$[B] = [C^+] / [A^+] (k t_R).$$

Taking  $k = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ,  $t_R = 10^4 \text{ s}$ , and a minimum measurable ion abundance ratio,  $[C^+] / [A^+] = 10^{-4}$ , one obtains a minimum detectable

$[B] = 10 \text{ cm}^{-3}$  corresponding to a volume mixing ratio on the order of  $10^{-16}$  in the middle stratosphere.

Various trace gases (Table 3) have already been detected using PACIMS. Particularly interesting ones are  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3$ , as they are involved in stratospheric aerosol formation (Fig. 10).

It seems that  $\text{H}_2\text{SO}_4$ -vapor is supersaturated with respect to  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  solution droplets at altitudes below about 30-35 km depending on season. Thus,  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  aerosols can exist only below these heights. It also seems that  $\text{HSO}_3$  becomes abundant at the lower heights, possibly suggesting [53, 56] that aerosols are formed from  $\text{HSO}_3^-$  rather than  $\text{H}_2\text{SO}_4$ -vapor. It is conceivable that  $\text{H}_2\text{SO}_4$  is formed in the aerosols rather than in the gas phase, which would be in contrast to most current models of the stratospheric sulfur chemistry.

This example clearly demonstrates the kind of interesting new information on trace gases which was recently obtained from stratospheric in situ ion composition measurements.

Very recently, active chemical ionization mass spectrometry (ACIMS) was employed for stratospheric trace gas detection [57]. Here ions are created in the stratospheric medium by an electron bombardment ion

TABLE 3 - *Stratospheric trace gases detected by chemical ionization mass spectrometry. Altitude range and positive (PI) or negative (NI) ion composition measurements are indicated. Parentheses (+) denote that identification is uncertain.*

| Trace gas                | PI  | NI  | Altitude Range |
|--------------------------|-----|-----|----------------|
| $\text{H}_2\text{O}$     | +   | +   | 33 - 42        |
| $\text{CH}_3\text{CN}$   | +   |     | 15 - 42        |
| $\text{CH}_3\text{OH}$   | +   |     | 15 - 34        |
| $\text{CH}_3\text{NO}_2$ | (+) |     | 15 - 34        |
| $\text{HNO}_3$           |     | +   | 33 - 42        |
| $\text{HCN}$             |     | (+) | 34             |
| $\text{HSO}_3$           |     | +   | 28 - 34        |
| $\text{H}_2\text{SO}_4$  |     | +   | 15 - 40        |
| $\text{HNO}_2$           |     | (+) | 34             |

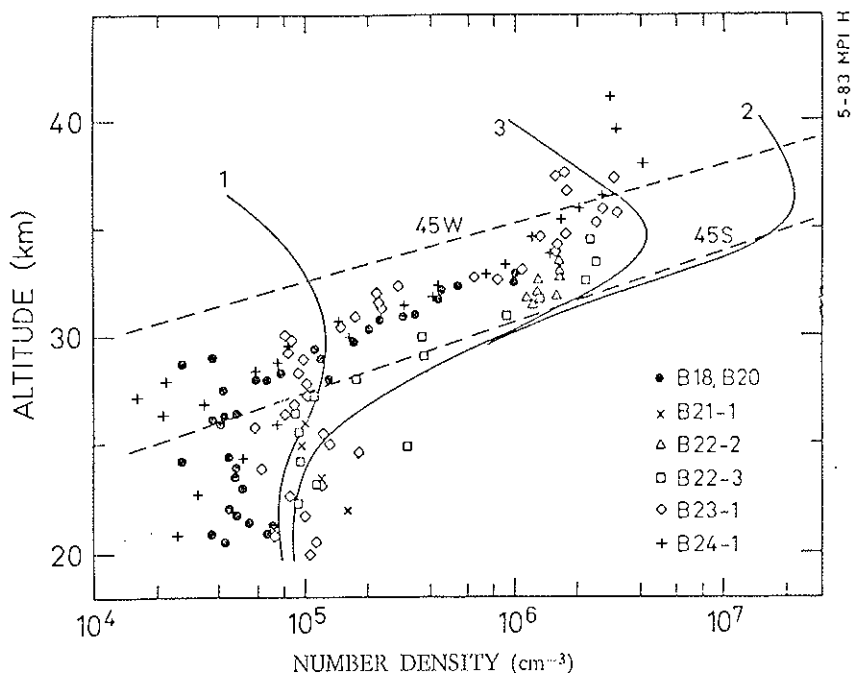


FIG. 10. Sulfuric acid vapor abundances as obtained by passive chemical ionization mass spectrometry. Curves 1, 2, and 3 are model predictions of Turco *et al.* [58]. Broken curves are equilibrium saturation vapor concentrations for 45° latitude summer (S) and winter (W). (Figure from Qiu and Arnold, Ref. [26]).

source and sampled by an ion mass spectrometer after they have flown with the neutral gas over a distance of about 50 cm. The ions reside for about 20 seconds in the medium before they are sampled. Within this time, they react with trace gases whose concentration can be inferred from the measured abundances of reactant and product ions.

ACIMS has already provided information on  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{CN}$ , and  $\text{H}_2\text{O}$  [57]. Since the large cluster ions interact with condensable vapors similar to aerosols, in situ compositional measurements of large compositional cluster ions also provide interesting information on the composition and thermodynamics of aerosols which exist in the same medium [53]. It was found that large negative cluster ions around 30 km altitude are composed mostly of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  which is rather similar to the expected aerosol composition. Bond energies for  $\text{H}_2\text{SO}_4$ -ligands were found to be about 20 kcal mole<sup>-1</sup> which is close to the heat



of vaporization for a bulk  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  solution. It was also found that the  $\text{HSO}_3$ -radical bonds similarly strongly to large negative ion clusters such as  $\text{H}_2\text{SO}_4$ . This finding is of great interest as no laboratory information on  $\text{HSO}_3$  is as yet available.

Thus, in situ ion composition measurements can provide new and interesting information on neutral trace gases and aerosols.

## ASSESSMENT OF TROPOSPHERIC ION CHEMISTRY

The nature of tropospheric ions and their possible role in trace gas and aerosol processes is, as already mentioned, largely unknown. Building on recent progress in our understanding of stratospheric ion processes and first in situ ion composition measurements which were recently made in the upper troposphere, an assessment of tropospheric ion chemistry will be attempted in the following section.

In the troposphere the most important sources of ionization are radioactivity and galactic cosmic rays [60]. The former, which is due to  $\alpha$ ,  $\beta$ , and  $\gamma$  radiations from thoron and radon, is dominant up to about one kilometer altitude. Above this height, as in the stratosphere, galactic cosmic ray ionization is most important.

The total ionization rate,  $Q$ , is on the order of  $1\text{-}10\text{ cm}^{-3}\text{ s}^{-1}$  in the troposphere.

Removal of free ions occurs by two mechanisms: ion-ion recombination (essentially saturated ternary ion-ion recombination; effective binary coefficient  $\alpha = 2 \cdot 10^{-6}\text{ cm}^3\text{ s}^{-1}$ ) and ion-attachment to aerosol particles. The latter process leads to so-called "large ions" which are, in fact, electrically-charged aerosols rather than ions in a strictly physical sense [60]. Usually, ion-attachment is the most important sink for free ions throughout the troposphere as the tropospheric aerosol content is relatively large (Fig. 2). In this respect, the tropospheric ionization-deionization balance differs greatly from the stratospheric one.

On the average, the free ion lifetime in the troposphere is on the order of  $10^2\text{-}10^3$  seconds. Taking typical  $Q$ -values of  $1\text{-}10\text{ cm}^{-3}\text{ s}^{-1}$ , a steady-state free ion concentration,  $n$ , on the order of  $10^2\text{-}10^4\text{ cm}^{-3}$  is obtained. Due to temporal and spatial changes of the aerosol content, tropospheric free ion concentrations may undergo marked changes.

The chemical evolution of tropospheric free ions is rather uncertain. Stages one and two of the positive and negative ion evolutions may be

similar to those occurring in the stratosphere. A marked difference, however, may arise from the relatively large tropospheric water vapor abundance possibly leading to marked hydration as early as stages one and two. It is conceivable that in certain cases hydration changes the reactivity of the core ion. For example, reaction of  $O_3^-(H_2O)_n$  with  $CO_2$  is much slower or even inefficient compared to that of  $O_3$  [37].

For typical ground level conditions the most prominent positive and negative ions should contain about 10-20 water molecules. This has been found from mass spectrometric studies of ions created in ground level air carried out by our group (unpublished data).

Most uncertain, however, are stages three of the positive and negative ion evolutions, particularly as reactant trace gases are not known. Taking the above free ion lifetimes of  $10^2$ - $10^3$  seconds and a maximum rate coefficient for an ion molecule reaction on the order of  $10^{-9}$   $cm^3 s^{-1}$ , reactant trace gases having abundances of only  $10^6$ - $10^7$   $cm^{-3}$  (corresponding volume mixing ratio:  $10^{-16}$ - $10^{-15}$ ) can convert a significant fraction of the free ion population.

Potential reactant trace gases may, as in the stratosphere, include molecules possessing large proton affinities or large gas phase acidities. A major difference, however, arises from the fact that trace gases which can be depleted by heterogeneous interaction with aerosols may have small and possibly strongly variable abundances. Such interactions may involve condensation, dissolution, or surface as well as liquid phase chemical reactions.

Since such trace gases seem to be particularly efficient reactants for ions, it is conceivable that the tropospheric ion composition responds sensitively to aerosol conditions and meteorological factors.

This may be illustrated by discussing a possible influence of sulfuric acid vapor, which is a potential reactant trace gas. It may react with negative ions leading to  $H_2SO_4^-(H_2SO_4)_\ell(H_2O)_m$  mixed clusters, and it may also react with large positive water clusters leading to a ligand "shell" composed of a mixture of  $H_2SO_4$  and  $H_2O$ .

In the troposphere, sulfuric acid is formed from sulfur-bearing precursor gases and ultimately leads to  $H_2SO_4$ - $H_2O$  aerosol solution droplets, as in the stratosphere. However, in contrast to the tropospheric situation, significant  $H_2SO_4$  supersaturation with respect to the  $H_2SO_4$ - $H_2O$  phase should occur not under all conditions. Thus, the atmospheric  $H_2SO_4$ -vapour concentration should be roughly equal to the equilibrium saturation concentration over the aerosol which depends critically on the relative humidity and on temperature. Consequently, the influence of tropospheric sulfuric

acid vapour on the ground level ion composition may vary from negligible to important, depending on conditions.

This example demonstrates the possible response of tropospheric ions to aerosol and meteorological conditions.

Other potential reactant trace gases besides  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  are  $\text{NH}_3$ ,  $\text{CH}_3\text{CN}$ , and acids such as  $\text{HNO}_3$  and  $\text{HCl}$ . Ammonia, for example, is highly soluble in water and therefore may become depleted from the gas phase. According to in situ measurements, tropospheric ammonia vapor abundances greatly exceed the critical reactant trace gas level. Consequently,  $\text{NH}_3$  may markedly influence the positive ion chemistry. The same may be true for  $\text{CH}_3\text{CN}$  which seems to originate from the troposphere.

Thus, positive mixed cluster ions of the type  $\text{NH}_4^+(\text{NH}_3)_k(\text{CH}_3\text{CN})_l(\text{H}_2\text{O})_m$  may be formed. However, it is conceivable that other trace gases which have the potential to react with positive cluster ions are also present in sufficiently large abundances.

For both  $\text{NH}_3$  and  $\text{CH}_3\text{CN}$  it was found in the laboratory [44, 59] that only a few molecules can be incorporated into the cluster, forming an "inner" ligand shell, and that  $\text{H}_2\text{O}$  becomes the preferred ligand in the "outer" ligand shell.

Potential reactant gases for negative ions under conditions of low  $\text{H}_2\text{SO}_4$ -vapor abundances are acids such as  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{HNO}_2$ , where mixed cluster ions of the type  $\text{NO}_3^-(\text{HNO}_3)_l(\text{H}_2\text{O})_m$  may be most prominent.

In order to investigate tropospheric ion chemistry, several so-called "simulation experiments" involving ionization of laboratory air at atmospheric or elevated pressures and subsequent ion detection by differentially-pumped mass spectrometers have been carried out during recent years. However, due to the comparatively small ion residence times encountered in these experiments as a result of ion losses to the walls of the apparatus, at best only stages one and two of the ion evolution can be simulated. The decisive stage three which determines the nature of the terminal ions cannot be simulated as its characteristic time scale of  $10^2$ - $10^3$  s is much larger than the ion residence time. Therefore, these "simulation studies" have to be interpreted with care.

The first in situ ion composition measurements in the upper troposphere which were recently made by our group [12, 28] using an aircraft-borne mass spectrometer revealed the presence of large negative and positive cluster ions.

Observed negative ion masses and tentative ion identifications are

given in Table 4. It appears that the major species can be grouped in two families containing  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  cores with  $\text{NHO}_3$  and other acidic ligands.

Measured fractional count rates are shown in Figure 11. At the upper heights,  $\text{NO}_3^-$ -clusters are most prominent while  $\text{HSO}_4^-$ -clusters become about equally abundant at the lower altitudes.

Observed positive ion masses are given in Table 5 along with tentative ion identifications. These ions are mostly fragments of larger ambient cluster ions. Electric field dissociation was intendedly employed in order to facilitate ion identification. Other measurements [28] not using the dissociation revealed the presence of much larger positive ions which, however, were difficult to identify due to a lower mass resolution setting.

It appears that the major positive ions around the tropopause are  $\text{H}^+(\text{H}_2\text{O})_n$  clusters and cluster species which may fit the  $\text{H}^+(\text{CH}_3\text{CN})_l(\text{H}_2\text{O})_m$  sequence. So far, no definitive indication for  $\text{NH}_4^+$  cores exists in this region.

As in the stratosphere, the ions can be used as probes for neutral

TABLE 4 - *Negative ion masses as measured in the upper troposphere. Maximum fractional count rates and tentative ion identifications are also given (after Heitmann and Arnold; Ref. 12).*

| Mass        | Max. | Ion  |
|-------------|------|--|
| $62 \pm 3$  | 22.2 | $\text{NO}_3^-$  |
| $80 \pm 3$  | 3.8  | $\text{NO}_3^-\text{H}_2\text{O}$  |
| $125 \pm 2$ | 22.2 | $\text{NO}_3^-\text{HNO}_3$  |
| $143 \pm 3$ | 2.4  | $\text{NO}_3^-\text{HNO}_3 \cdot \text{H}_2\text{O}$ , $(\text{NO}_3\text{HSO}_3)^-$   |
| $160 \pm 3$ | 15.0 | $\text{HSO}_4^-\text{HNO}_3$   |
| $188 \pm 2$ | 66.7 | $\text{NO}_3^-(\text{HNO}_3)_2$  |
| $209 \pm 3$ | 22.6 | $\text{HSO}_4^-(\text{HNO}_3)_2\text{H}_2\text{O}$ ; $\text{HSO}_4^-\text{HSO}_3\text{H}_2\text{O}$ ; $\text{HSO}_4^-\text{HSO}_5$                                   |
| $223 \pm 2$ | 11.3 | $\text{HSO}_4^-(\text{HNO}_3)_2$   |
| $241 \pm 3$ | 14.3 | $\text{HSO}_4^-(\text{HNO}_3)_2\text{H}_2\text{O}$ ; $\text{HSO}_4^-\text{HSO}_3 \cdot \text{HNO}_3$   |
| $251 \pm 3$ | 5.7  | $\text{NO}_3^-(\text{HNO}_3)_3$  |
| $273 \pm 3$ | 7.5  | $\text{HSO}_4^-(\text{HNO}_3)_3\text{H}_2\text{O}$ ; $\text{HSO}_4^-\text{HSO}_3\text{HNO}_3\text{H}_2\text{O}$ ;<br>$\text{HSO}_4^-\text{HSO}_5 \cdot \text{HNO}_3$ |
| $286 \pm 3$ | 2.6  | $\text{HSO}_4^-(\text{HNO}_3)_3$   |
| $297 \pm 3$ | 2.7  | $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2$  |
| $352 \pm 3$ | 2.1  | $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2\text{HNO}_3$  |

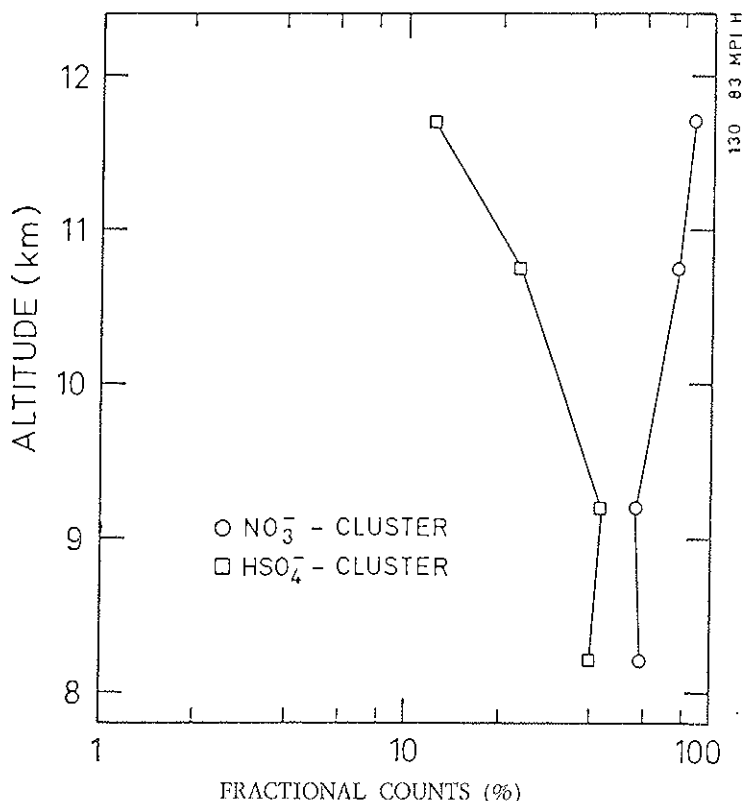


FIG. 11. Total fractional count rates for  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  cluster ions as measured in flights F1 and F2 [after Heitmann and Arnold; Ref. 12].

trace gases. Attempts to infer  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  are shown in Figures 12 and 13. The  $\text{HNO}_3$ -data fill an observational gap which existed between about 7 km and the stratopause. They fall mostly into the range of model predictions. However, more measurements are needed also due to the expected variability of  $\text{HNO}_3$ -abundances induced by heterogeneous removal of this trace gas.

The sulfuric acid vapour measurements (Figure 13) are the first ones in the troposphere. They compare also reasonably well with model predictions. In particular, they reveal that  $\text{H}_2\text{SO}_4$ -vapour appears to be highly supersaturated with respect to the condensed  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  phase which is important for nucleation considerations. For a more detailed discussion of  $\text{HNO}_3$ - and  $\text{H}_2\text{SO}_4$ -data see reference [12].

TABLE 5 - Positive ion masses as measured in the upper troposphere by a fragment ion mass spectrometer. Maximum fractional count rates and tentative ion identifications are also given (after Hauck and Arnold; Ref. 29).

| Mass    | Percent | Ion   |
|---------|---------|---|
| 19 ± 2  | 4.3     | H+H <sub>2</sub> O  |
| 28 ± 1  | 7.1     | H+A   |
| 32 ± 1  | 3.0     | H+B   |
| 37 ± 1  | 12.2    | H+ (H <sub>2</sub> O) <sub>2</sub>  |
| 42 ± 2  | 2.0     | H+CH <sub>3</sub> CN  |
| 50 ± 1  | 4.4     | H+B · H <sub>2</sub> O  |
| 55 ± 1  | 21.6    | H+ (H <sub>2</sub> O) <sub>3</sub>  |
| 60 ± 1  | 15.8    | H+CH <sub>3</sub> CN · H <sub>2</sub> O                                   |
| 73 ± 1  | 4.7     | H+ (H <sub>2</sub> O) <sub>4</sub>  |
| 78 ± 1  | 9.0     | H+CH <sub>3</sub> CN (H <sub>2</sub> O) <sub>2</sub>                      |
| 88 ± 1  | 6.0     | H+CH <sub>3</sub> CN · C<br>H+B · D                                       |
| 90 ± 2  | 3.4     | H+ (H <sub>2</sub> O) <sub>5</sub>  |
| 96 ± 2  | 6.8     | H+CH <sub>3</sub> CN (H <sub>2</sub> O) <sub>3</sub>                      |
| 106 ± 2 | 2.7     | H+CH <sub>3</sub> CN · C · H <sub>2</sub> O<br>H+B · D · H <sub>2</sub> O |
| 115 ± 1 | 8.3     | H+CH <sub>3</sub> CN (H <sub>2</sub> O) <sub>4</sub>                      |
| 126 ± 1 | 5.8     | H+ (H <sub>2</sub> O) <sub>7</sub>  |
| 132 ± 1 | 4.0     | H+CH <sub>3</sub> CN (H <sub>2</sub> O) <sub>5</sub>                      |
| 164 ± 2 | 1.4     | H+B · CH <sub>3</sub> CN (H <sub>2</sub> O) <sub>5</sub>                  |
| 201 ± 2 | 2.0     | H+ (CH <sub>3</sub> CN) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub>      |

A: HCN (172.7); C<sub>2</sub>H<sub>2</sub> (182.6)

B: CH<sub>3</sub>NH<sub>2</sub> (211.3); CH<sub>3</sub>OH (182.2)

C: CH<sub>2</sub>O<sub>2</sub> (178.1); C<sub>2</sub>H<sub>6</sub>O (187.0); (CH<sub>3</sub>)<sub>2</sub> NH (225.3)

D: CH<sub>3</sub>CHCO (200.0)

Another important tropospheric trace gas which should be detectable via ion composition measurements is ammonia. It reacts, as already mentioned, with positive ions yielding NH<sub>4</sub> cores. So far, however, such cores could not be detected in the upper troposphere which sets an upper limit to the ammonia vapour abundance (mole fraction) of only about  $2 \cdot 10^{-12}$  around the tropopause [29].

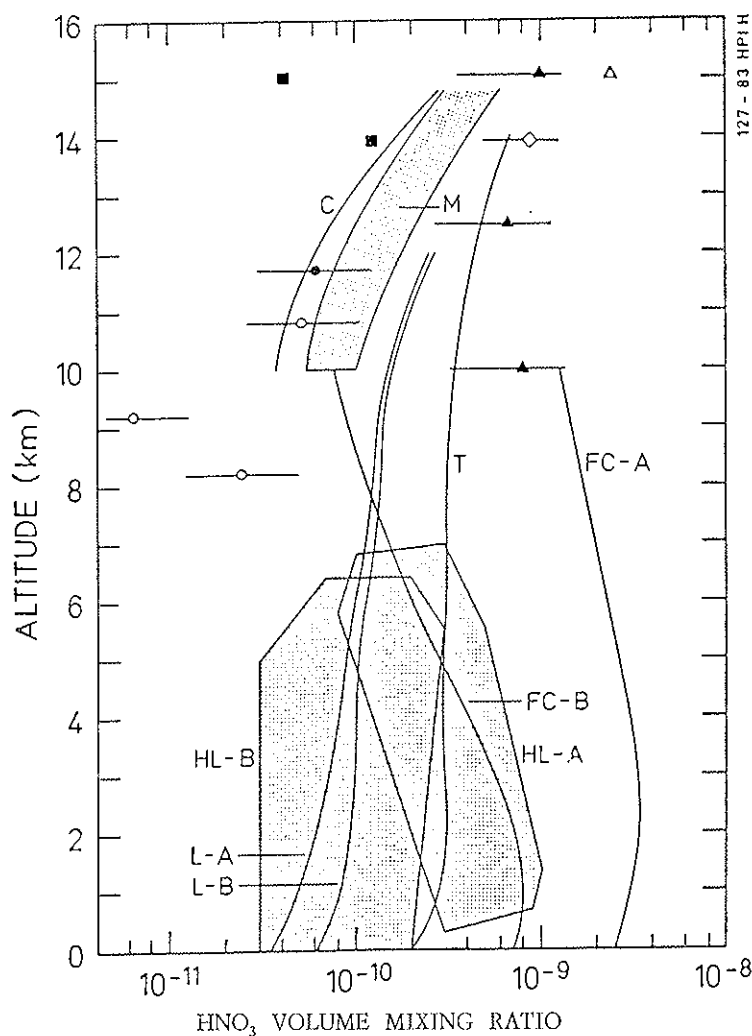


FIG. 12. Nitric acid vapour abundances as inferred from negative ion composition data (circles). Comparison is made with other measurements (symbols) and various model predictions (lines). [After Heitmann and Arnold; Ref. 12].

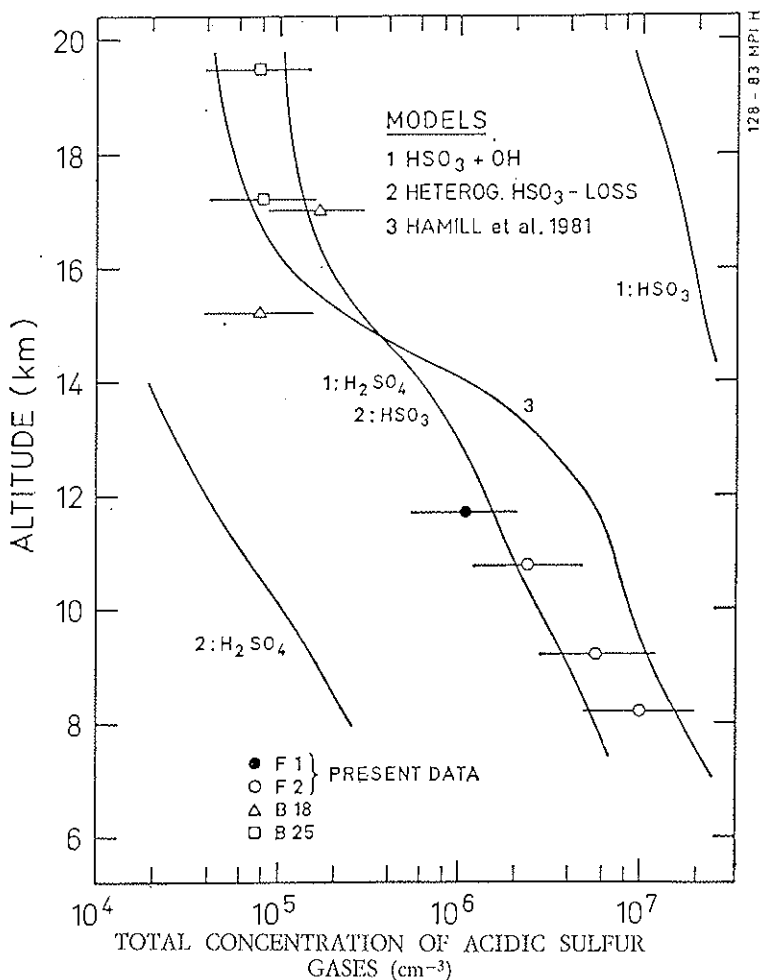


FIG. 13. Total abundances of acidic sulfur gases as inferred from negative ion composition measurements (circles). Comparison is made with model predictions (lines). [After Heitmann and Arnold; Ref. 12].

Now a possible role of free ions in tropospheric trace gas and aerosol processes will be discussed.

As far as aerosol formation is concerned, conventional ion nucleation (IN) which requires relatively large supersaturation ratios ( $S \geq 4$ ) is probably inefficient. Due to the relatively large tropospheric aerosol content, large  $S$  values can hardly build up but supersaturated vapors



should condense on preexisting aerosols. Polyion nucleation may be operative but it is not known whether small polyions can grow to condensation nuclei sizes before they are scavenged by preexisting aerosols.

Concerning a possible role of ions in tropospheric trace gas processes little can be said at present. Besides ion-molecule reactions, ion-ion recombination and ion-catalyzed reactions may in this respect be important. The latter may also include "quasi liquid phase reactions" occurring in relatively large cluster ions or polyions. Maximum rates for trace gas destruction and formation are similar to those estimated for the stratosphere (see section on Potential Role of Ions in Stratospheric Trace Gas and Aerosol Processes).

As in the stratosphere, in situ ion composition measurements should offer an enormous potential for neutral trace gas detection. Likely candidates for PACIMS trace gas detection are the reactant trace gases discussed above. Diagnostic applications for probing aerosol properties also seem promising. Since tropospheric cluster ions are relatively large, they should resemble aerosol solution droplets.

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## DISCUSSION

LIBERTI

Will you please give us some details about how you make the sampling. Since most measurements are made in the stratosphere, I presume this has been done by aircraft. Now, and since you have been using as experimental device a mass spectrometer, how are you able to make a distinction between ions and molecules? And the second question: if the species you describe in your slides have been really shown, in other words have been experimentally demonstrated with this pathway which you assume that the ions are recombined.

ARNOLD

Let me answer the first question first. The sampling is essentially similar for the various ridges and also it is a little bit optimized for the specific conditions prevailing in the different layers of the atmosphere. Of course the rocket sampling will be different from the aircraft sampling. In the case of the rocket you form a molecular beam by a skimmer, this conically shaped sampling electrode, the gas approaches this skimmer under an angle of zero degrees with respect to the skimmer axis, so you sweep out a cone and you form a molecular beam, and you take care that this molecule beam is not scattered inside by freezing it out directly. So there is no dramatic disturbance of the molecular beam inside the instrument because you have raised it out . . . liquid neon or liquid helium temperature on the cold surface. And from this molecular beam you extract the ions by means of electric fields, focus them and inject them into an electric mass filter. That is in brief the technique used in the case of the rocket experiments. For balloon and aircraft measurements the sampling is somewhat different. I do not want to discuss this in detail, unless you would like it; but I may just draw your attention to a major problem of this ion sampling, which is condition-induced fragmentation. That means while you employ the electric field you will increase the condition energy of the ions with regard to the background gas, and this causes internal excitation, and dissociation of ligand molecules. We have investigated this problem in great detail in the laboratory in simulation type experiments, and we found that in fact dissociation takes place but it is not as dramatic as one may expect. Usually

only one ligand is dissociated under most of the sampling conditions encountered. At the lower heights there is an additional problem: adiabatic cooling, due to adiabatic expansion, and one has to be very careful. But the main effect of this adiabatic cooling would be additional clustering of water vapor. Except you are particularly interested in the water cluster distribution, this would not hurt too much because you know essentially the only molecular species which can cluster to the ion in the adiabatically expanding gas jet would be water vapor under typical atmosphere conditions. It turns out that the opposite effect of dissociation is even stronger, so this is over-compensated by the electric field. It means you dissociate more ligands than you can add under these sampling conditions we are encountering.

About your second question, we measure plus lines (or ions) of a certain mass charge ratio, and of course we are confronted with a problem of identifying these species and the larger they are the larger the masses are, the more difficult this job gets, so you need additional information. One additional piece of information which is of experimental nature is the collisionally induced dissociation. You can dissociate the clusters stepwise, strip off the ligands in the experiment in the atmosphere by changing electric field conditions, and then you can measure fragment ion patterns. And this helps quite a lot as you may imagine.

BROSSET

This makes clear the question of sulphate, but do you agree that nitric acid has a quite different problem?

ARNOLD

There has been discussion of the possibility of a ternary aerosol system in the stratosphere involving also nitric acid besides sulphuric acid and water. This has been published several years ago in *Nature*; as far as I remember, the paper was not quite conclusive about this point. There is still a possibility that nitric acid might be involved in stratospheric aerosol. I may just briefly mention a finding from the ion cluster studies. I mentioned before that the sulphuric acid clusters containing, or carrying a negative charge are easily hydrated under atmospheric conditions, and that the degree of hydration, interestingly, increases with the size of the cluster, which cannot be explained by a pure electrostatic interaction between the so-called core ion and the water ligand. Interestingly, we found a similar behavior also for nitric acid clusters

which contain an  $\text{NO}^-$  core; and both these behaviors we found first in the atmospheric data and then went back to the laboratory, produced these ions in high pressure ion sources, studied the hydration and we have at least half quantitatively reproduced the increase of hydration efficiently.

BROSSET

But in fact the drop of activity of sulphuric acid with additional water is much more than the drop of nitric acid because in rather dilute solution we have an appreciable pressure of nitric acid.

ARNOLD

I agree.

CANUTO

Just an information: do you know if any of these chains of reaction that you studied have been used by those who study the composition of comets because they have a type of reaction in cometary physics that reminds me very closely of what you are doing. Since you have direct data, you have no comparison if your reaction is reliable or not. That would be most useful to check with people who have spent their lives trying to make sense out of the data out of cometary nuclei.

ARNOLD

In fact the method may be strong in getting information on neutrons in comets, and in fact at our laboratory a mass spectrometer probe for the cometary mission of Halley's comet is prepared. But the scenario is a little bit different. Of course the gas tail of the comet has a very complex chemistry and you have gradients in concentrations and change in direction with the radiation field, that the ultimate goal would be to trace back the so-called OH. In order to get these, of course you have to translate or to unravel the entire chemistry — you measure a gas constituent which was produced by possibly not very well known processes. You have to evaporate first the material from the comet, then it is exposed to the UV radiation field of the sun, it's processed photochemically, it may undergo some reactions, so that would be very difficult. But there is a chance to get some information.

CRUTZEN

Is there a possibility that  $\text{SO}_2$  can directly react with the clusters? You mentioned too that at some point  $\text{H}_2\text{O}$  may be also involved. If anything like that happens, then this may become very interesting.

ARNOLD

In fact this has been measured. One measurement of this kind was mentioned in the morning's talk on the quantum chemistry, namely that  $\text{SO}_2$  reacts with  $\text{NO}^-_2$ . We have heard that this is a particularly strong bonding, and we have heard that this must be due to some additional bonding mechanism which cannot simply be explained by the bipolar charge induced by polar interaction which shows that  $\text{NO}^-_3$  bonds very strongly to  $\text{SO}_2$ . There is the indication that the  $\text{SO}_2$  molecule at least clusters very efficiently to negative ions but only to the small ones, to the  $\text{NO}^-_2$ ,  $\text{NO}^-_3$  ions. We have recently tried to find out if also larger negative ion clusters attach to  $\text{SO}_2$  without any positive results.

CRUTZEN

And what about  $\text{H}_2\text{O}_2$  You mentioned that also in your talk.

ARNOLD

This has also been measured at the NOAA lab, and it was found that  $\text{H}_2\text{O}_2$  bonds very strongly to  $\text{NO}^-_3$ , and we make use of this reaction in trying to measure the  $\text{H}_2\text{O}_2$ . What we do is the following: we measure the  $\text{NO}^-_3$  ion in the stratosphere by mass spectro in the more or less undisturbed environment. The flow or the resonance time is about 1". The flow is simply due to a relative motion of the balloon gondola with respect to the surrounding atmosphere. So this is a kind of a flow reactor experiment; and since  $\text{H}_2\text{O}_2$  should be there, it should attach to the  $\text{NO}^-_3$  ion. The advantage of this active method is that only small ions are involved which are known to attach to  $\text{H}_2\text{O}_2$ , whereas by contrast the natural atmospheric ions grow much larger in a time scale during which they have no chance to collide with an  $\text{H}_2\text{O}_2$ . So we hope this way to get  $\text{H}_2\text{O}_2$  measurements in the stratosphere.



PULLMAN

You mentioned that  $\text{SO}_2$  binds to  $\text{NO}^{-}_2$  and  $\text{NO}^{-}_3$  but not to larger negative ions. What larger negative ions?

ARNOLD

Well, we were naturally interested in those negative ions which are the most abundant ones in some parts of the stratosphere, as well as the  $\text{NO}^{-}_3$  with two nitric acid ligands. I may mention just very briefly why we were interested in that. One may not necessarily expect  $\text{SO}_2$  to cluster with these larger ions, but we have observed an increase of an ion which may be interpretative in terms of  $\text{SO}_2$  clustering to nitric acid clusters in the stratospheric eruption cloud of the volcanos. If this ion does not contain  $\text{SO}_2$  the missing ligand must be nitric acid, which has a mass number which is just one a.m.w. from the  $\text{SO}_2$ . The measurements would probably indicate that there was a marked enhancement of nitric acid vapor concentration in the eruption cloud and that could be of interest.

PULLMAN

This is just a clarification for my information. Could you give me the words for PCIMS what does it stand for?

ARNOLD

Passive chemical ionization mass spectrology. It is the term used for chemical ionization. First of all we invented the term: passive because we were using already existing natural ions, and then after we employed this method by which we formed ions in the atmosphere and we measured them.

ANDERSON

Two questions: the first, do you see any correlation between the nitric acid observations and the local water vapor concentration? Secondly, what is the altitude resolution of the method for nitric acid?

ARNOLD

Let me answer the second question first. The altitude resolution at present can be as small as of the order of 100 meters. Usually we scan the entire mass spectrum, but we could focus only on those ions which are needed in order to infer the nitric acid vapor concentration, that means we gain time, and that means we get sufficiently good ion counting statistics in a shorter time scale, and that means we can improve resolution even below 100 meters.

And the first question was if we find correlations between the nitric acid vapor content and the water vapor. To which hydrogen are you referring?

ANDERSON

To the  $H_2O$ .

ARNOLD

We do not measure water vapor directly in the stratosphere. Again we can possibly infer it from the hydrate ion distribution, but this is more difficult because here you have to rely on a thermodynamic equilibrium distribution, which can be altered due to the electric field. Therefore we feel that this method is not very useful because there exist better methods for measuring water vapor. Therefore I simply cannot argue the question. There are no parallel water vapor measurements. As far as the troposphere is concerned, the dew point is measured on the earth in parallel to the nitric acid measurements. But here, as you have seen, we have only so far obtained four data points and that would be premature to discuss anything.

HOWARD

How confident are you of the identification of the  $HSO_3$  particle in a particular distance in the stratosphere?

ARNOLD

The  $HSO_3$  molecule, or the molecule X which we tentatively identify as  $HSO_3$ , is clustered to the negative ions which contain also sulphuric acid molecules. And now there are two possibilities, or this additional information

in order to get more than only the mass number. The mass number has been pinched down unambiguously — it is 81 atomic mass units. Unfortunately the same mass number would apply to an adduct nitric acid and water. And this is one of the problems: how to distinguish between the two possibilities. There could be mixed clusters which contain nitric acid besides the sulphuric acid and water in addition. If we accelerate these ions in an electric field we get a product which is usually an ion smaller by 81 atomic mass units, and not by 18 or 63, which would correspond to fragments of the nitric acid in the water complex. However, we cannot absolutely exclude the possibility of for instance nitric acid and water being contained in this system, and it would be very helpful to have accompanying laboratory measurements of this system — not of the  $\text{HSO}_3$  system. That may be very tough in the laboratory, but at least the nitric acid-water-sulphuric acid mix could certainly be studied with the methods available at your laboratory.

MALONE

Have you been able to examine the distribution and mobility of ions in relation to the potential gradient which is related to the many lightning discharges daily?

ARNOLD

We have done no mobility measurements in the atmosphere. We have done mobility measurements in the laboratory, using a drift tube technique and we have studied the mobility of the major ion clusters which we find in the atmosphere, including also these recently observed sulphuric acid clusters, and one can then use these laboratory data in order to calculate the mobility on the basis of the in situ ion composition measurements. It seems that usually the average mobilities are consistent with mobility measurements made by Rosen and Hoffmann using modern techniques. But there may be one thing which might be interesting to know in this regard. The recent tropospheric measurements which we made revealed the presence of thin layers of very massive cluster ions. In other words, while you are scanning the altitude range, you find more or less ions which fit usual average mobilities. But you also find thin layers where there are very massive ions, even so massive that they appear to fall outside the mass range of the instrument, which is 800 atomic mass units.

WANDIGA

It was interesting to note some of the neutral molecules you were able to detect; but your missing some of the ones that one would expect is also striking, like the freons. Can you give an explanation for that?

ARNOLD

Well, they are interesting, but unfortunately they are not very favorable particles for reactions. They react with ions but they do not lead to stable ions. The product ions are further converted to those ions which we have seen in the compilation. And this has already been shown by laboratory measurements, particularly at the NOAA Laboratory, but unfortunately the freons which would be of interest are not good candidates for this method.

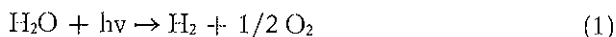
# OXYGEN CYCLE IN THE ATMOSPHERE

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The introduction of oxygen into the Earth's atmosphere is, on a geological timescale, only a relatively recent phenomenon. It now seems clear that outgassing of the young Earth resulted in the formation of a mildly reducing atmosphere, consisting in the main of  $\text{N}_2$  and  $\text{CO}_2$  (Abelson, 1966). An earlier hypothesis (Urey, 1952) requiring the existence of a strongly oxidizing paleo-atmosphere containing significant quantities of  $\text{CH}_4$  and  $\text{NH}_3$  now appears untenable. The atmospheric lifetimes of such materials would be too short for their chemistry to play an important role in, for example, the eventual synthesis of amino acids either through photochemistry, in electric discharges, or on hot surfaces.

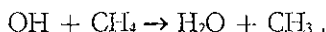
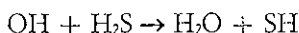
Biological sources account for the overwhelming fraction of  $\text{O}_2$  found in the present atmosphere. Considerable controversy and no small degree of uncertainty surrounds the mechanism of oxygen formation in the *pre-biological* atmosphere (Levine *et al.*, 1981; Levine, 1982). The attractive suggestion that the photodecomposition of  $\text{H}_2\text{O}$  by vacuum ultraviolet light in



fails to take account of the many chemical processes which lead to the reoxidation of  $\text{H}_2$  with subsequent water formation. Indeed, the rate of  $\text{O}_2$  formation following (1) actually depends on the rate of  $\text{H}_2$  gravitational escape from the atmosphere and not the photolysis rate itself. An alternative chemical process involving the disproportionation of OH radicals

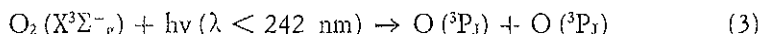


must compete with other reactions of OH that yield H<sub>2</sub>O, *viz*,

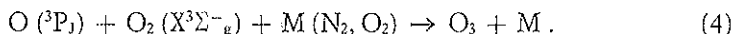


The actual quantity of O<sub>2</sub> predicted on the basis of model calculations appears to vary wildly depending on the assumed gas phase chemistry, the role of O<sub>2</sub> reactions with Fe<sup>2+</sup> in the early oceans, and the transport mechanism. Oxygen levels reported as the result of recent theoretical calculations (Levine, 1982) range between 10<sup>-14</sup> and 10<sup>-1</sup> of the present atmospheric level (PAL). Enhanced levels of solar activity would have significantly increased the prebiological O<sub>2</sub> levels. At the current level of uncertainty, relatively little can be deduced about the actual chemical mechanism responsible for fixing the O<sub>2</sub> density prior to the establishment of photosynthetic sources of oxygen.

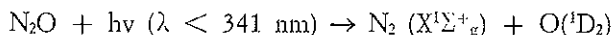
The development of oxygen in the early atmosphere led to a concomitant buildup in the ozone density and hence a significant decrease in middle ultraviolet radiation impinging upon the Earth's surface. As will be discussed in detail below, ozone arises following the photodissociation of O<sub>2</sub> in the far ultraviolet below 242 nm,



followed by the combination of atomic and molecular oxygen,



The dependence of the ozone column density upon the oxygen level is a matter of considerable interest for it will fix the degree of UV-B penetration through the atmosphere and hence presumably would establish the surface conditions for the emergence of life onto land from the sea during the Silurian period (Berkner and Marshall, 1965). Recent calculations seem to suggest that the column density of O<sub>3</sub> exceeded 10% of its current value even at O<sub>2</sub> densities as low as 1% PAL (Levine *et al.*, 1981). This behavior (Figure 1) at relatively low O<sub>2</sub> densities is attributed to the increased penetration of actinic radiation capable of O<sub>2</sub> photolysis in (3) and the enhanced rate of N<sub>2</sub>O photodissociation



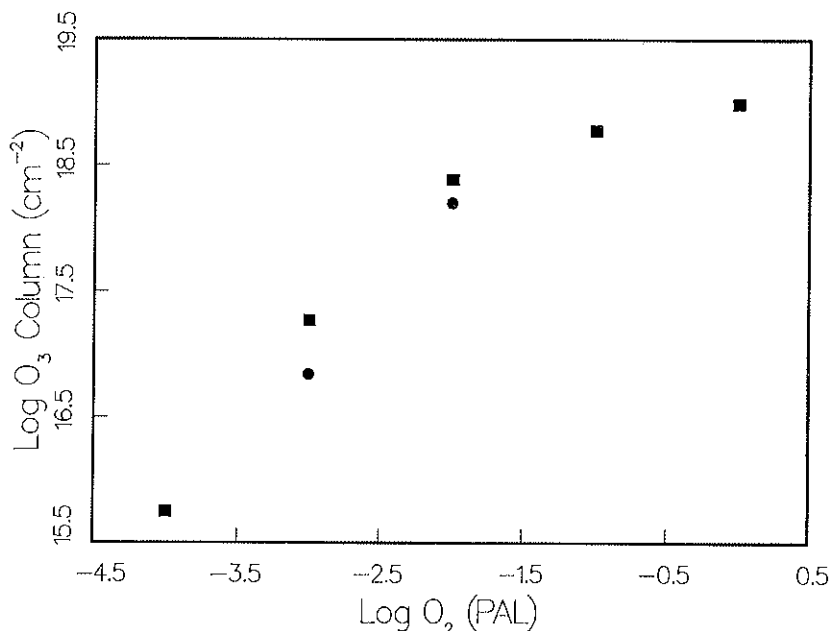
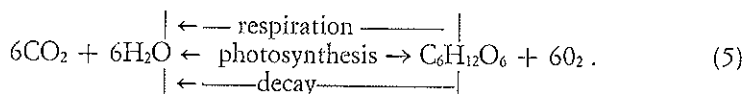


FIG. 1. Dependence of ozone column density upon level of O<sub>2</sub> in early atmosphere in the presence (●) and absence (■) of chlorine chemistry. [Source: Levine, 1982].

which would decrease the NO density (and hence rate of catalytic O<sub>3</sub> destruction) in the upper atmosphere. Clearly all such model calculations of the early atmosphere depend critically upon currently unknown parameters such as the prebiological rate of N<sub>2</sub>O formation; they do however provide an interesting backdrop against which to examine the current role of oxygen chemistry in the atmospheric environment.

The O<sub>2</sub> level of the present atmosphere is fixed primarily by the biological photosynthesis/respiration cycle which converts CO<sub>2</sub> and O<sub>2</sub>,



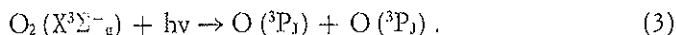
A minute fraction of the O<sub>2</sub> produced in (5) is 'fixed' in association with deep ocean sedimentation of organic material. Consumption of O<sub>2</sub> by combustion of the Earth's entire inventory of recoverable hydrocarbons (*ca.* 10<sup>19</sup> gm) would only result in a 2% decrease in the atmospheric O<sub>2</sub>

level. Whether the concomitant production of  $\text{CO}_2$  would lead to significant changes in climate and hence environment is quite another (and far more worrying) matter.

In contrast to the case of atmospheric  $\text{O}_2$ , the continued integrity of the stratospheric ozone layer remains a matter of intense concern to environmental chemists. Here, we must deal with the characterization of the photochemical system in which  $\text{O}_2$  photolysis (3) followed by recombination (4) forming ozone is balanced by parallel, largely catalytic cycles involving trace constituents. Detailed discussions of these reactive cycles are presented in other contributions to these proceedings. This paper will primarily be concerned with a discussion of the photodissociation of  $\text{O}_2$  and  $\text{O}_3$  as well as the chemistry of the reactively labile electronically excited oxygen atoms which result from such photolysis processes. Particular emphasis will be placed on the details of energy flow and deposition both following photodissociation and in bimolecular collisions. Of special interest will be the characterization of elementary reactions that may profitably be included in the further development of refined models of atmospheric chemistry.

### *Photodissociation of Molecular Oxygen*

The entire cycle of odd oxygen chemistry in the upper atmosphere is initiated by the photolysis of  $\text{O}_2$  below 242 nm, the thermochemical threshold (Table 1) for dissociation into ground state atomic oxygen formation in



Several laboratory measurements of the total absorption cross-section for the critical  $\text{O}_2(\Lambda^3\Sigma^+_u \leftarrow X^3\Sigma^-_g)$  Herzberg continuum have been reported

TABLE 1 - Threshold wavelengths for photolytic production of oxygen atoms from  $\text{O}_2$ .

| Atomic products                                   | Wavelength (nm) |
|---|-----------------|
| $\text{O}(^3\text{P}_1) + \text{O}(^3\text{P}_1)$ | 242.4           |
| $\text{O}(^3\text{P}_1) + \text{O}(^1\text{D}_2)$ | 175.0           |
| $\text{O}(^3\text{P}_1) + \text{O}(^1\text{S}_0)$ | 133.2           |



(Ditchburn and Young, 1962; Shardanand, 1969; Hasson and Nicholls, 1971; Ogawa, 1971; Shardanand and Rao, 1977). Special attention has been focussed on the region 200-230 nm for it is in this range that the solar flux in the stratosphere is not so strongly attenuated by mesospheric  $O_2$  or stratospheric  $O_3$  (Nicolet, 1980). Severe experimental problems make the measurement of  $\sigma_{O_2}(\lambda)$  (Figure 2) especially difficult. The exceptionally low cross-section for this transition, *ca.*  $10^{-24} \text{ cm}^2$ , can be overcome by the use of long pathlengths, but not high pressures, for the Herzberg continuum intensity displays a strong pressure dependence, presumably due to collisional perturbation and/or dimer formation. The end result is that the observed cross-section,  $\sigma_{\text{Total}}(\lambda)$ , represents the sum  $\sigma_{O_2}(\lambda) + \sigma_{O_3-O_2}(\lambda) n_{O_2}$ . As a consequence, experimental determination of  $\sigma_{O_2}(\lambda)$  requires that measured values of  $\sigma_{\text{Total}}(\lambda)$  must be extrapolated to zero oxygen pressure. This, in turn, appears to introduce significant random uncertainty and perhaps systematic error in the final result, for dimer absorption dominates at  $P_{O_2} > 500$  torr, the pressure

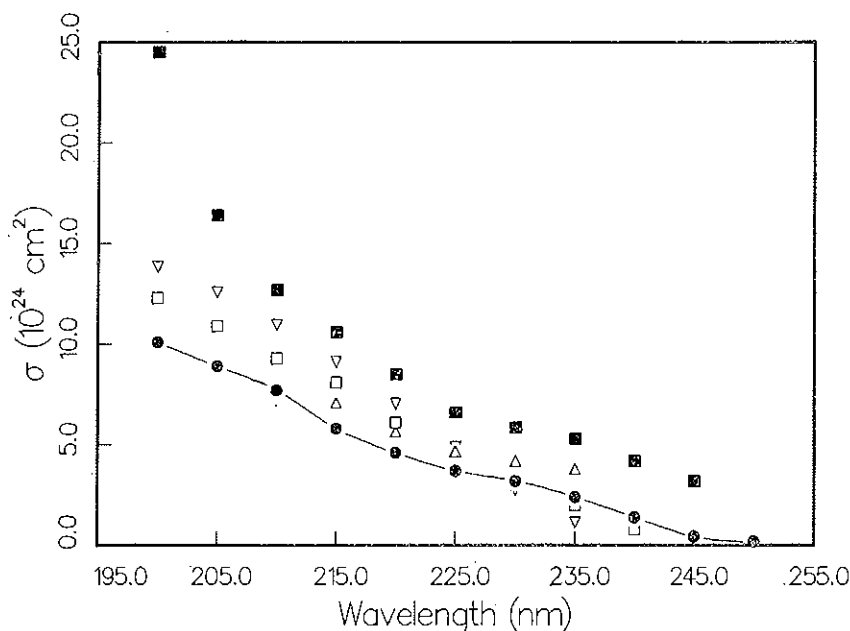


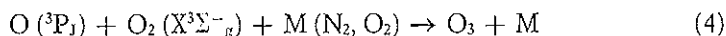
Fig. 2. Cross section for oxygen absorption in the Herzberg continuum region above 200 nm. [Sources: ( $\square$ ) Ditchburn and Young, 1962, ( $\blacksquare$ ) Shardanand, 1969, ( $\triangle$ ) Ogawa, 1971, ( $\nabla$ ) Hasson and Nicholls, 1971, ( $\bullet$ ) Shardanand and Rao, 1977].

at which absorption by  $O_2$  over a one meter pathlength would be 1%! The trend in  $\sigma_{O_2}(\lambda)$  with time appears to be downward, with the most recently reported laboratory values being smaller by at least 30% than earlier results.

Field studies of solar irradiance in the stratosphere suggest that even the latest values of  $\sigma_{O_2}(\lambda)$  derived from the laboratory studies are still too large by a factor of at least 30%. The most recent estimates obtained for  $\sigma_{O_2}(205)$  using balloon-borne spectrometers (Herman and Mentall, 1982; Frederick and Mentall, 1982; Anderson and Hall, 1983) are in the range  $6.6\text{--}7.0 \times 10^{-24} \text{ cm}^2$  in contrast to the laboratory values for this wavelength which are between  $8.9$  and  $16.4 \times 10^{-24}$ . This discrepancy leads not only to difficulties in calculating the rate of odd oxygen formation but also to uncertainties in the rate of trace constituent photolysis in the narrow atmospheric window between the peak of the Hartley continuum absorption by  $O_3$  near 250 nm and the intense Schumann-Runge bands of  $O_2$  below 200 nm. A recent model calculation of stratospheric chemistry (Froidevaux and Yung, 1982) suggests a reduction in  $\sigma_{O_2}(\lambda)$  by 0.6 would lead to a significant decrease in the computed concentrations of  $N_2O$ ,  $CF_2Cl_2$ , and  $CFCl_3$  in the upper stratosphere without a corresponding change in  $CH_4$ ,  $H_2$  or  $CO$ , none of which are photodissociated by actinic radiation in the region near 200 nm.

Recent measurements of the line strength of the Schumann-Runge  $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$  (Yoshino *et al.*, 1983) transitions have resolved outstanding uncertainties concerning the intensity of this structured absorption region. The determination of a quantitatively reliable cross-section in a region of continuous absorption is more challenging. In view of the importance of (3) to the generation of odd oxygen species in the upper stratosphere and, potentially, the partial restoration of ozone column density resulting from enhanced  $O_2$  dissociation at lower altitudes in response to  $O_3$  destruction above, it seems imperative that a reliable value of  $\sigma_{O_2}(\lambda)$  be obtained. Laser-based techniques for measurement of weak absorption signals should be considered in order to perform the required determination at low pressures where dimer absorption is not significant and over pathlengths that are of reasonable dimension, multi-pass cells being limited in utility by the mediocre performance of high reflectance coatings at 200 nm.

Turning to the second process of importance to ozone formation, the recombination of atomic oxygen with  $O_2$  in



has been studied by a variety of experimental techniques in order to obtain what now seem to be reliable kinetic parameters over the range of atmospherically important temperatures and pressures (Huie *et al.*, 1972; Klais *et al.*, 1980; Lin and Leu, 1982). Reaction (4) is well within the third-order regime at  $P_{N_2} < 200$  torr; the most recent experimental studies have been carried out using highly direct detection of  $O(^3P_1)$  by resonance fluorescence or absorption at the 130 nm transition,  $3^3S_1 \leftarrow 2^3P_1$ , following vacuum ultraviolet photolysis of  $O_2$ . The results obtained in this manner (Table 2) seem to be in reasonable agreement, especially near 298 K. Greater discrepancies exist over the broad temperature range of stratospheric relevance and further examination of the low temperature kinetics may be warranted. Because third-order reactions such as (4) are relatively slow, significant corrections must be made for diffusion of  $O(^3P_1)$  out of the reaction zone as well as for reactions with trace contaminants such as  $O_3$ . The formation of the ozone product of (4) has been monitored using time-resolved absorption spectroscopy (Kleindienst, *et al.*, 1980). From these observations it was concluded that over half of the  $O_3$  was formed in a low-lying metastable state, possibly  $^3B_2$ . This observation would be of atmospheric significance if these metastable  $O_3$  molecules could undergo reaction prior to being quenched to the ground state.

### Photodissociation of $O_3$

The wavelength thresholds for  $O_3$  photodissociation into specific atomic and molecular fragments are presented in Table 3. There are two

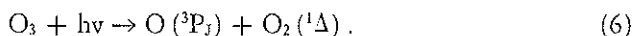
TABLE 2 - Kinetic parameters,  $k_4 = A \exp (C/T)$ , describing three-body reaction of  $O + O_2 + M \rightarrow O_3 + M$ .

| M              | A (cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup> ) | C (K) | Reference                  |
|----------------|---|-------|----------------------------|
| N <sub>2</sub> | $5.04 \times 10^{-35}$  | 724   | Lin and Leu, 1982          |
|                | $8.82 \times 10^{-34}$  | 575   | Klais <i>et al.</i> , 1980 |
|                | $1.82 \times 10^{-35}$  | 995   | Arnold and Comes, 1979     |
| O <sub>2</sub> | $6.40 \times 10^{-35}$  | 663   | Lin and Leu, 1982          |
|                | $2.15 \times 10^{-34}$  | 345   | Klais <i>et al.</i> , 1980 |
|                | $6.75 \times 10^{-35}$  | 635   | Arnold and Comes, 1979     |

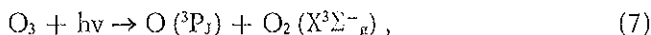
TABLE 3 - Threshold wavelengths (nm) for photolytic production of oxygen atoms and molecules from O<sub>3</sub>.

| O                           | X <sup>3</sup> Σ <sup>-</sup> <sub>g</sub> | O <sub>2</sub><br>a <sup>1</sup> Δ <sub>g</sub> | b <sup>1</sup> Σ <sup>+</sup> <sub>g</sub> |
|-----------------------------|--|---|--|
| <sup>3</sup> P <sub>j</sub> | 1180                                       | 611   | 463  |
| <sup>1</sup> D <sub>2</sub> | 411  | 310   | 266  |
| <sup>1</sup> S <sub>0</sub> | 237  | 200   | 180  |

main regions of absorption by O<sub>3</sub> which are of interest to atmospheric photochemists. The first of these, the Chappuis bands, occurs in the visible region between 450 and 800 nm with a peak cross-section of only σ<sub>o<sub>2</sub></sub>(600) = 5.2 × 10<sup>-21</sup> cm<sup>2</sup>. That the peak of this 1<sup>1</sup>A<sub>1</sub> ← 1<sup>1</sup>A<sub>1</sub> transition coincides roughly with the threshold for formation of O (<sup>3</sup>P<sub>j</sub>) + O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>), might suggest that this channel plays a significant role in the photodissociation process, *viz.*



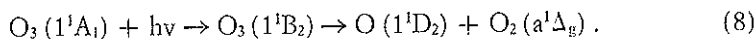
However, the total quantum efficiency for O<sub>3</sub> destruction following photolysis is not observed to depend upon the wavelength of actinic radiation in this region (Castellano and Schumacher, 1962). Rather, the value of Φ<sub>-o<sub>3</sub></sub> is measured as 2 both above and below the 611 nm threshold. In addition, lovely observations of the O<sub>2</sub> product of O<sub>3</sub> photolysis in the Chappuis bands using Coherent Anti-Stokes Raman Spectroscopy (CARS) have confirmed (Valentini, 1983) that it is only O<sub>2</sub> (X<sup>3</sup>Σ<sup>-</sup><sub>g</sub>) which is formed in



process (6) playing no observable role. These same experimental studies revealed that the vibrational distribution of the O<sub>2</sub> (X<sup>3</sup>Σ<sup>-</sup><sub>g</sub>) fragment produced in (7) peaks in v'' = 0 with an apparent population inversion occurring between v'' = 3 and v'' = 2. The rotational state distributions peak in the region 30 < J'' < 38, with a shift observed toward lower J'' in the higher vibrational levels. About 65% of the total available dissociation energy appears in relative translation of the fragments, the internal energy being roughly equally divided between vibration and

rotation. Neither a simple impulsive nor a statistical model yields population distributions that are in satisfactory agreement with the observed results.

The ultraviolet Hartley band of  $O_3$  spans the region 200-320 nm. This strong absorption feature,  $\sigma_{O_3}(255) = 1.1 \times 10^{-17} \text{ cm}^2$ , is associated with the  $1^1B_2 \leftarrow 1^1A_1$  allowed transition arising from the charge transfer of the  $p\pi$  orbital of the central oxygen to that of a terminal atom (Hay and Dunning, 1977). The identity of the absorption transition has been confirmed by determining the angular distribution of the photofragments of the dissociation at 266 nm (Fairchild *et al.*, 1978). The  $1^1B_2$  excited state correlates with electronically excited products,



This is in good agreement with classical photochemical measurements which clearly demonstrated that the large quantum yield for ozone removal following excitation in the Hartley band was consistent with reactions of the electronically excited photofragments and subsequent chemical products (Wayne, 1969).

We next examine the details of energy deposition in the fragments of  $O_3$  photodissociation in the Hartley continuum. Recent time-of-flight studies (Sparks *et al.*, 1980) of the internal energy distribution in the  $O_2(a^1\Delta_g)$  product of (8), have revealed that over 50% of the products are formed in  $v'' = 0$ , 24% in  $v'' = 1$ , 12% in  $v'' = 2$  and 7% in  $v'' = 3$ . Rotational excitation accounts for another 17% of the available energy in  $v'' = 0$ . These results can be rationalized on the basis of an impulsive release of energy on the excited state potential surface with a weak minimum at an elongated bond length, but similar bond angle as the ground state.

CARS measurements have revealed an unexpected propensity for population of the even rotational levels in  $v'' = 0$  and  $v'' = 1$  (Moore *et al.*, 1983). No explanation based on symmetry or dynamical constraints for this interesting observation is immediately forthcoming. Further elucidation of the dynamics of (8) will probably require refinement of our understanding of the role of symmetry conservation in the dissociation of triatomic molecules.

Because of its importance to the chemistry of both the troposphere and stratosphere, it is the wavelength dependence of the  $O(1^1D_2)$  yield which is of greatest interest to the atmospheric chemist. From the

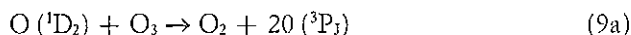
relative yield,  $\Phi_{O(^1D_2)}(\lambda) = O(^1D_2) / \{O(^1D_2) + O(^3P_1)\}$ , the absorption cross-section,  $\sigma_{O_3}(\lambda)$ , and the solar flux,  $F(\lambda)$ , the rate coefficient for  $O(^1D_2)$  production may be calculated directly,

$$J_{O(^1D_2)} = \int \sigma_{O_3}(\lambda) \Phi_{O(^1D_2)}(\lambda) F(\lambda) d\lambda.$$

Until quite recently, direct measurements of  $\Phi_{O(^1D_2)}(\lambda)$  were limited by the very real experimental difficulties associated with the highly efficient deactivation of  $O(^1D_2)$  by  $O_3$ , as well as the need to provide a sensitive probe for atomic oxygen atoms in the ground  $^3P_1$  state as well as in the electronically excited  $^1D_2$  state. The development of resonance spectroscopic techniques for time-resolved detection of  $O(^3P_1)$  has permitted monitoring of this state at densities of *ca.*  $10^{12} \text{ cm}^{-3}$  with an instrumental bandwidth in excess of 10 MHz. When combined with the use of high intensity photolysis sources such as the excimer lasers and frequency quadrupled Nd/YAG, it has proved possible to measure directly the yield of  $O(^1D_2)$  and  $O(^3P_1)$  at several discrete wavelengths in the middle ultraviolet.

Two basic schemes have been utilized in the direct measurement of  $\Phi_{O(^1D_2)}(\lambda)$  in the Hartley band region. The first (Brock and Watson, 1980a; Wine and Ravishankara, 1982) permits the use of slower detection methods because the yield of  $O(^3P_1)$  following ozone photolysis in the presence of known quenchers of  $O(^1D_2)$  (such as  $N_2$ ) that convert all of the excited atoms to the ground state is compared to that observed when all of the  $O(^1D_2)$  is collisionally deactivated by a molecule (e.g.,  $CH_4$ ) that is known to undergo chemical reaction with the excited state. Thus the total oxygen atom yield and that associated with processes (6) and (7) only may be obtained in separate experiments. Although this scheme is conceptually relatively simple, its successful execution requires that the apparatus remain stable over the long times required to achieve good signals for data analysis.

In our laboratory at Cornell, an alternative scheme has been developed (Amimoto *et al.*, 1980; Greenblatt and Wiesenfeld, 1983) in which the magnitude of the  $O(^3P_1)$  signal *immediately* following laser photolysis is compared quantitatively to that seen following the deactivation of  $O(^1D_2)$  by  $O_3$ , a process which is known (Davenport *et al.*, 1972; Amimoto *et al.*, 1978) to yield one ground state atom for each  $O(^1D_2)$  deactivated, probably in (Arnold and Comes, 1980 a,b)



where  $k_{9a} = k_{9b}$ . The temporal profile of  $\text{O} (^3\text{P}_1)$  obtained in these experiments provides an estimate of  $\Phi_{\text{O} (^1\text{D}_2)}(\lambda)$  for each laser pulse. The nonlinear least squares procedures employed to yield the desired photochemical parameter require good signal quality (Figure 3), so tens of thousands of laser pulses are sometimes averaged in order to achieve satisfactory results.

A compendium of  $\Phi_{\text{O} (^1\text{D}_2)}(\lambda)$  values reported to date is presented in Table 4. In the region near the peak of the Hartley continuum, namely at 248 and 266 nm, the yields of  $\text{O} (^1\text{D}_2)$  are in the range 0.88-0.94, but certainly not unity as was earlier assumed. The value of  $\Phi_{\text{O} (^1\text{D}_2)}(308)$  is especially important in that it places on an absolute scale the body of *relative* measurements of  $\Phi_{\text{O} (^1\text{D}_2)}(\lambda)$  in the wavelength region above 300 nm which is so important in tropospheric photochemistry (Moortgart and Kudszus, 1978). These had been made using a variety of methods based either on chemical analysis or chemiluminescent detection of photolysis products; all were indirect when compared to the schemes described above. Results were normalized to a value of  $\Phi_{\text{O} (^1\text{D}_2)}(300) = 1.0$ . The most recent direct measurements of  $\Phi_{\text{O} (^1\text{D}_2)}(308)$  suggest that a more appropriate value of  $\Phi_{\text{O} (^1\text{D}_2)}(300)$  would be 0.96-0.97. Apparently the yield of  $\text{O} (^1\text{D}_2)$  actually *increases* to the long wavelength side of the Hartley band peak.

Several recent studies have centered on the theoretical description of  $\text{O}_3$  spectroscopy in the Hartley continuum. Potential energy surfaces for the four  $^1\text{A}'$  states which play an important role in (8) have been calculated using the generalized valence bond multiconfiguration SCF technique (Hay *et al.*, 1982). Analytic surfaces were fitted to a set of 18 reference configurations for each of these states. The  $1^1\text{B}_2$  surface, upon which occurs the dissociative interaction leading to production of  $\text{O} (^1\text{D}_2)$  and  $\text{O}_2 (a^1\Delta_g)$ , is characterized by an asymmetric equilibrium geometry. The  $2^1\text{A}_1$  state which also correlates with electronically excited products but cannot be accessed by an electric dipole-allowed transition from the ground  $1^1\text{A}_1$  state lies very close in energy to the  $1^1\text{B}_2$ . Both of these states are crossed by a repulsive state at an  $\text{O}_2\text{-O}$  bond distance of *ca.* 0.17 nm when the bond angle is  $110^\circ$ . The calculated absorption spectrum in the middle ultraviolet agrees well with that observed experimentally. Dynamics calculations designed to probe the

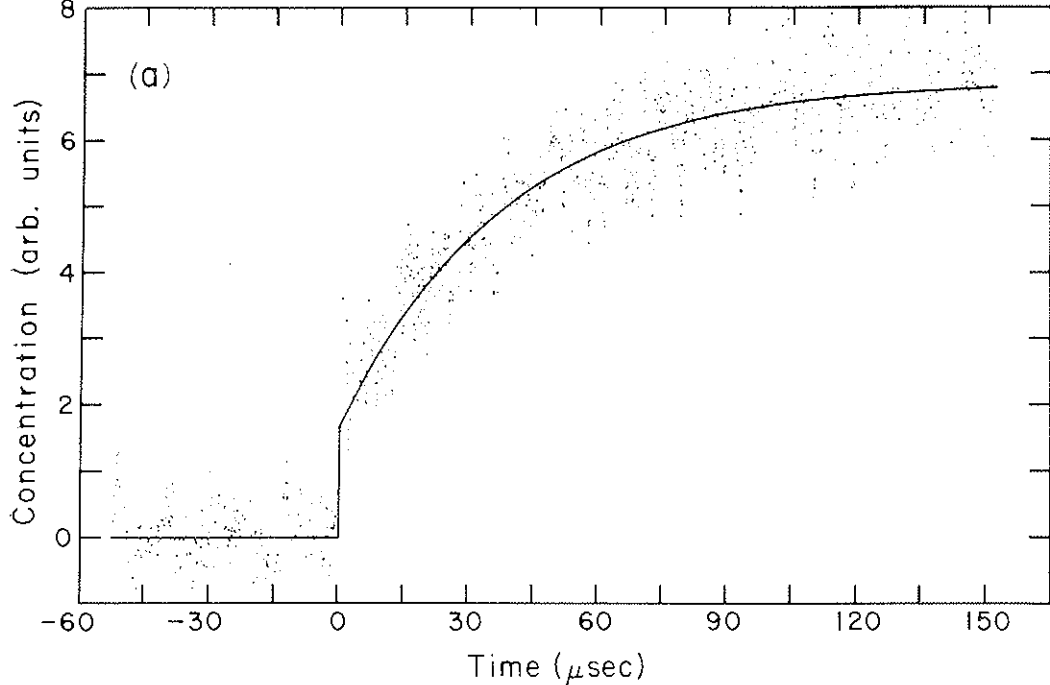


FIG. 3. Transient profile of  $O(^3P_j)$  density obtained by monitoring the vacuum ultraviolet atomic resonance fluorescence signal following laser photodissociation of  $O_3$ . (a) Photolysis at 308 nm,  $P_{O_3} = 1$  mTorr,  $P_{He} = 5.7$  Torr, 40288 averaged. (b) Photolysis at 248 nm,  $P_{O_3} = 1$  mTorr,  $P_{He} = 9.7$  Torr, 8192 shots averaged. The solid lines through the points representing non-linear least squares fit to the data, [Source: Greenblatt and Wiesenfeld, 1983].

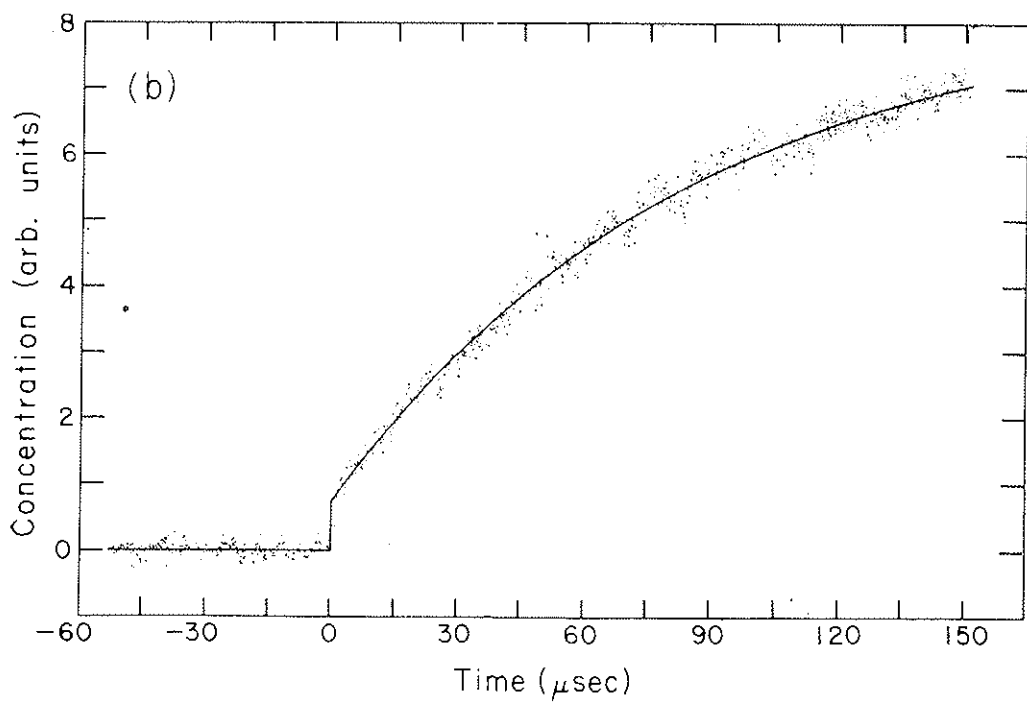




TABLE 4 - Direct determinations of  $\Phi_{O(^1D_2)}$  following photodissociation of  $O_3$  in the Hartley band.

| Wavelength<br>(nm) | $\Phi_{O(^1D_2)}$ |                                 |
|--------------------|-------------------|---------------------------------|
| 308                | 0.79 (0.02)       | Greenblatt and Wiesenfeld, 1983 |
| 266                | 0.88 (0.02)       | Brock and Watson, 1980          |
| 266                | ca. 0.90          | Sparks <i>et al.</i> , 1980     |
| 248                | 0.94 (0.01)       | Greenblatt and Wiesenfeld, 1983 |
| 248                | 0.91 (0.03)       | Wine and Ravishankara, 1982     |
| 248                | 0.85 (0.02)       | Amimoto <i>et al.</i> , 1980    |

Numbers in parentheses represent reported errors.

distribution of internal energy in the fragments of photodissociation have not yet been reported. The observed lack of dependence of  $\Phi_{O(^1D_2)}(\lambda)$  in the region 248-300 nm seems difficult to explain in view of the calculated curve crossing, for the velocity of system passage through the region of nonadiabaticity near 0.17 nm would vary widely depending upon the wavelength of actinic radiation. The J distribution of the  $O(^3P_r)$  produced in  $O_3$  photolysis at 266 nm has been determined in our laboratory using resonance enhanced multiphoton ionization techniques (Figure 4). These results (Sivaram and Wiesenfeld, in progress) suggest that the spin-orbit levels are formed in a statistical distribution, the population ratios being roughly in proportion to the degeneracies of the  $J = 0, 1$ , and 2 levels. Such information may shed further light on the nature of the excited state potential surfaces governing  $O_3$  photodissociation in the gas phase.

A relatively simple spectroscopic model of  $O_3$  absorption in the middle ultraviolet has been proposed (Adler-Golden *et al.*, 1982). This model assumes that the internal energy of an  $O_3$  molecule adds fully to that of the absorbed ultraviolet photon and that the quantum yield of  $O(^1D_2)$  varies smoothly from zero at some threshold energy (calculated as being  $32900\text{ cm}^{-1}$ ) to unity  $600\text{ cm}^{-1}$  above this threshold. The model, which is quite successful in rationalizing the observed Hartley band spectrum for vibrationally excited  $O_3$ , accurately reflects the experimental temperature dependence of the  $O(^1D_2)$  yield at 313 nm and also predicts a dependence of  $\Phi_{O(^1D_2)}(\lambda)$  upon wavelength in the region above 304 nm that is quite similar to that observed in a previous experimental study

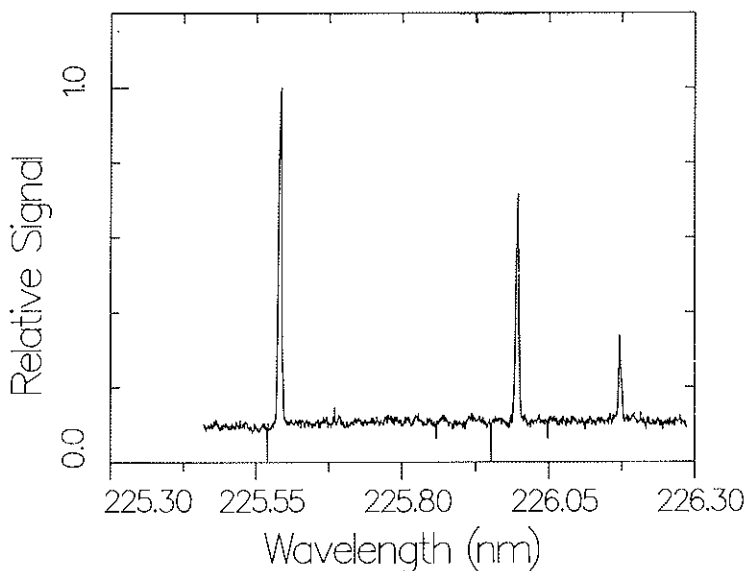


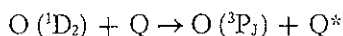
FIG. 4. Resonance enhanced, three-photon spectrum of atomic oxygen,  $3P_{2,1,0}$  observed following excitation of the  $3^3P_J \leftarrow 2^3P_J + 2h\nu$  transition in a flow discharge apparatus. Atomic oxygen at a density of *ca.*  $10^{13} \text{ cm}^{-3}$  was generated in the  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$  reaction.

(Brock and Watson, 1980b). This latter set of observations noted the presence of a pronounced 'tail' in the  $\text{O}(^1\text{D}_2)$  yield which would play an important role in tropospheric chemistry at high solar zenith angles; earlier experiments did not reveal the existence of this absorption feature. The values of  $\Phi_{\text{O}(^1\text{D}_2)}(\lambda)$  at these longer wavelengths seem quite worthy of further experimental and theoretical examination.

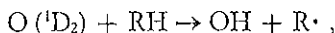
### *Oxygen chemistry*

The profusion of reactive atomic and molecular oxygen species (including  $\text{O}_3$ ) present in the atmosphere suggests an important role for these materials in fixing its physical structure and chemical composition. This is, in fact, the case. Other contributions to the present proceedings will describe many of the complex chemical cycles involving oxidizers such as  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{O}_3$ , and  $\text{O}$  that have been identified in both the troposphere and stratosphere. Hydrogen peroxide appears to be responsible for a significant fraction of  $\text{SO}_2$  oxidation in the aqueous aerosol,

hence contributing strongly to wet deposition of acidic materials. Atomic oxygen and  $O_2(a^1\Delta_g)$  react with olefins in polluted air yielding free radicals. In the remainder of this contribution, attention will be focussed upon the pivotal role played by the primary photoproduct of the ultra-violet dissociation of  $O_3$ , namely  $O(^1D_2)$ . Because these highly reactive atoms can either be *physically quenched* to the electronic ground state



where  $Q^*$  represents internal excitation, or undergo *chemical reaction* to yield distinct chemical products, as in



the following discussion will be organized along these logical lines (see also, Wiesenfeld, 1982).

The magnetic dipole allowed transition  $O(^1D_2) \rightarrow O(^3P_{1,2}) + h\nu$  ( $\lambda = 630$  nm) may be observed in the aurora. Below the mesosphere, collision times are short in comparison to the optical lifetime of  $O(^1D_2)$  ( $\tau = 143$  sec) so bimolecular encounters dominate the removal of excited oxygen atom at these altitudes. The development of sophisticated atmospheric models requires specification of the detailed rate constants for particular deactivation processes. Thus, it becomes necessary not only to know the total rate of  $O(^1D_2)$  removal, but also to account for the relative efficiency with which the various possible product species are formed (NASA, 1981). For all deactivators, the relative contributions of quenching and chemical reaction must be assessed. The role of energy transfer should be understood for quenching processes, and the excitation efficiency of the available internal modes of the collision partner determined. In the case of chemical reaction, the high energy of  $O(^1D_2)$ ,  $\Delta H^\circ_f = 105$  kcal/mole, often makes necessary the characterization of a potential profusion of reactants. To some extent, such kinetic parameters were obtained from classical chemical experiments carried out in the 1960's (see Schiff, 1972, and Nicolet, 1972), but detailed information has primarily become available over the course of the last decade during which have been developed highly specific diagnostic techniques, often based on laser spectroscopy.

Measurement of absolute rate constants for  $O(^1D_2)$  removal requires the application of techniques which permit time-resolved monitoring of

either the excited atom or some product. In the earliest of these direct studies (Heidner *et al.*, 1972, 1973), the attenuation of the O ( $^1P_1 \leftarrow ^1D_2$ ) resonance line at 115 nm was monitored in the vacuum ultraviolet following the broad-band photolysis of ozone in the presence of various deactivators. The bimolecular rate constants for deactivation,  $k_d$ , were estimated from the variation in the observed removal rate with collision partner concentration,  $[D]$ ,

$$[O(^1D_2)]_t = [O(^1D_2)]_{t=0} \exp(-k_d [D] t).$$

This technique required that the observed attenuation signal be corrected for non-linearity induced by the mismatch between the atomic absorption line and the resonance emission from the microwave-powered resonance lamp which was used as the source of the 115 nm radiation. This empirical correction appears to have resulted in a systematic discrepancy between the values obtained in these measurements and those reported in later work in which the temporal progress of the O ( $^1D_2$ ) deactivation process was followed by monitoring either the profile of the weak 630 nm emission (Davidson *et al.*, 1976, 1977; Streit *et al.*, 1976) or the growth in the O ( $^3P_1$ ) resonance absorption or fluorescence at 130 nm (Amimoto *et al.*, 1979, Wine and Ravishankara, 1981). The later technique also makes possible the estimation of relative quenching efficiencies for specific deactivating molecules because not only the temporal profile but also the magnitude of the O ( $^3P_1$ ) signal is obtained. The rates of O ( $^1D_2$ ) deactivation by a wide range of molecules have now been reliably measured at room temperature (Table 5), and the temperature effect over the range of stratospheric and tropospheric importance demonstrated to be insignificant.

As noted above, development of reliable atmospheric models requires the elucidation of detailed rate constants for specific deactivation pathways. Presented below is a discussion of the collisional dynamics of O ( $^1D_2$ ) deactivation by molecules of atmospheric interest. Additional species which are not of primary importance to environmental chemistry will also be mentioned in order to illustrate the general behavior of O ( $^1D_2$ ) in gas phase encounters with quenching and reactive substrates.

*Nitrogen.* The overwhelming fraction of electronically excited oxygen atoms formed in the photolysis of O<sub>3</sub> in the atmosphere are deactivated by collisions with N<sub>2</sub> and O<sub>2</sub>, with  $k_{N_2} [N_2]/k_{O_2} [O_2] = 2.4$ . This de-

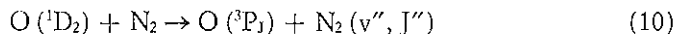
TABLE 5 - Overall rate constants and quenching efficiencies for deactivation of  $O(^1D_2)$  as determined at Cornell by laser photolysis-resonance absorption spectroscopy.

| Deactivator                     | $10^{10} \times k_d$ (cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup> ) |          | $k_q/k_d$ |
|---------------------------------|--|----------|-----------|
| O <sub>3</sub>                  | 2.4  | (0.11)   | 0.0       |
| N <sub>2</sub>                  | 0.24   | (0.01)   | 1.0       |
| O <sub>2</sub>                  | 0.42   | (0.02)   | 1.0       |
| N <sub>2</sub> O                | 1.2  | (0.1)    | 0.0       |
| CO <sub>2</sub>                 | 1.3  | (0.1)    | 1.0       |
| H <sub>2</sub> O                | 1.9  | (0.3)    | 0.0       |
| CH <sub>4</sub>                 | 1.6  | (0.1)    | 0.0       |
| CH <sub>3</sub> F               | 1.4  | (0.1)    | 0.25      |
| CHF <sub>3</sub>                | 0.084  | (0.008)  | 0.75      |
| CF <sub>4</sub>                 | 0.0018   | (0.0001) | 1.0       |
| CH <sub>3</sub> Cl              | 2.1  | (0.2)    | <0.1      |
| CH <sub>2</sub> Cl <sub>2</sub> | 2.7  | (0.2)    | <0.1      |
| CHCl <sub>3</sub>               | 3.0  | (0.2)    | 0.1       |
| CCl <sub>4</sub>                | 3.5  | (0.3)    | 0.15      |
| CFCI <sub>3</sub>               | 2.4  | (0.2)    | 0.15      |
| CF <sub>2</sub> Cl <sub>2</sub> | 1.4  | (0.2)    | 0.15      |
| CF <sub>3</sub> Cl              | 1.12   | (0.02)   | 0.50      |

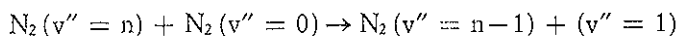
Numbers in parentheses represent errors.

References: Animoto *et al.*, 1978, 1979; Force and Wiesenfeld, 1981.

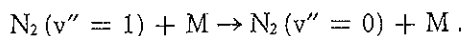
activation accounts for a significant degree of heating in the stratosphere when the energy released in



is eventually degraded into translation probably via the efficient self-relaxation of N<sub>2</sub>



and the far slower



The efficiency of electronic-to-vibrational energy transfer in (10) is in some doubt, the only measurement reported to date suggesting that *ca.* 40% of the available 45 kcal/mole is converted into vibration (Slanger and Black, 1974). However, in the related deactivation process,

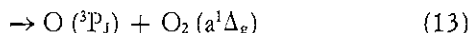
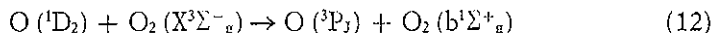


small signal absorption measurements using a tunable laser probe beam (Lin and Shortridge, 1974; Shortridge and Lin, 1976) revealed that only 21% of the electronic quantum in the excited atom was transferred to CO.

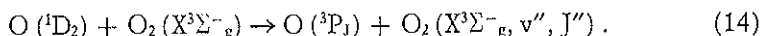
Processes such as (10) and (11) have been treated theoretically using models in which long-lived intermediates ( $\text{N}_2\text{O}$  and  $\text{CO}_2$ , respectively) are formed as the result of collisional encounters between  $\text{O} (^1\text{D}_2)$  and the quencher (Tully, 1974; Zahr *et al.*, 1975). These intermediate species are strongly bound, the ground electronic state of the molecules correlating with the diatomic and  $\text{O} (^1\text{D}_2)$ , not the lower-lying  $^3\text{P}_1$  ground state. Multiple traversals of the region of non-adiabatic interaction between the singlet and triplet state, the latter correlating with  $\text{O} (^3\text{P}_1)$ , can occur during the long lifetime (in excess of  $10^4$  vibrational periods) of the collision intermediate. Thus, even relatively weak coupling between the two surfaces can, given enough opportunity, result in a quenching efficiency which is quite high (roughly corresponding to one quenching event for every 5-10 gas kinetic collisions). That the lifetime of the collision complex is relatively long is confirmed by the observation of a distribution of vibrational energy in the CO product of (11) which would be expected by a statistical partitioning of energy in the  $\text{CO}_2$  intermediate complex.

The collisional deactivation of  $\text{O} (^1\text{D}_2)$  by  $\text{N}_2$  (and  $\text{O}_2$  as well) will result in the formation of *translationally* excited  $\text{O} (^3\text{P}_1)$  atoms. These will, through further collisions with the major constituents, become thermalized to the ambient temperature. However, it has been recognized (Logan and McElroy, 1977), that, at any given instant, there must exist a distribution of oxygen atom velocities which is certainly not thermal. Indeed, the density of energetic oxygen atoms arising from (10) is quite comparable to that of  $\text{O} (^1\text{D}_2)$  especially in the lower atmosphere where direct photolysis of  $\text{O}_3$  in the Chappuis band in (3) gains in relative importance. The chemistry of thermally excited atoms is only beginning to be explored and we can expect to develop a significantly better understanding of such interesting processes in the near future.

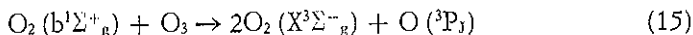
*Oxygen.* The deactivation of  $O(^1D_2)$  by  $O_2$  is interesting for it offers several exoergic spin-conserving pathways leading to electronic excitation of the collision partner,



in parallel with the quenching pathway analogous to (10) and (11)



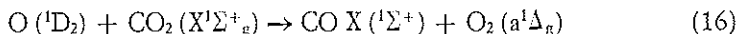
Process (12) is probably of atmospheric interest because the subsequent deactivation of  $O_2(b^1\Sigma^+_g)$  by  $O_3$



is both relatively fast,  $k_{15} = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , and efficient in destroying  $O_3$ , roughly 25-50% of the deactivating collisions resulting in decomposition (Slanger and Black, 1979). This may be contrasted with a similar dissociative deactivation of the lower-lying  $a^1\Delta_g$  state of  $O_2$  which proceeds with a rate constant  $10^4$  X smaller than  $k_{15}$ .

A variety of experimental techniques has been applied to the study of  $O(^1D_2)$  deactivation by  $O_2$ . The total yield of atomic oxygen following (12) followed by (14) has been determined to be in the range 0.5-0.6 (Slanger and Black, 1979; Amimoto and Wiesenfeld, 1980), which suggests that  $0.6 < k_{12}/k_{O_2} < 1.0$ . On the basis of these measurements, it has been concluded that these processes may play a role in  $O_3$  destruction at high altitudes, reducing its density by as much as 12%.

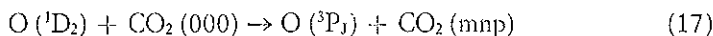
*Carbon Dioxide.* Collisional deactivation of  $O(^1D_2)$  by  $CO_2$  is intriguing from a number of different viewpoints. Chemical reaction to yield CO and  $O_2(a^1\Delta_g)$



is both highly exothermic and conservative of electronic spin and orbital angular momentum. Yet experiments clearly demonstrate (Shortridge and Lin, 1975; Amimoto *et al.*, 1979) that  $k_{16}/k_{CO_2} \ll 0.01$ , i.e., the deactivation proceeds entirely by physical quenching and not chemical reaction,

albeit at a rate essentially identical to the rapid reaction of O ( $^1D_2$ ) with  $N_2O$ . This behavior, which is all the more striking because  $N_2O$  and  $CO_2$  are isoelectronic, has been rationalized (Wiesenfeld, 1977) in terms of *adiabatic* correlations of reactants with high-lying product states, in particular those arising from the interaction of *two* O ( $^1D_2$ ). Avoided crossings between the states correlating with reactants and those correlating with low-lying molecular excited states of  $N_2O$  (such as  $^3\Sigma^+$  and  $^3\Delta$ ) occur at thermally accessible energies. Because no such low-lying states exist in  $CO_2$ , there is a substantial barrier to formation of products.

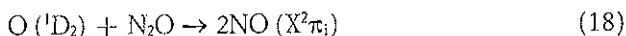
That the rates of O ( $^1D_2$ ) deactivation by  $N_2O$  and  $CO_2$  are similar is fortuitous, the high efficiency of quenching by  $CO_2$  arising from the intermediacy of a long-lived  $CO_3$  complex, the existence of which can be inferred from isotope scrambling studies (Baulch and Breckenridge, 1966). Excitation of the internal modes of  $CO_2$  following



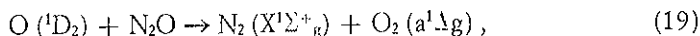
can be monitored by observation of the infrared emission at 4300 nm following laser photolysis of  $O_3/CO_2$  mixtures (Robertshaw and Smith, 1980). This emission arises from the  $CO_2(mnp \rightarrow mnp-1)$  transition. Insertion of a  $CO_2$  sample between the photolysis cell and infrared detector selectively removes the fundamental emission,  $001 \rightarrow 000$ , even at low pressures, while use of higher  $CO_2$  pressures removes the  $011 \rightarrow 010$  contribution as well. Preliminary measurements carried out in our laboratory (Greenblatt, 1983) suggest strongly that formation of either the 001 or 011 states is quite inefficient; electronic-to-vibrational energy transfer appears to strongly favor deposition of energy in higher-lying states. This is somewhat surprising, for models based on a statistical distribution of energies in the  $CO_3$  intermediate would predict substantial population of the lowest-lying states. Interestingly the vibrational population distribution of the  $CO_2$  resulting from (17) seems to be quite similar to that observed (Moore *et al.*, 1983) following the deexcitation by  $CO_2$  of translationally excited hydrogen atoms with energies quite similar to that of the electronic quantum in O ( $^1D_2$ ). Whether the mechanisms of these two seemingly different interactions are similar remains to be determined.

*Nitrous Oxide.* With  $N_2$ , attention is turned to those molecules which undergo chemical reaction with O ( $^1D_2$ ). Specifically, it is the formation of NO in





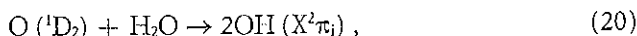
which has profound consequences for stratospheric chemistry, the resultant nitric oxide being the catalytic agent primarily responsible for  $\text{O}_3$  destruction in the unperturbed atmosphere. Reaction (18) proceeds in competition with



the critical ratio  $k_{18}/k_{19}$  apparently remaining constant at 0.60 over the atmospheric temperature range (Marx *et al.*, 1979; Voltrauer *et al.*, 1979; Lam *et al.*, 1981). It is not yet completely clear whether there exists any dependence of this ratio upon the kinetic energy of the  $\text{O} (^1\text{D}_2)$ . The very latest studies discern no such dependence.

The dynamics of (18) have been the subject of considerable recent interest in our laboratory. An earlier study of the NO product energetics following (18) using kinetic absorption spectroscopy (Chamberlain and Simons, 1975) revealed the presence of vibrational levels as high as  $v'' = 6$ . Approximately one quarter of the overall exothermicity of (18) appeared in product vibration. A long-lived ONNO intermediate complex was inferred. Because of the importance of (18) to stratospheric chemistry, we have been engaged in a detailed examination of the NO product energetics. Photolysis with a KrF laser of an  $\text{O}_3/\text{N}_2\text{O}$  mixture leads to production of the  $\text{O} (^1\text{D}_2)$  reactant. State-resolved detection of NO is accomplished at some fixed time delay following photolysis (typically in the range 50-2000 nsec) through the use of one-photon enhanced, two-photon laser ionization spectroscopy. This technique involves the generation of tunable far ultraviolet radiation in the region 220-300 nm. Excitation of the  $\text{NO} (A^2\Sigma^+ \leftarrow X^2\pi_i)$  transition and subsequent ionization,  $\text{NO}^+ (X^1\Sigma^+) + e^- \leftarrow \text{NO} (A^2\Sigma^+)$  is detected using a pair of biased electrodes and a charge sensitive amplifier (Figure 5). To date, vibrational levels as high as  $v'' = 12$  have been observed (Greenblatt *et al.*, 1983) and significant rotational excitation of product NO detected. Currently, these experimental results are being analyzed in order to provide quantitative information concerning product distributions. We hope to extend these measurements using isotopic labelling to provide detailed, hitherto unavailable information concerning energy flow during the course of (18).

*Water.* The reaction of  $\text{O} (^1\text{D}_2)$  with  $\text{H}_2\text{O}$  proceeds exclusively via



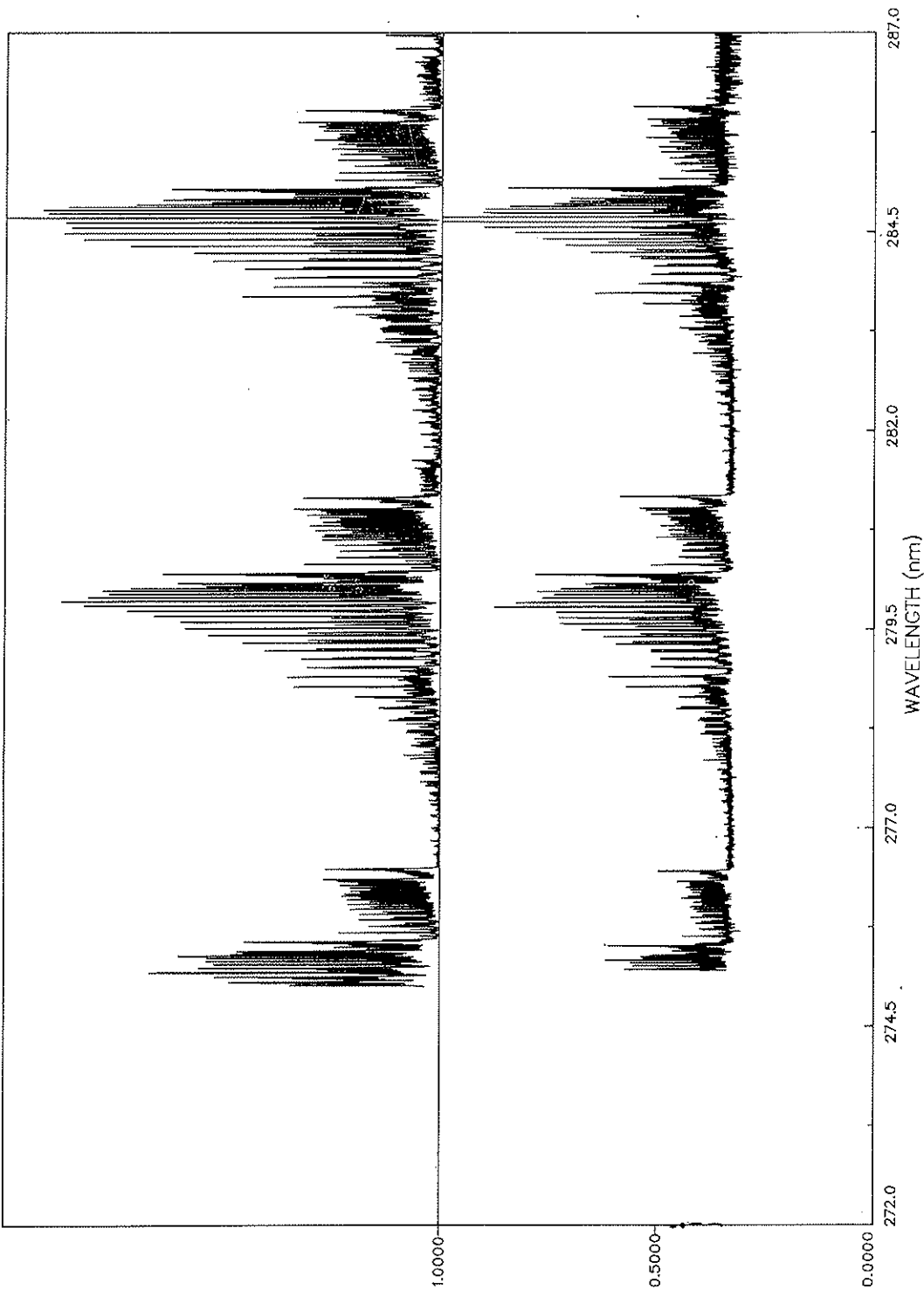
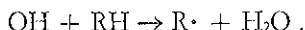


Fig. 5. Resonance enhanced, two-photon spectrum of rotationally relaxed NO produced in reaction (18) initiated by the KrF laser photolysis of an  $\text{O}_3/\text{N}_2\text{O}/\text{He}$  mixture, the helium having been added to achieve rotational relaxation of the product molecule. This small

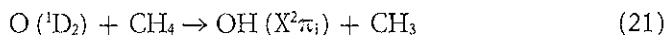
both physical quenching and reaction to form  $\text{H}_2 + \text{O}_2$  (Zellner *et al.*, 1980) appearing to play no significant role. Reaction (20) is of special importance in the troposphere where the resultant OH is involved in the oxidation of CO to  $\text{CO}_2$  and the formation of free radicals as in



The dynamics of (20) have now been subjected to exhaustive examination primarily using laser induced fluorescence (Butler *et al.*, 1981) and laser absorption (Gericke *et al.*, 1981) detection of the  $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi_i$  transition in the wavelength region near 300 nm. The absorption technique, although experimentally much more difficult because it requires exceptionally narrow laser linewidths, offers the significant advantage of being capable of detecting ground state vibrational levels that are inaccessible to the fluorescence technique because of predissociation of the excited state. As in the case of the  $\text{O} (^1\text{D}_2) + \text{N}_2\text{O}$  experiments, the nascent population distribution of the OH product can be detected by careful selection of the time delay between the laser pulse that causes  $\text{O}_3$  photodissociation and that which probes the OH spectrum.

Perhaps the most elegant of the experiments carried out on (20) involved the detection of products arising from the reaction of  $^{16}\text{O} (^1\text{D}_2)$  with  $\text{H}_2^{18}\text{O}$  (Gericke *et al.*, 1981). Spectroscopic discrimination of the  $^{18}\text{OH}$  and  $^{16}\text{OH}$  fragments revealed that the 'old'  $^{18}\text{OH}$  fragment is primarily formed in the ground vibrational state, while about half of the 'new'  $^{16}\text{OH}$  fragments are formed in vibrational states above  $v'' = 1$ . Rotational state distributions for both fragments are quite similar and over half of the total reaction exoergicity is released in translation. Analysis of the spectroscopic data suggests that (20) proceeds via a direct abstraction of an H atom by  $\text{O} (^1\text{D}_2)$  and does not involve the intermediacy of a long-lived complex as do so many other reactions of electronically excited oxygen atoms.

*Organics.* The current interest in the reactions of  $\text{O} (^1\text{D}_2)$  with organic molecules stems only in part from the importance of

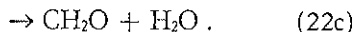
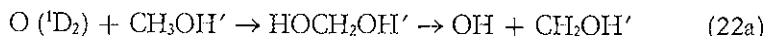


in the stratosphere. In addition, these reactions serve as useful models for a variety of chemical processes involving the isoelectronic carbene,  $\text{CH}_2 (^1\text{A}_1)$ . By studying the dynamics of reactions involving excited oxygen,

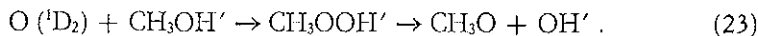
it is possible to gain considerable insight into a variety of reaction schemes which are of significance in synthetic organic chemistry.

Turning first to (21) and analogous oxidation reactions involving heavier saturated hydrocarbons, an insertion/elimination mechanism involving the formation of internally excited alcohols, e.g.,  $\text{CH}_3\text{OH}$ , seems to play a major role. Direct abstraction of hydrogen is manifest by the observation of bimodal rotational population distributions following (21) (Luntz, 1980). In larger hydrocarbons, alternative routes involving C-C bond scission become important and abstraction appears to become of increasing significance. Because the product of direct abstraction is characterized by a rotational distribution similar to that seen in the reaction of  $\text{O}(^3\text{P}_1)$  with hydrocarbons (Andresen and Luntz, 1980; Luntz and Andresen, 1980), it has been hypothesized that abstractions involving  $\text{O}(^1\text{D}_2)$  actually proceed *via* a triplet surface.

A study of the analogous reaction of  $\text{O}(^1\text{D}_2)$  with alcohols (Goldstein and Wiesenfeld, 1983), while of no direct atmospheric importance, reveals interesting details concerning the reactive characteristics of electronically excited oxygen atoms and provides information about the unimolecular dissociation dynamics of chemically activated molecules. In the generic case of  $\text{O}(^1\text{D}_2)$  reaction with methanol, a variety of reactive pathways are available:



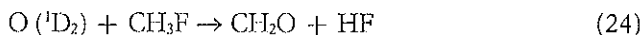
Note that (22a-c) represent the interesting case of a spatially symmetric molecule being formed with an initially asymmetric energy distribution. In addition to direct abstraction processes which appear to play no significant role, there is the attack of  $\text{O}(^1\text{D}_2)$  upon the hydroxylic moiety



Laser induced fluorescence studies of the  $\text{O}(^1\text{D}_2)$  reaction with alcohols as heavy as butanol revealed that attack upon the O-H site in (23) is favored as would be expected of an electrophillic reagent such as  $\text{O}(^1\text{D}_2)$ . From an analysis of the fragmentation pattern following reaction (22), it was concluded that energy redistribution is not complete prior to bond

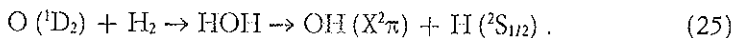
scission. Interestingly the elimination of  $\text{H}_2\text{O}$  from the *gem*-diol in (22c) appears to play no significant role whatsoever. This is in agreement with the observation (Casavecchia *et al.*, 1980) that  $\text{H}_2$  is not formed in the reaction of  $\text{O}(^1\text{D}_2)$  with  $\text{CH}_4$  although hydrogen atoms *are* produced in low yield.

The deactivation of  $\text{O}(^1\text{D}_2)$  by halocarbons has been studied in a number of laboratories and both the overall kinetics and reaction mechanisms quite thoroughly examined (Fletcher and Husain, 1976; Davidson *et al.*, 1978; Force and Wiesenfeld, 1981). Both quenching and reaction play significant roles here, although reaction dominates except in the cases of  $\text{CF}_4$  and  $\text{CHF}_3$ . Electrophillic attack upon the chlorine atom may well dominate deactivation of  $\text{O}(^1\text{D}_2)$  by the chlorocarbons (Addison *et al.*, 1979). Molecular elimination of hydrogen halides as in



must represent a significant pathway because laser emission can be obtained from the diatomic product of this and similar reactions (Burks and Lin, 1978). The extent to which (24) contributes to the overall deactivation of  $\text{O}(^1\text{D}_2)$  by the partially halogenated hydrocarbons is not known, nor is it clear how the availability of alternate pathways leading from the chemically activated intermediate complexes, e.g.,  $\text{CH}_2\text{FOH}$  in the case of the example, would affect the observed deposition of energy into the OH fragment produced in parallel with the hydrogen halide.

*Hydrogen.* The reaction of  $\text{O}(^1\text{D}_2)$  with  $\text{H}_2$  takes place on the ground state potential surface of water,  $\text{H}_2\text{O}(^1\text{A}_1)$ . On the basis of trajectory calculations, (Whitlock *et al.*, 1982) it has been suggested that, as is true for the hydrocarbons, parallel mechanisms involving insertion/elimination and direct abstraction govern the course of this reaction. The observation using laser induced fluorescence spectroscopy (Luntz *et al.*, 1979; Smith and Butler, 1980) of a highly excited, non-Boltzmann rotational distribution and a nearly statistical vibrational distribution for  $v'' = 1$  and  $v'' = 0$  is consistent with the insertion/elimination



Laser induced fluorescence cannot detect  $\text{OH}(X^2\pi)$  in vibrational levels above  $v'' = 1$  because of the previously mentioned predissociation in the

$A^2\Sigma^+$  state. Calculations predict that the direct abstraction of hydrogen atoms by O ( $^1D_2$ ) would result in the production of an OH vibrational distribution peaked at  $v'' = 2$ . Quite recently, highly vibrationally excited products of (25) have, in fact, been detected by observation of infrared chemiluminescence (Butler *et al.*, 1983). Because of the relative facility with which reliable potential surfaces for this simple reaction may be calculated and trajectory studies performed, complete characterization of the products seems most worthwhile.

### *Summary*

The importance of odd oxygen chemistry in fixing the chemical composition and physical structure of the atmosphere has encouraged the application of the most sophisticated methods of modern physical chemistry to its study. Overall rate constants and, to a large extent, chemical branching ratios have now been quite well established for the deactivation of O ( $^1D_2$ ) and precise yields for its formation following O<sub>3</sub> photolysis in the Hartley continuum are now known. Currently, attention is being focussed on the detailed energetics of these important processes and information concerning the distribution of available energy in photodissociative and reactive fragments is increasingly becoming available. Such data will permit the identification of the mechanisms by which such processes occur and lead to their theoretical description at a microscopic level. To what extent this information will be included in future atmospheric models remains a matter of speculation, but it seems certain that, at the very least, energy transfer mechanisms must be identified in order to understand the various airglow phenomena, radiative energy loss, etc. Much depends on the degree to which chemical reactivity is enhanced by internal excitation, a question which is still being addressed. An especially attractive area for future research is the field characterization of internal energy distributions of small molecules in the atmosphere using laser-based, state-selective analytical methods.

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## DISCUSSION

KNABE

I had expected a report on oxygen cycles which would be more concerned with the more general atmospheric problems of its formation and changes that might occur under certain regimes.

ROWLAND

I wonder if the speaker might like to state briefly, for people whose science might be geology, forestry, or agriculture, the important problems of current interest involving the atmospheric chemistry of oxygen.

WIESENFELD

In a sense, the chemistry of  $O_2$  itself represents something of a "non-problem"; the photosynthetic cycle keeps in balance the production and removal (through respiration) of molecular oxygen. Net removal of  $O_2$  accompanies the combustion of fossil fuel but even were the Earth's entire reserve of carbon burned to yield  $CO_2$ , the concomitant decrease in partial pressure of  $O_2$  would be small and probably of little environmental consequence when compared to the enormous increase in atmospheric carbon dioxide. Our research efforts are primarily concerned with the establishment of a reliable base of kinetic and photochemical data that may be applied to the development of advanced models of atmospheric chemistry. Field measurements alone provide only part of the answer in that one cannot measure everything simultaneously and there are certain minor constituents (such as  $HO_2$ ) which even now cannot be adequately monitored at ambient concentrations. All models are in a sense underdefined in that were one to vary freely the available parameters, perfectly good fits to the limited field data would be possible. The goal of laboratory studies is to constrain the number of free parameters that are available; to a large extent I think that we have been successful.

LAG

Have you investigated the possible influences of artificial nitrogen fertilizers?

WIESENFELD

No not personally, but this has been a matter of some concern. It requires knowledge of nitrogen balances between the hydrosphere and atmosphere; to the best of my knowledge, it is not a serious problem, but I would certainly welcome hearing more about this problem.

ROWLAND

In some respects, the oxygen cycle in the atmosphere is most concerned with ozone chemistry which will be discussed later today. The effect of nitrogen fertilizers on the atmosphere would be most strongly felt through perturbation of stratospheric ozone. The general consensus now seems to be that the effect of nitrogen fertilizers upon the atmosphere will be small compared to the magnitude of other sources.

FIOCO

When you were discussing the photodissociation of ozone. I noticed that you left out the Huggins bands; the dissociation efficiency and  $O(^1D)$  branching ratio for this absorption feature would be interesting. Upon going from the Hartley to the Huggins region, I believe that one witnesses the onset of structured absorption. This is of interest not only from the standpoint of photochemistry, but also for diagnostics. So far, devices being used to measure atmospheric ozone are crude and we are not yet able to definitively state whether the total ozone column is being depleted. Improvement of these techniques requires a better knowledge of the absorption spectrum.

WIESENFELD

Where does the Hartley region end and the Huggins region begin? To what extent can they be considered separate features? Structured absorption features can be observed even for bound-free transitions. The only information concerning the photochemistry of ozone in the Huggins band is derived from classical photochemical studies which suggest that the dissociation of  $O_3$  in this region leads to the formation of ground state atomic oxygen and either  $O_2(^1\Delta)$  or  $O_2(^1\Sigma)$ . Thus from the standpoint of the major photochemical cycles which were described by other speakers, the role of Huggins band absorption seems relatively minor. Because of the importance of excited oxygen atoms to tropospheric chemistry, direct field measurements of ozone photodissociation rates in

the middle ultraviolet are currently being actively pursued and our laboratory hopes to apply new techniques to the determination of the wavelength dependence of the yield of excited atoms.

CRUTZEN

Is anything other than  $O(^1D)$  and  $O_2(^1\Delta)$  produced at the high energy end of the Hartley continuum?

WIESENFELD

The thermochemical threshold for production of  $O_2(^1\Sigma)$  in a spin-allowed process is 266 nm so one cannot *a priori* exclude the possibility of its formation in ozone photolysis. However I know of no evidence which would confirm the production of these higher excited states at high energies in the Hartley continuum. Looking at the characteristic red emission at 763 nm would make detection of  $O_2(^1\Sigma)$  possible; a very real experimental problem arises because deactivation of  $O(^1D)$  by the trace of  $O_2$  invariably present in any  $O_3$  sample yields  $O_2(^1\Sigma)$ . This issue certainly deserves closer scrutiny.

ROWLAND

For the nonphotochemists, it should be pointed out that the interest in such excited states as  $O_2(^1\Sigma)$  derives from the observation that their chemistry differs significantly from that of the electronic ground state. Because these excited states can be produced photochemically from ozone especially at short wavelengths the question is whether these molecules may be important to trace species chemistry.

LIBERTI

You mentioned the reaction between oxygen and nitrous oxide. Most environmental chemists pay attention to NO and  $NO_2$  as well as their interconversion, but little attention is paid to  $N_2O$ . Does  $N_2O$  have a part in the nitrogen cycle? We are very curious about the fact that it is present uniformly in the troposphere at about 0.25 ppm. Is the reaction of oxygen and  $N_2O$  of direct relevance to the atmosphere?

WIESENFELD

Definitely yes. In the troposphere, to which I think you may be referring,  $\text{N}_2\text{O}$  is relatively inert. It is in the stratosphere where reaction (18) plays such an important role releasing the nitrogen oxides which dominate the catalytic destruction of ozone.

LIBERTI

As far as the troposphere is concerned, do you think it is absolutely inert?

ROWLAND

Because the estimated lifetime is 100 years or more, it must be completely inert.

LIBERTI

Why is the  $\text{N}_2\text{O}$  constant? What are its sources and sinks? Is it increasing or decreasing and does its concentration vary? If it is important to the chemistry of the stratosphere, then its concentration in the troposphere should certainly be relevant.

ROWLAND

The concentration in the stratosphere is directly dependent upon that in the troposphere and as the  $\text{N}_2\text{O}$  in the troposphere increases there will be more nitrogen oxides in the stratosphere. One sees no difference in  $\text{N}_2\text{O}$  concentrations at remote locations around the world because its lifetime is very long. Those gases with lifetimes in excess of 10 years display similar concentrations throughout the atmosphere.

ANDERSON

In searching for mechanisms involving excited oxygen atoms have you discovered any processes involving the vibrationally excited states of either the ground electronic state or low-lying excited states of  $\text{O}_2$  which would drive these chemical cycles backward? Have you considered candidate reactions other than those already identified for the production of odd oxygen in the stratosphere?

## WIESENFELD

No, we have not although I should emphasize that, using the newly developed laser spectroscopic tools described in my paper, studies of the chemistry of vibrationally excited states now become feasible. Destruction of ozone following collisions with vibrationally excited molecules is known, but the importance of vibrationally excited species in the atmosphere is a matter of some debate. Collisional quenching of these molecules must always compete with chemistry and so the question becomes one of understanding the relative efficiencies of such processes.

# THE GLOBAL SULFUR BUDGET

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## *Introduction*

My presentation here on the global sulfur budget has been very much facilitated as I earlier this year received from Professor M.V. Ivanov a monograph (not yet published in English) with the following title: "The global biogeochemical sulfur cycle and influence on it of human activity" (\*).

The monograph seems to include probably all our present knowledge concerning the behaviour of sulfur in the environment. All data given are well documented by a very comprehensive list of references. For that reason this monograph will be used as a general reference for all those data and ideas which are discussed in it. Concerning data taken from elsewhere they will be documented in the usual way.

## *The objective of the present survey*

In a paper from 1978 (Atm. Env. Vol. 12), H. Rhode points out that making estimates of the global sulfur budget can be formulated as seeking answers to the following two questions earlier presented in a paper by Kellogg *et al.* (Science 175, pp. 587-596, 1972):

1. What are the sources (natural and man-made), sinks and residence times of sulfur compounds in the atmosphere-ocean-soil system?

(\*) General editing: G. K. Skryabin. Editors in chief: M.V. Ivanov (USSR) and J.R. Freney (Australia). This monograph is the result of an international project organized by SCOPE and the Academy of Sciences of USSR. The project has been sponsored by UNEP.

2. How do man's activities compare with nature's in determining the overall budget of atmospheric sulfur compounds?

It is meant that the material compiled below from the monograph mentioned above and from other papers may give at least a tentative answer to these questions.

### *The box model*

It is generally recognized that the use of box models is a very convenient way to present environmental budgets. This method is also used in the monograph, whereby the time scale has been chosen to one year.

Concerning the space scale it is recognized that *global* budgets may provide limited information because of high local variations in emission density. For that reason several space scales are used.

For the total global model the space scale applied is illustrated in Figure 1.

As shown, the respective states of aggregation are represented by the following reservoirs.

|               |  |
|---------------|--|
| Gas phase:    | Continental atmosphere<br>Oceanic atmosphere   |
| Liquid phase: | Ocean water<br>Intracontinental water sheds    |
| Solid phase:  | Oceanic sediments<br>Pedosphere<br>Lithosphere |

The budgets of the separate boxes are discussed first. Concerning the continental atmosphere it is, to begin with, subdivided into three smaller boxes, i.e., the atmosphere over industrial and urban regions, dusty continental atmosphere, meaning arid regions hit by wind blown dust, and clean continental atmosphere.

The sulfur budgets of all these boxes and also of the total combination of them will be presented below.

### *Relevant sulfur compounds and some of their properties*

There are certainly many sulfur compounds participating in the fluxes



among the different boxes. The most important ones and the correspondent valence states of sulfur have been listed in Table 1.

Of these compounds only  $\text{H}_2\text{SO}_4$  and the ion  $\text{SO}_4^{2-}$  are stable in air and aerated water.

The compounds of sulfur having the valence state 2- are only stable in systems with much lower oxidation potential.

They are formed biogenetically (coastal zones, decomposition of org. material) or in some cases, pyrolytically (volcanoes).

The gas  $\text{SO}_2$  has an intermediate position. It is formed in the first step of the oxidation of  $\text{S}^{2-}$ -compounds. Further it is produced by thermal decomposition of some sulfates and, as well known, by the combustion of S-containing fuels.

### *Oxidation of $\text{S}^{2-}$ -compounds*

As is evident from the above said, all  $\text{S}^{2-}$ -compounds in Table 1 will be oxidized in air. The principal process is a homogeneous oxidation reaction, usually comprising several steps before the end product  $\text{H}_2\text{SO}_4$  is arrived at. The main role in this reaction is played by the hydroxy radical. In the troposphere this one is formed according to the following reaction:

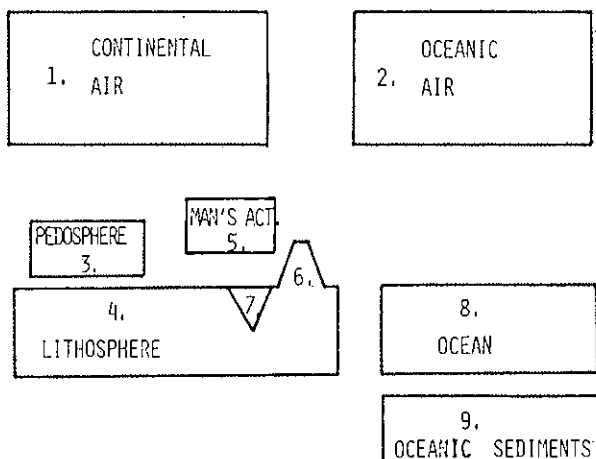
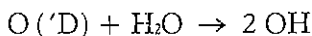
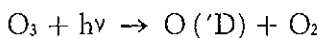


FIG. 1. The global sulfur budget. (Figures in brackets indicate anthropogenic contributions).

TABLE 1

| Compound  | Valence state of S |
|---|--------------------|
| H <sub>2</sub> S  | 2—                 |
| (CH <sub>3</sub> ) <sub>2</sub> S and other org. sulfides | 2—                 |
| CS <sub>2</sub>   | 2—                 |
| COS   | 2—                 |
| SO <sub>2</sub>   | 4+                 |
| H <sub>2</sub> SO <sub>4</sub> and its salts              | 6+                 |

As already mentioned the first product of the reactions of S<sup>-2</sup>-compounds with this radical is SO<sub>2</sub>. The rate of the respective reactions is rather dependent on the type of the compound, which is seen in Table 2. For that reason in the monograph these compounds are divided into two groups which we may call reactive ((CH<sub>3</sub>)<sub>2</sub>S and H<sub>2</sub>S) and non-reactive (CS<sub>2</sub> and COS). In budget calculations the last ones are simply treated as precursors to SO<sub>2</sub>.

It may, however, be observed that according to P.J. Crutzen (Geophys. Res. Lett. 1976, Vol. 3, pp. 73-76) the slow oxidation of COS makes possible that this compound is responsible for the sulfate layer in the stratosphere.

### *Oxidation of SO<sub>2</sub>*

The most studied reaction in this context is probably the oxidation of SO<sub>2</sub>.

TABLE 2

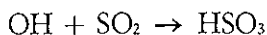
| Compound                          | Rate constant<br>cm <sup>3</sup> molecules <sup>-1</sup> sec <sup>-1</sup> |
|-----------------------------------|--|
| (CH <sub>3</sub> ) <sub>2</sub> S | $9 \times 10^{-12}$  |
| H <sub>2</sub> S                  | $5 \times 10^{-12}$  |
| CS <sub>2</sub>                   | $0.4 \times 10^{-12}$  |
| COS                               | $0.04 \times 10^{-12}$   |

Three types of reactions seem to be possible:

1. Homogeneous gas phase reaction
2. Reaction in water solution
3. Reaction on surfaces

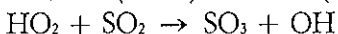
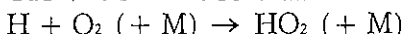
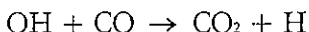
It has been shown that several kinds of homogeneous gas phase reactions (reactions with photochemically generated radicals) are occurring. The most important (rapid) ones are the following (Eggleton and Cox, *Atm. Env.* 1978, Vol. 12, pp. 227-230):

1. The OH-reaction

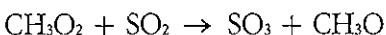


It has been established that the radical  $\text{HSO}_3$  is readily converted to  $\text{H}_2\text{SO}_4$

2. The  $\text{HO}_2$ -reaction

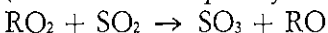


3. The  $\text{CH}_3\text{O}_2$ -reaction



4. The  $\text{RO}_2$ -reaction

( $\text{RO}_2$  stands for peroxy radicals excluding  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$ )



The importance of these four reactions are closely connected to the respective reaction rates. These and also the rate constants are given in Table 3 (Eggleton and Cox, 1.c.).

All other photochemically generated reactive species seem to give negligible contributions as compared with those in Table 3.

Earlier it was thought that catalytic oxidation (with Mn as principal catalyst) was mainly responsible for the liquid phase oxidation of  $\text{SO}_2$ .

However, it has been observed that the decrease in some regions of

TABLE 3

| Species                        | Rate constant for reaction<br>with SO <sub>2</sub><br>(cm <sup>3</sup> molecules <sup>-1</sup> sec <sup>-1</sup> ) | SO <sub>2</sub> oxidation rate<br>(% h <sup>-1</sup> ) |
|--------------------------------|--|--|
| OH                             | $0.5 - 1.0 \times 10^{-12}$  | 1.2 - 2.5  |
| HO <sub>2</sub>                | $9 \times 10^{-16}$  | 0.84   |
| CH <sub>3</sub> O <sub>2</sub> | $\leq 10 \times 10^{-15}$  | $\leq 0.8$   |
| RO <sub>2</sub>                | $\leq 10 \times 10^{-15}$  | $\leq 1.84$  |

the concentration of smoke particles (carrier of a.o. Mn) was not followed by a decrease of sulfate in precipitation.

In fact, an increase was measured. Therefore, an uncatalyzed reaction seemed to be more probable and was suggested by Penkett (Nat. 240, 105, 1972). In this connection the oxidizing agents O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were tested (H<sub>2</sub>O<sub>2</sub> is produced in the atmosphere mainly by the reaction HO<sub>2</sub> + HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>). The result of this test is given in Table 4 (Cox and Penkett from Acid Deposition, Ed. Beilke and Elshout. D. Reidel Publ. Comp. 1983).

TABLE 4

| CALCULATED RATES OF SO <sub>2</sub> OXIDATION IN WATER SOLUTION<br>BY O <sub>2</sub> , O <sub>3</sub> AND H <sub>2</sub> O <sub>2</sub> AT 10°C. |  |  |   |
|--|--|--|---|
| INITIAL REACTANT CONCENTRATIONS:<br>SO <sub>2</sub> = 5 ppbv, O <sub>3</sub> = 50 ppbv, H <sub>2</sub> O <sub>2</sub> = 1 ppbv                   |  |  |   |
| pH   | O <sub>2</sub><br>μM min <sup>-1</sup> | O <sub>3</sub><br>μM min <sup>-1</sup> | H <sub>2</sub> O <sub>2</sub><br>μM min <sup>-1</sup> |
| 4.0  | 0.0001                                 | 0.1                                    |   |
| 4.3  |  |  | 13.4  |
| 5.0  | 0.003                                  | 2.5                                    |   |
| 5.4  |  |  | 28.5  |
| 6.0  | 0.6                                    | 67.6                                   |   |
| 6.6  |  |  | 73.4  |

The oxidation of  $\text{SO}_2$  in rain drops by means of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  is consequently the dominant non-catalytic reaction. It is interesting to note that the  $\text{H}_2\text{O}_2$ -oxidation is rather insensitive to decrease of pH. These reactions due to their rates are probably quite capable of producing enough sulfate in rain water to account for observed levels.

There has been much work spent on investigations of  $\text{SO}_2$  oxidation by means of surface reactions. Results hitherto obtained indicate, however, that conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  on atmospheric particles at room temperature does not take place in considerable extent (Liberti *et al.*, *Atm. Env.* 12, 255, 1978).

### *The distribution of sulfur compounds between air and water*

It is well known that compounds of sulfur in different oxidation states have rather different properties, e.g. volatilities and solubilities in water.

A combination of the two last properties is, however, expressed by the respective distribution constants (or Henry law constants). Hence a change in the oxidation state implies a change in the distribution of the compound in question between air and water. This in its turn usually results in a transfer of this compound from one box in the model to another.

The magnitude of this effect is illustrated in Table 5. Here the Henry law constant,  $(K_a)_T$ , at  $20^\circ\text{C}$  for  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  is given and also an example concerning the respective equilibrium concentrations in mole  $\text{l}^{-1}$  for water and mole  $\text{m}^{-3}$  for air.

TABLE 5

| Compound                | $K_a$ (Total) $20^\circ\text{C}$<br>dimensionless | Equilibrium conditions           |                                |
|-------------------------|---|----------------------------------|--------------------------------|
|                         |   | mole $\text{l}^{-1}$<br>in water | mole $\text{m}^{-3}$<br>in air |
| $\text{H}_2\text{S}$    | 6.8   | 1                                | 6800                           |
| $\text{SO}_2$           | 0.12  | 1                                | 120                            |
| $\text{H}_2\text{SO}_4$ | $\sim 0$  | 1                                | $\sim 0$                       |

It shall be pointed out that these "total" constants (Henry law constants) refer to the total content of the respective species in water including hydration and dissociation products.

The right part of Table 5 is a good illustration of what happens if  $\text{H}_2\text{SO}_4$  in water solution is reduced to  $\text{H}_2\text{S}$ . As is seen almost everything of  $\text{S-H}_2\text{SO}_4$  will leave the water phase and enter the air as  $\text{S-H}_2\text{S}$ . If the last one now will be oxidized back to  $\text{H}_2\text{SO}_4$  it will, of course, return as  $\text{S-H}_2\text{SO}_4$  to the water phase. Such a process is a true cyclic one.

Now, suppose a sulfidic ore has been dug out by man somewhere from the lithosphere and oxidized giving  $\text{SO}_2$ , which is released into the atmosphere. Here it will be subsequently oxidized to  $\text{H}_2\text{SO}_4$  and washed out by precipitation into some water shed. By one or another process it may now be reduced to  $\text{H}_2\text{S}$ . It could happen that this one instead of leaving the water phase will react with some heavy metal ions present forming almost insoluble sulfides. The sulfur atoms originating from somewhere in the lithosphere will now be confined in the sediments of the water shed.

As such a process may not readily be considered as a cyclic one, this type will in the following discussion be called a transfer.

For the reason that sulfur displacements in the environment may be both of the cyclic and of the transfer type it is preferred here for the overall processes to use the term budget instead of cycle.

### *The atmospheric sulfur budget*

In the monograph mentioned a very comprehensive examination is presented concerning hitherto published relevant data about concentrations, reaction rates, estimation of emissions and depositions and of fluxes and resident times as well.

The whole material has been evaluated into a number of partial budgets and finally in a total global one.

Special attention has been given to the very important budget of the atmosphere. As already shown in Fig. 1, the total box of the atmosphere has been primarily divided into two: the continental atmosphere and the oceanic one.

Further, the continental atmosphere has been subdivided into 1) The polluted atmosphere over industrial and urban regions, 2) The atmosphere over remote dusty (arid) regions, and 3) The atmosphere over remote clean regions.

For all these regions graphs are given in the monograph. These graphs have here been disguised into tables which seem to facilitate calculation of the total budgets.

All masses in the tables below are given in Tg. The time scale is, as mentioned earlier, one year. The main figures concerning masses in the boxes and fluxes between them are the estimates of the authors of the monograph. In brackets after the main figures are presented the minimum and maximum values found in the literature.

As is seen, Table 6 gives the budget of the industrial and urban atmosphere. The total mass of sulfur within the box has been estimated to 0.145 Tg and its residence time to 0.5 day. It has been suggested that here the contribution from natural sources is negligible.

Steady-state is assumed as in all boxes concerning the gas phase. This assumption has given here a net export of 88 Tg  $y^{-1}$ . Half of it is thought to be transferred to the clean continental atmosphere, the other half to the oceanic atmosphere. The total balance for the industrial and urban atmosphere has, in this way, been estimated to 113 Tg  $y^{-1}$ .

Table 7 represents the opinion of the authors that the importance of wind blown dust has earlier been underestimated. Their own conclusions indicate that in the budget of the atmosphere, the wind blown dust should be considered as an entry of  $\sim 20$  Tg  $y^{-1}$ .

In Table 8 data for the continental clean atmosphere are collected. The total mass is 0.42 Tg and the residence time is estimated to 1.5 days. The total balance amounts to  $\sim 103.5$  Tg  $y^{-1}$ .

Summarizing the Tables 6, 7 and 8 one gets for the total continental atmosphere the figures in Table 9.

As is seen the mass of sulfur obtained is 0.59 Tg, the residence time 1.2 days and finally, the grand total balance including transfers from and into oceanic atmosphere 184.5 Tg  $y^{-1}$ .

The conditions for the oceanic atmosphere are given in Table 10. Here, the mass of sulfur has been estimated to 0.765 Tg and the residence time to 1.0 day. For the grand total balance (including transfers from and into continental atmosphere) the figure 278 Tg  $y^{-1}$  has been obtained.

The data in Tables 9 and 10 finally are summarized in Table 11, which now should give the budget of the total global atmosphere. It should be pointed out that all figures hitherto discussed are valid for the year 1980.

Hence, for this total budget we have got:

|                        |                        |
|------------------------|------------------------|
| Total mass of sulfur   | 1.36 Tg                |
| Average residence time | 1.4 days               |
| Total balance          | 342 Tg y <sup>-1</sup> |

*The total global sulfur budget and the transfer processes of sulfur*

Using the data in the Tables 6-11 and also data concerning the liquid and solid phases and with the application of the model in Fig. 1, the authors of the monograph have finally arrived at an estimation of the total global sulfur budget. It is presented in Figure 2.

As the atmospheric boxes have earlier been described in detail and moreover as steady-state has been assumed to prevail in the gas phase it remains now to discuss the fluxes concerning the lithosphere-pedosphere and the ocean (also the intracontinental water sheds).

TABLE 6

THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE.  
INDUSTRIAL AND URBAN REGIONS

TOTAL MASS OF S: 0.145 Tg

RESIDENCE TIME: 0.5 Day

| INPUT                             |                                 | OUTPUT                                      |                                 |
|-----------------------------------|---------------------------------|---|---------------------------------|
| Process                           | Flux: S Tg y <sup>-1</sup>      | Process                                     | Flux: S Tg y <sup>-1</sup>      |
| Antropog. emission                |                                 |   |                                 |
| S-SO <sub>2</sub>                 | 98 (83-113)                     | Wet dep.                                    | 11 (9-13)                       |
| S-SO <sub>4</sub> <sup>2-</sup>   | 12 (10-14)                      | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> ) | 2 (1-7)                         |
| S-S <sub>R</sub> <sup>2-</sup> x/ | 3 (1-5)                         | Dry dep. (S-SO <sub>2</sub> )               | 12 (5-19)                       |
| Natural emission                  | negligible                      | Transfer into clean cont. atmosphere        | 44 (34-54)                      |
|                                   |                                 | Transfer into oceanic atmosphere            | 44 (34-54)                      |
| Total                             | 113 (94-132) Tg y <sup>-1</sup> | Total                                       | 113 (83-147) Tg y <sup>-1</sup> |

x/Index R Stands for Reactive, Such as (CH<sub>3</sub>)<sub>2</sub>S



TABLE 7

## THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE.

## REMOTE ARID REGIONS

TOTAL MASS OF S: 0.035 Tg

RESIDENCE TIME: 0.6 Day

| INPUT      |                               | OUTPUT                                      |                                  |
|------------|-------------------------------|---|----------------------------------|
| Process    | Flux: Tg y <sup>-1</sup>      | Process                                     | Flux: Tg y <sup>-1</sup>         |
| Dust susp. | 20 (10-30)                    | Wet dep.                                    | 3 (1.5-4.5)                      |
|            |                               | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> ) | 9 (2-23)                         |
|            |                               | Transfer into clean cont.<br>atmosphere     | 8 (3-13)                         |
| Total      | 20 (10-30) Tg y <sup>-1</sup> | Total                                       | 20 (6.5-40.5) Tg y <sup>-1</sup> |

TABLE 8

## THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE.

## REMOTE CLEAN REGIONS

TOTAL MASS OF S: 0.42 Tg

RESIDENCE TIME: 1.5 Days

| INPUT  |                                   | OUTPUT                                      |                                   |
|--|-----------------------------------|---|-----------------------------------|
| Process  | Flux Tg y <sup>-1</sup>           | Process                                     | Flux Tg y <sup>-1</sup>           |
| Oxid. of COS and<br>CS <sub>2</sub> -S-SO <sub>2</sub> | 1.5 (1-2)                         | Transfer into oceanic<br>atmosphere         | 56.5 (31-82)                      |
| Transfer from<br>ind. and urban<br>atmosphere          | 44 (34-54)                        | Wet dep.                                    | 37 (27-47)                        |
| Transfer from<br>remote dusty<br>atmosphere            | 8 (3-13)                          | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> ) | 5 (2-17)                          |
| Volcanic emission                                      | 14 (7-21)                         | Dry dep. (S-SO <sub>2</sub> )               | 5 (2-8)                           |
| Nat. emission<br>(S-S <sub>R</sub> <sup>-2</sup> )     | 16 (4-30)                         |   |                                   |
| Transfer from<br>oceanic atm.                          | 20 (10-30)                        |   |                                   |
| Total  | 103.5 (59-160) Tg y <sup>-1</sup> | Total                                       | 103.5 (62-154) Tg y <sup>-1</sup> |

TABLE 9

## THE SULFUR BUDGET OF THE CONTINENTAL GLOBAL ATMOSPHERE (1980)

TOTAL MASS OF SULFUR: 0.59 Tg

RESIDENCE TIME: 1.2 Days

| INPUT                             |                                    | OUTPUT                             |                                    |
|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Process                           | Flux Tg y <sup>-1</sup>            | Process                            | Flux Tg y <sup>-1</sup>            |
| Antropog. emission                |                                    | Wet dep.                           | 51 (37.5-64.5)                     |
| S-SO <sub>4</sub> <sup>2-</sup>   | 12 (10-14)                         | Dry dep.                           | 16 (5-47)                          |
| S-SO <sub>2</sub>                 | 98 (83-113)                        | (S-SO <sub>4</sub> <sup>2-</sup> ) |                                    |
| S-S <sub>R</sub> <sup>2-</sup>    | 3 (1-5)                            | Dry dep.                           |                                    |
| Volcanic emission                 | 14 (7-21)                          | (S-SO <sub>2</sub> )               | 17 (7-27)                          |
| Dust susp.                        |                                    |                                    |                                    |
| S-SO <sub>4</sub> <sup>2-</sup>   | 20 (10-30)                         |                                    |                                    |
| Nat. emission                     |                                    |                                    |                                    |
| S-S <sub>R</sub> <sup>2-</sup>    | 16 (4-30)                          |                                    |                                    |
| Oxid. of COS and                  |                                    |                                    |                                    |
| CS <sub>2</sub> S-SO <sub>2</sub> | 1.5 (1-2)                          |                                    |                                    |
| Total                             | 164.5 (116-215) Tg y <sup>-1</sup> | Total                              | 84 (49.5-138.5) Tgy <sup>-1</sup>  |
| Transfer from                     |                                    | Transfer into                      |                                    |
| oceanic atm.                      | 20 (10-30)                         | oceanic atm.                       | 100.5 (50.5-150.5)                 |
| Grand total                       | 184.5 (126-245) Tg y <sup>-1</sup> | Grand total                        | 184.5 (100-239) Tg y <sup>-1</sup> |

TABLE 10

## THE SULFUR BUDGET OF THE OCEANIC GLOBAL ATMOSPHERE (1980)

TOTAL MASS OF SULFUR: 0.765 Tg

RESIDENCE TIME: 1.0 Day

| INPUT                                 |                                       | OUTPUT                                      |                                  |
|---------------------------------------|---------------------------------------|---|----------------------------------|
| Process                               | Flux Tg y <sup>-1</sup>               | Process                                     | Flux Tg y <sup>-1</sup>          |
| Nat. emission                         |                                       | Wet dep.                                    | 230 (160-300)                    |
| S-S <sub>R</sub> <sup>2-</sup>        | 20 (0-40)                             | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> ) | 17 (3-48)                        |
| Volcanic emission                     | 14 (7-21)                             |   |                                  |
| Sea spray                             | 140 (77-203)                          | Dry dep. (S-SO <sub>2</sub> )               | 11 (5-17)                        |
| Oxid. of COS                          |                                       |   |                                  |
| and CS <sub>2</sub> S-SO <sub>2</sub> | 3.5 (2.5-4.5)                         |   |                                  |
| Total                                 | 177.5 (86.5-268.5) Tg y <sup>-1</sup> | Total                                       | 258 (168-365) Tg y <sup>-1</sup> |
| Transfer from                         |                                       | Transfer into                               |                                  |
| continental                           |                                       | continental atm.                            | 20 (10-30)                       |
| atmosphere                            | 100.5 (50.5-250.5)                    |   |                                  |
| Grand total                           | 278 (137-419) Tg y <sup>-1</sup>      | Grand total                                 | 278 (178-395) Tg y <sup>-1</sup> |

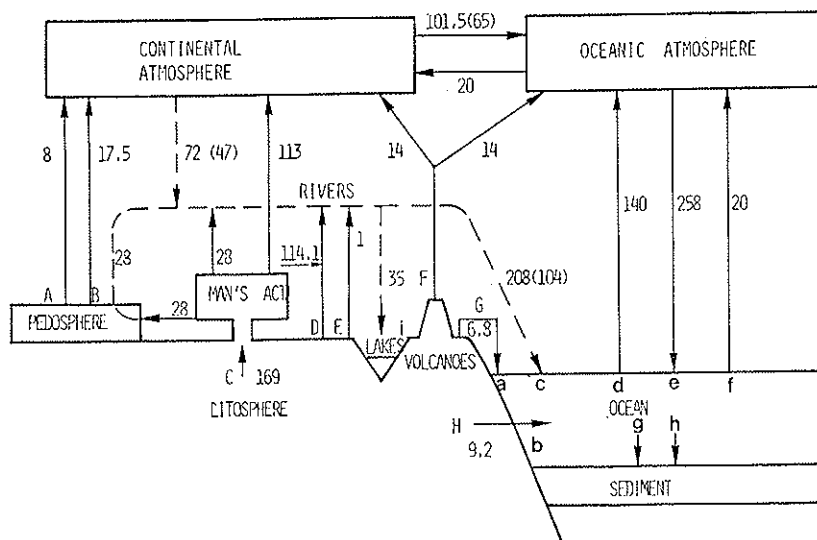


FIG. 2. The space scale of the global box model.

1. Continental atmosphere
2. Oceanic atmosphere
3. Pedosphere
4. Lithosphere
5. Man's activity
6. Volcanoes
7. Intracontinental water sheds
8. Ocean
9. Oceanic sediments

TABLE 11

THE TOTAL SULFUR BUDGET OF THE GLOBAL ATMOSPHERE (1980)

TOTAL MASS OF SULFUR: 1.36 Tg

RESIDENCE TIME: 1.4 Days

| INPUT            |                                      | OUTPUT           |                                      |
|------------------|--------------------------------------|------------------|--------------------------------------|
| Continental part | 164.5 (116-215)                      | Continental part | 84 (49.5-138.5)                      |
| Oceanic part     | 177.5 (86.5-268.5)                   | Oceanic part     | 158 (168-365)                        |
| Total            | 342 (202.5-483.5) Tg y <sup>-1</sup> | Total            | 342 (217.5-503.5) Tg y <sup>-1</sup> |

TABLE 12

| GLOBAL TRANSFER PROCESS OF SULFUR             |                       |                                 |                         |                              |  |
|---|-----------------------|---------------------------------|-------------------------|------------------------------|--|
| OUTPUT<br>FROM LITOSPHERE<br>AND PEDOSPHERE   |                       |                                 | INPUT<br>INTO THE OCEAN |                              |  |
| Symbol<br>in<br>fig. 2                        | Process               | Flux ( $\text{Tg y}^{-1}$ )     | Symbol<br>in<br>fig. 2  | Process                      | Flux ( $\text{Tg y}^{-1}$ )                |
| A.  | Net. part. matter     | 8                               | a.                      | Dry dep. (biog. gases)       | 6.8  |
| B.  | Biogenic gasem.       | 17.5                            | b.                      | Underground stream           | 9.2  |
| C.  | Litosphere            | 169                             | c.                      | Transfer with river<br>water | 208.1                                      |
| D.  | Weathering            | 114.1                           | d.                      | Sea spray                    | 140  |
| E.  | Acid mine water       | 1                               | e.                      | Wet and dry<br>dep.          | 258  |
| F.  | Volcanoes             | 28                              | f.                      | Biog. emission               | 20   |
| G.  | Biogenic gasem.       | 6.8                             | e-d-f                   | Net. input from<br>atm.      | 98   |
| H.  | Underground<br>stream | 9.2                             |                         |                              |  |
|   | Total                 | 353.6 $\text{Tg y}^{-1}$        | Total                   |                              | 322.1 $\text{Tg y}^{-1}$                   |
| OUTPUT FROM OCEAN<br>INTO SEDIMENT            |                       |                                 |                         |                              |  |
|   | g.                    | Dep. of $\text{S-S}^{2-}$       |                         |                              | 98.4                                       |
|   | h.                    | Dep. of $\text{S-SO}_4^{2-}$    |                         |                              | 27.8                                       |
|   |                       | Total                           |                         |                              | <u>126.2 <math>\text{Tg y}^{-1}</math></u> |
|   |                       | Net. dep. in the<br>ocean water |                         |                              | <u>322.1-126.2</u>                         |
|   |                       |                                 |                         |                              | <u>195.9 <math>\text{Tg y}^{-1}</math></u> |
| INPUT<br>INTO INTRACONTINENTAL<br>WATER SHEDS |                       |                                 |                         |                              |  |
|   | i.                    |                                 |                         |                              | 35   |
|   | Total                 |                                 |                         |                              | <u>35 <math>\text{Tg y}^{-1}</math></u>    |

For the sake of clarity, in Fig. 2 the fluxes from the lithosphere-pedosphere have been denoted with capital letters and the fluxes from and into the ocean and the intracontinental water sheds with small letters.

These fluxes and the respective processes, which all correspond to the data in the monograph, are collected in Table 12 and summarized in Table 13. (There seems to be a small error somewhere giving a difference of  $\sim 1\%$  in the balance).

The conclusions from the figures in Table 13 can be formulated as follows:

TABLE 13

| GLOBAL TRANSFER BALANCE OF SULFUR        |                          |                                |                          |
|--|--------------------------|--------------------------------|--------------------------|
| Emission from lithosphere and pedosphere | 353.6 Tg y <sup>-1</sup> | Deposition in ocean water      | 195.9                    |
|  |                          | In oceanic sediment            | 126.2                    |
|  |                          | In intracontinental watersheds | 35                       |
|  |                          | Total deposition               | 357.1 Tg y <sup>-1</sup> |

In 1980 a mass of about 355 Tg of sulfur has been removed from somewhere in the lithosphere-pedosphere. Of this mass 195 Tg has been deposited in the ocean water, 35 Tg in intracontinental water sheds and 125 Tg in oceanic sediments.

### *Some comparisons*

Of all the partial budgets given, the one in Table 6 (The sulfur budget of the industrial and urban atmosphere) gives probably the most direct information on the magnitude of man's contribution to the sulfur budget. However, the scale of Table 6 is still too large to give an impression of what is going on in our own European environment. Therefore, an evaluation by H. Rhode (paper given at IVL Symposium, Gothenburg March 9, 1983) valid for northern Europe will be cited (Table 14).

When comparing Rhode's figures with the ones in Table 6 it may seem that Europe still is responsible for a rather small fraction (~12%) of the total anthropogenic sulfur pollution. However, this fraction seems to have a rather dramatic effect on our nearby environment.

It should be mentioned that in the monograph also the atmospheric budgets for preindustrial time have been estimated. These are given in Tables 15 and 16. From these tables the total preindustrial atmospheric budget can be calculated (Table 17).

As is seen the balance arrived at is 228 Tg y<sup>-1</sup> which figure has to be compared with 342 Tg y<sup>-1</sup> valid for 1980 (Table 11).

TABLE 14

## THE ATMOSPHERIC SULFUR BUDGET FOR N. EUROPE (H. Rhode, 1983)

| INPUT                  |                          | OUTPUT                      |                              |
|------------------------|--------------------------|-----------------------------|------------------------------|
| Process                | Flux Tg y <sup>-1</sup>  | Process                     | Flux Tg y <sup>-1</sup>      |
| Anthropogenic emission | 13                       | Wet dep. of anthropogenic S | 4                            |
| Natural emission       | 0.3                      | Wet dep. of natural S       | 0.5                          |
|                        |                          | Dry dep. of anthropogenic S | 3-6                          |
|                        |                          | Dry dep. of natural S       | 0.2-0.3                      |
|                        |                          | Net export                  | 3-6                          |
| Total                  | 13-16 Tg y <sup>-1</sup> | Total                       | 10.7-16.8 Tg y <sup>-1</sup> |

TABLE 15

## GLOBAL ATMOSPHERE - PREINDUSTRIAL ERA - CONTINENTAL PART

| INPUT  |                         | OUTPUT  |                         |
|--|-------------------------|---|-------------------------|
| Process  | Flux Tg y <sup>-1</sup> | Process   | Flux Tg y <sup>-1</sup> |
| Vulcanic activity (S-SO <sub>2</sub> )   | 14                      | Wet dep. (S-SO <sub>4</sub> <sup>2-</sup> , S-SO <sub>2</sub> ) | 26                      |
| Wind erosion (S-SO <sub>4</sub> <sup>2-</sup> )                                    | 20                      | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> )                     | 13                      |
| Emission (S-S <sub>R</sub> <sup>2-</sup> )   | 16                      | Dry dep. (S-SO <sub>2</sub> )                                   | 5                       |
| Oxid. or red. of COS and CS <sub>2</sub> (S-SO <sub>2</sub> or S-H <sub>2</sub> S) | 1                       |   |                         |
| Total  | 51 Tg y <sup>-1</sup>   | Total   | 44 Tg y <sup>-1</sup>   |
| Transfer from oceanic atmosphere   | 20 Tg y <sup>-1</sup>   | Transfer into oceanic atmosphere                                | 27 Tg y <sup>-1</sup>   |
| Grand total  | 71 Tg y <sup>-1</sup>   | Grand total   | 71 Tg y <sup>-1</sup>   |

TABLE 16

| THE SULFUR BUDGET OF THE GLOBAL ATMOSPHERE.<br>PREINDUSTRIAL ERA - OCEANIC PART         |                         |   |                         |
|---|-------------------------|---|-------------------------|
| INPUT   |                         | OUTPUT  |                         |
| Process   | Flux Tg y <sup>-1</sup> | Process   | Flux Tg y <sup>-1</sup> |
| Emission (S-S <sub>R</sub> <sup>2-</sup> )  | 20                      | Wet dep. (S-SO <sub>4</sub> <sup>2-</sup> , S-SO <sub>2</sub> ) | 161                     |
| Volcanic activity (S-SO <sub>2</sub> )  | 14                      | Dry dep. (S-SO <sub>4</sub> <sup>2-</sup> )                     | 12                      |
| Sea spray (S-SO <sub>4</sub> <sup>2-</sup> )  | 140                     | Dry dep. (S-SO <sub>2</sub> )                                   | 11                      |
| Oxid. or red.<br>of COS and CS <sub>2</sub><br>(S-SO <sub>2</sub> , S-H <sub>2</sub> S) | 3                       |   |                         |
| Total   | 177 Tg y <sup>-1</sup>  | Total   | 184 Tg y <sup>-1</sup>  |
| Transfer from<br>continental atm.   | 27 Tg y <sup>-1</sup>   | Transfer into<br>continental atmosphere                         | 20 Tg y <sup>-1</sup>   |
| Grand total   | 204 Tg y <sup>-1</sup>  | Grand total   | 204 Tg y <sup>-1</sup>  |

TABLE 17

| THE TOTAL SULFUR BUDGET OF THE GLOBAL ATMOSPHERE.<br>PREINDUSTRIAL ERA |                        |                  |                        |
|--|------------------------|------------------|------------------------|
| INPUT  |                        | OUTPUT           |                        |
| Continental part   | 51 Tg y <sup>-1</sup>  | Continental part | 44 Tg y <sup>-1</sup>  |
| Oceanic part   | 177 Tg y <sup>-1</sup> | Oceanic part     | 184 Tg y <sup>-1</sup> |
| Total  | 228 Tg y <sup>-1</sup> | Total            | 228 Tg y <sup>-1</sup> |

However, the figure 342 Tg y<sup>-1</sup> is composed of three main terms:

|                                  |                        |
|----------------------------------|------------------------|
| Anthropogenic emission (Table 6) | 113 Tg y <sup>-1</sup> |
| Sea spray (Table 10)             | 140 »                  |
| Other emissions                  | 89 »                   |
| Total (Table 11)                 | 342 Tg y <sup>-1</sup> |

If from this sum of  $342 \text{ Tg y}^{-1}$  the anthropogenic part ( $113 \text{ Tg y}^{-1}$ ) is subtracted, one arrives at  $229 \text{ Tg y}^{-1}$  in good agreement with the result of the little more complicated calculation in Tables 15, 16 and 17.

Surveys similar to this one usually contain a final paragraph describing the conditions which will be met with in, say, the year 2025.

Such forecasts are usually based on statistics indicating the probable increase of the global consumption of sulfur containing combustibles. However, in these very complicated times I think extrapolations of that kind may be rather misleading. For that reason no such forecast will be given here.



## DISCUSSION

REVELLE

Did I read your diagram right to understand that there is a net influx of the ocean waters of about 100 million tons a year? That there is a net influx into the ocean waters?

BROSSET

Yes, that is exactly what it is.

REVELLE

If this continued over geologic time, the ocean would consist of nothing but sulphate. You must have some sink in the ocean. There is a possible sink that is the hydrothermal circulation in the bottom of the ocean. The entire volume of ocean water apparently passes through the top one or two kilometers of the crust every ten million years, and the sulphate is probably taken out at that time.

The other question I had is: what about volcanic emissions that go up into the upper atmosphere? They must have a half life a lot longer than one day.

BROSSET

Probably yes. They are only mentioned as a total volcanic emission of 28 teragrams in the air, and they are simply divided into two parts, 14 and 14 for the oceanic and continental atmosphere. That is everything with that. But I am quite aware that part of it does not go up to the stratosphere.

KNABE

You gave different figures on the pre-industrial time and the present time, if I got the number correctly. It was 224 teragrams a year in the pre-industrial time and 342 at present. I would like to see the last of your tables, and then I could make my question more precisely.

BROSSET (showing the table and explaining)

These are the anthropogenic emissions in the atmosphere. These are the sea spray, and these are all other emissions. Now if you put them together, you will get the 342 of today.

KNABE

So far I can follow you, but at the very end of it that means total minus and volcanic conditions... Would this be the pre-industrial budget: 228?

BROSSET

If you just subtract from the total the anthropogenic of today — or from the total of today the anthropogenic of today — you will get there a figure that is identical with the calculation of the pre-industrial.

KNABE

But how much is the sea spray the result of the input by rivers? Any meaning?

BROSSET

Yes, you are quite correct. That is now the total anthropogenic input from the rivers: 208; the anthropogenic part of it is 104; and the sea spray total is 140.

ANDERSON

I would like to speak to the gas phase oxidation rates which you mentioned, and particularly the reaction OH with COS. We have examined that reaction in the laboratory by looking both at reacted products and find it to be 100 times slower than your quotation  $0,04 \cdot 10^{-12}$ .

CRUTZEN

I would like to make a few corrections here. First of all, the El Chichón volcano did not put out 100 million tons of sulphate — it put out maybe 3. The other thing is that the ocean already contains so much sulphate that I

do not think on the short-time scale man's input has modified anything. So the sea spray I think it is pre-industrial. About the sulphur reaction, for many of them it seems that when OH reacts with sulphur compounds there is a very strong oxygen effect. It is not noticed for COS, so I think for COS we can forget about reactions of OH in the atmosphere, but regarding CS<sub>2</sub> and dimethylsulphide very strong oxygen effects have been discovered, mainly work in Germany in the laboratory of Becker.

#### CHAMEIDES

On this question of COS, the evidence is that CS<sub>2</sub> + OH reaction produces COS, and the problem with that is that COS does not react with OH. We have a real problem removing COS from the atmosphere. I do not think the question of the COS and OH has been properly addressed and I would not be surprised that in low temperature like in the upper troposphere it turns out that that reaction does in fact occur. But at the moment it is a real problem for the sulphur budget where the COS goes.

#### CRUTZEN

I think that where it goes is rather clear — it will go into the plants. Plants like the stuff, and that has not been considered in the budget so far.

#### PHILLIPS

I was interested in the results you commented on briefly about the oxidation of sulphur dioxide in the aqueous phase, and you said that there were different oxidizing powers, if you like, and precipitations corresponding to different meteorological conditions, and I think you said that air masses from central Europe have the strongest oxidizing power. Could you comment on what is different about those air masses? What is it in the precipitation which causes this? I mean, how is air from central Europe different from that which has traveled across the North Sea, for instance?

#### BROSSET

I am not able to do that, and the only thing I can say is that there were a number of special measurements and we observed that we had two or three times higher oxidation powers in the precipitation for southern winds as compared with other wind directions.

LIBERTI

It is quite ambitious for a scientist to describe a natural phenomenon in terms of a specific reaction. The situation in the atmospheric environment is however more complicated as a variety of reactions are occurring simultaneously and a certain species may take part in different reactions affecting the relative equilibria. Most data are coming from laboratory work and experimental conditions are definitely different from the ones observed in the troposphere. As an example the mechanism of oxidation of sulphur dioxide, in gas phase is usually reported occur to a large extent through free radicals. If the presence of humidity and of particulated matter is considered, specifically in the lower part of the troposphere, definitely also heterogeneous reactions play a very important role. I feel that experiments carried on in the atmosphere yield more consistent results to elucidate the chemistry of the atmospheric environment.

BROSSET

Thank you very much, Dr. Liberti. May I ask you now. I avoided to mention the work of Novakov in Berkeley, California; he studied in a number of papers the oxidation of sulphur dioxide on black particles claiming that there is a kind of oxidation power of the amorphous carbon itself. Now I never understood myself if carbon is the active re-agent of the catalyst and oxidation is going on on the surface field. Have you any opinion on that?

LIBERTI

I will try to answer your questions. Experiments definitely show that  $\text{SO}_2$  absorbed on carbon particles is rapidly oxidized to sulphate and this mechanism is one of the more important for the oxidation of  $\text{SO}_2$  in a heterogeneous process. Not all particulated material behaves, however, in the same way and the specific nature of the surface and humidity play an important role on this mechanism.

WANDIGA

Could you also kindly try to elaborate a little more on your biogenic sources of emissions, because I think they may be on the low side, particularly if you restrict yourself to the sources which are occurring in the temperate zones. When you include the biogenic emissions of sulphur which are

occurring in the tropical zone, the budget may be very different from what you are saying. In this sense I am referring to forest fires, but also to some of the work we have done on termites as being the source of dimethylsulphide.

BROSSET

You are quite correct, but I cannot elaborate more than I have done at this moment.

MARINI-BETTÒLO

I think it is very interesting this global presentation of the sulphur balance, I would say, more than the cycle. There are also some points that must be cleared, as Dr. Wandiga said, but even another point should be mentioned. We are considering pure reactions in the pure atmosphere. Sometimes it happens that there are also other products that might interfere like particulates. And I think we must bear in mind this when we pass from models to true reality.

# LABORATORY STUDIES OF ATMOSPHERIC RADICAL REACTIONS

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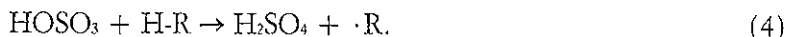
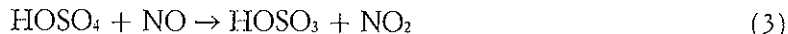
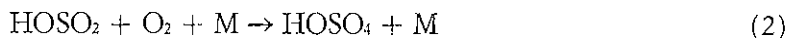
In this paper I will describe some aspects of important environmental problems from the point of view of the chemical reactions that occur in the atmosphere. An overview of the processes involved in stratospheric ozone depletion is given in the papers by Professor Rowland and Professor Anderson, in acid precipitation by Dr. Phillips, and in tropospheric photochemistry by Professor Chameides. It is not practical for me to discuss the details of all of these complicated systems, so I will concentrate on a few issues which are of current interest to me and which I believe touch on some of the key uncertainties in our understanding of the environmental problems. I will also limit my discussion to gas phase reactions, although we know that many liquid phase or heterogeneous reactions are taking place, especially in the troposphere.

## THE SO<sub>2</sub> OXIDATION MECHANISM

The topic acid precipitation has received a great deal of public attention in the US, Canada, and Europe recently. In their papers Dr. Brosset, Dr. Knabe, and Dr. Lag discuss various aspects of this critical problem. It is very surprising that we do not know the details of the chemical mechanisms by which gaseous SO<sub>2</sub> is converted to H<sub>2</sub>SO<sub>4</sub> in the atmosphere. There have been a number of different proposals for the homogeneous mechanism [1-3] but the only step that is well established is the initial attack of OH on SO<sub>2</sub>.



We assume that the bisulfite radical,  $\text{HOSO}_2$ , is the product because the reaction has been shown to be third order. Unfortunately this species has never been detected and nothing is known about its chemistry, so the remaining steps in the mechanism are speculative. A typical scheme is as follows:



Here the bisulfite radical is oxidized by  $\text{O}_2$  to a peroxybisulfate radical which is reduced by  $\text{NO}$  to a bisulfate radical. The  $\text{H-R}$  molecule is some species such as  $\text{H}_2\text{O}_2$  or  $\text{HO}_2$  with a relatively weakly bound hydrogen.

In order to model the homogeneous conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  it may not be necessary to know the rate coefficients for each of the steps as long as Reaction (1) is the rate limiting step. However, it is very important to know how many radicals are consumed in the overall mechanism. For example, Reaction (1) consumes one  $\text{OH}$ , so in the presence of a large concentration of  $\text{SO}_2$ , a condition that one might find in a power plant plume, the rate of  $\text{SO}_2$  oxidation is limited by the rate of  $\text{OH}$  production. In this situation, a reduction in  $\text{SO}_2$  concentration or emission may not be reflected in a proportionate reduction in  $\text{H}_2\text{SO}_4$  deposition [4], because the rate of  $\text{H}_2\text{SO}_4$  production is tied to the  $\text{OH}$  production rate not the  $\text{SO}_2$  concentration. Thus a knowledge of the  $\text{SO}_2$  oxidation mechanism is required to develop an effective strategy to control acid deposition. When all of the details of the mechanism are not known, it is common to use a simplified scheme such as that described by Atkinson *et al.* [5],



This shorthand version of the mechanism assumes that one odd hydrogen radical ( $\text{OH}$ ) is consumed per  $\text{SO}_2$  oxidized. This approach allows modellers to simulate  $\text{SO}_2$  oxidation in the troposphere.

Recently there have been two studies which cast serious doubt on the validity of Reaction (5) as a generalized reaction to describe  $\text{SO}_2$  oxidation. First, Stockwell and Calvert [6] made a kinetic study of the mechanism of the  $\text{OH-SO}_2$  reaction using a photochemical reactor with

long-path Fourier transform infrared spectroscopy. Mixtures of CO, HONO, NO, NO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> at ppm concentrations were prepared in synthetic air or N<sub>2</sub> at 700 torr. OH radicals were generated by the photolysis of HONO:



The OH initiates a chain reaction, the key steps include:



and



The chain is terminated by Reactions (10) and (11):



The steady state OH concentration was inferred from the rate of CO<sub>2</sub> formation via Reaction (7). The effect of SO<sub>2</sub> on this system was tested by adding SO<sub>2</sub> concentrations up to 172 ppm. The surprising result was that the rate of CO oxidation was not significantly reduced. This observation implies that the oxidation of SO<sub>2</sub> does not terminate the HO<sub>x</sub> chain and does not result in the net removal of OH radicals. Therefore the generalized Reaction (5) cannot be correct.

A second study by McKeen, Liu, and Kiang [7] supports the conclusion that SO<sub>2</sub> oxidation does not consume HO<sub>x</sub>. They modelled the oxidation of SO<sub>2</sub> in the stratosphere from the 1982 eruption of the El Chichón volcano. Using one and two dimensional models, they examined the photochemical effects on the injection of several megatons of sulfur into the stratosphere and compared the results with the chemical lifetimes of sulfur obtained from observations of stratospheric SO<sub>2</sub> and sulfate particles. The SO<sub>2</sub> to sulfate conversion scheme they tested assumed that odd hydrogen radicals were consumed (as in Reaction (5)). Under this condition their model predicted that the HO<sub>x</sub> species were significantly suppressed and that the chemical lifetime of SO<sub>2</sub> was greater than 100 days. This can be compared with the observations which imply a lifetime



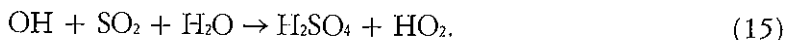
of the order of 30 to 40 days. McKeen *et al.* [7] found that it was necessary to assume that  $\text{HO}_x$  was not consumed by the  $\text{SO}_2$  oxidation in order to match the shorter lifetime of the observations. They adopted the scheme proposed by Stockwell and Calvert [6]:



and



which can be reduced to the generalized mechanism



The major difference between this mechanism and the one given in (5) is that  $\text{HO}_x$  radicals are not consumed in (15). The major weakness of this scheme is that the best available thermochemical data on sulfur species [8] indicates that Reaction (13) is endothermic by approximately  $6 \text{ kcal mol}^{-1}$ . This is an uncomfortably large figure but the uncertainty in the heat of formation of  $\text{HOSO}_2$  is probably large enough that one is not convinced that (15) is incorrect.

There is an additional piece of evidence that  $\text{O}_2$  is reactive toward the  $\text{OH} + \text{SO}_2$  adduct. A discharge-flow experiment by Leu [9] found that  $\text{OH}$  was regenerated when the  $\text{OH} + \text{SO}_2$  recombination reaction was studied in an  $\text{O}_2$  buffer gas. Although the author had no explanation for this observation, it is possible that the  $\text{NO}$  present in his experiment from the  $\text{OH}$  source reaction,  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ , was contributing to the regeneration of  $\text{OH}$  via the sequence Reactions (1), (13), and (9). We are presently developing some experiments to test this possibility by directly searching for the products  $\text{HO}_2$  and  $\text{SO}_3$  in my research group.

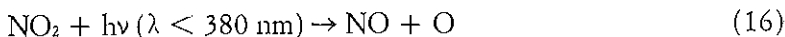
If the Stockwell and Calvert proposal that odd hydrogen radicals are not destroyed in the  $\text{SO}_2$  oxidation process is correct, a major revision of the models for the homogenous oxidation of  $\text{SO}_2$  is required. This revision will certainly change the predicted effects of reducing  $\text{SO}_2$  emission rates. The final result may be a clearer view of the strategy for reducing acid deposition rates.

## THE CO + OH REACTION

The reaction of carbon monoxide with hydroxyl radicals is a very important reaction in the lower atmosphere. It oxidizes CO, a highly toxic gas

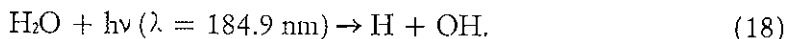


to CO<sub>2</sub>, it regulates the atmospheric HO<sub>x</sub>, and it contributes to the photochemical production of ozone in the lower atmosphere via the sequence (7), (8), (9), (16) and (17).



Reaction (7) is also very important in hydrocarbon combustion systems [10] where it has been shown to exhibit an unusual temperature behavior. The first observation of a pressure effect in the CO + OH reaction was reported by Overend, Paraskevopoulos, and Cvetanović [11] ten years ago. Several different groups subsequently confirmed the observation, but the best quantitative results that have been published are those of Biermann, Zetzsch, and Stuhl [12]. Details of other studies are given in reference 12. Biermann *et al.* used flash photolysis of water vapor to generate OH and observed OH decay rates by uv resonant absorption at pressures between 25 and 750 torr of He or N<sub>2</sub>. Their measurements were made at 300 K and showed a significant pressure effect only when O<sub>2</sub> was added. This observation led Biermann *et al.* to conclude that the CO + OH adduct, HOCO<sup>+</sup>, has three competing paths: (1) direct dissociation to products CO<sub>2</sub> + H, (2), stabilization by M and subsequent reaction of the stabilized product with O<sub>2</sub> to give CO<sub>2</sub> + HO<sub>2</sub> and (3) dissociation back to the reactants. They indicated some concern with their mechanism because the adduct, HOCO, hydroxycarbonyl, is very stable and therefore an O<sub>2</sub> reactant should not be required to observe the pressure enhancement. A satisfactory explanation of this problem has not been given. In the presence of O<sub>2</sub> the Biermann *et al.* result is described by the equation  $k(\text{CO} + \text{OH}) = (1.4 + 1.4 P) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  where P = the pressure of nitrogen in atmospheres. Thus the rate constant doubles between low pressure and one atmosphere pressure.

DeMore at the Jet Propulsion Laboratory has reexamined the  $\text{CO} + \text{OH}$  reaction system [13]. A sketch of his experiment is shown in Figure 1. A mixture of gases including the  $\text{CO}$  reactant, water vapor, and  $\text{Ar}$ ,  $\text{N}_2$ , or  $\text{SF}_6$  is continuously irradiated by 184.9 nm light from a mercury lamp. This photolyzes  $\text{H}_2\text{O}$  producing  $\text{OH}$ :



The steady state  $\text{OH}$  concentration that results is measured by laser induced fluorescence. The rate coefficient for Reaction (7) is determined by two methods: evaluating the steady state  $\text{OH}$  concentration and the amount

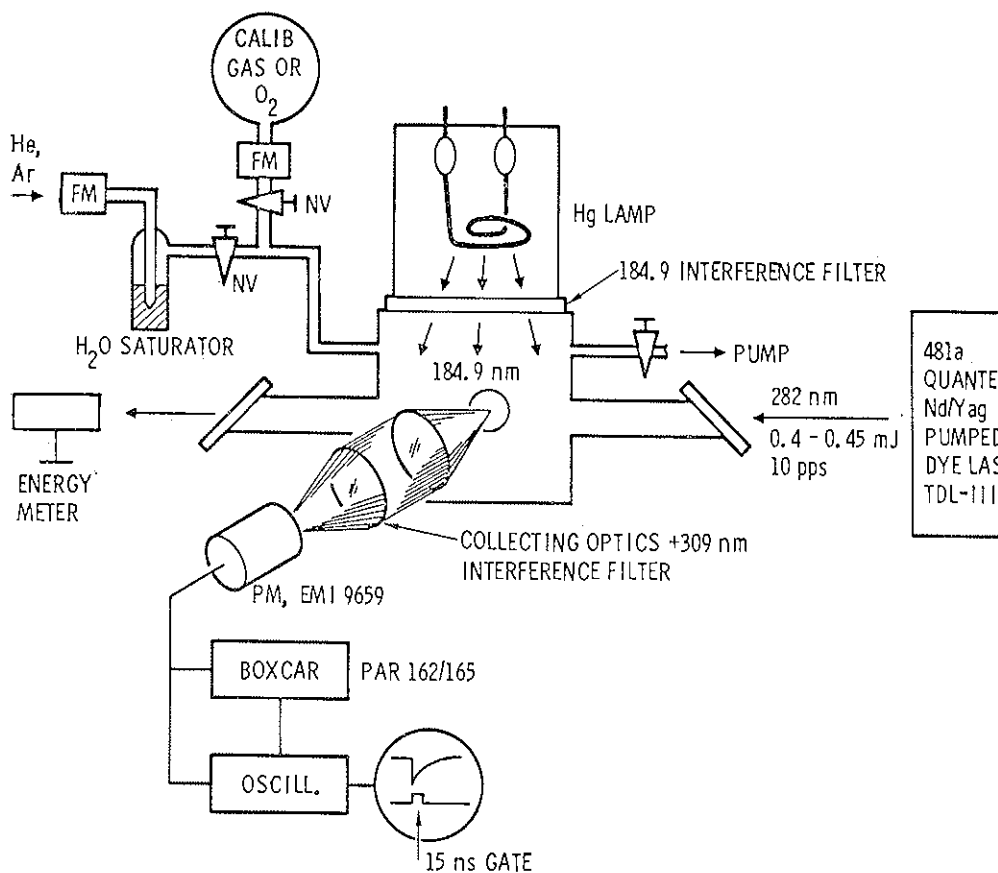


FIG. 1. Schematic of apparatus used by DeMore at Jet Propulsion Laboratory to study the reaction  $\text{CO} + \text{OH}$ . See text for details.

of CO oxidized to  $\text{CO}_2$  or by adding a reference reactant such as  $\text{H}_2$  or  $\text{CH}_4$  and evaluating the ratio of the  $\text{CO} + \text{OH}$  rate to the reference gas + OH rate. Preliminary results from DeMore's study are shown in Figure 2. This gives the factor by which the rate coefficient is increased for three different gases versus the pressure of the added gas. The ratio of the efficiencies of the gases is given by the ratio of their slopes and is in the order one expects for collisional stabilization by Ar,  $\text{N}_2$ , and  $\text{SF}_6$ . The efficiency of  $\text{N}_2$  is only about 40% of the value reported by Biermann *et al.* [12] DeMore also could not reproduce the  $\text{O}_2$  effect reported by Biermann *et al.* DeMore found that small amounts of  $\text{O}_2$  did not enhance the  $\text{CO} + \text{OH}$  rate coefficient even at high total pressures. He has proposed that the  $\text{O}_2$  enhancement reported by Biermann *et al.* may result from the sequence:



and

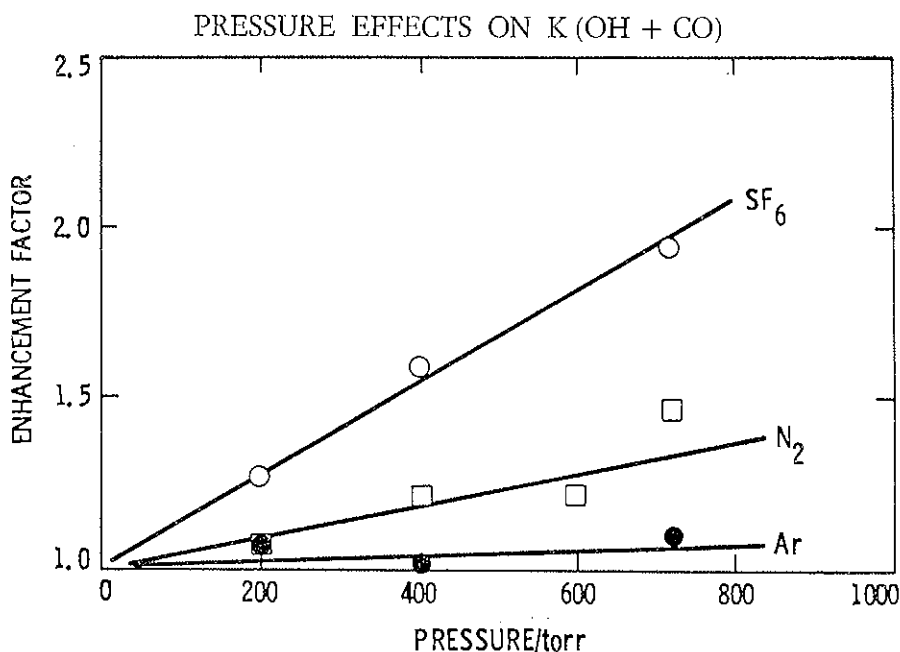


FIG. 2. Preliminary data from studies of the  $\text{CO} + \text{OH}$  reaction by DeMore. This shows the enhancement factor (the number by which the low pressure rate coefficient should be multiplied) as a function of pressure for three different collision gases.

This requires that the radical concentration in the Biermann *et al.* experiment be a factor of 3 to 10 times higher than they reported. A second problem is that Biermann *et al.* could see no enhancement with 750 torr of N<sub>2</sub> when no O<sub>2</sub> was present. According to the data of DeMore there should have been a 40% increase in the rate coefficient. I favor adopting the data from the DeMore study because his experiment is simpler than that of Biermann *et al.* and because his data is consistent with a straightforward kinetic model. Nevertheless this critical reaction requires some additional direct measurements.

### THE HO<sub>2</sub> + HO<sub>2</sub> REACTION

The HO<sub>2</sub> disproportionation reaction has a rich measurement history beginning with the classic mass spectrometric study of Foner and Hudson in 1962 [14].



This reaction is important in the atmosphere as a loss mechanism for hydroperoxyl radicals which are a critical oxidant. It is also the source of atmospheric hydrogen peroxide which may be responsible for the oxidation of SO<sub>2</sub> to sulfuric acid in droplets and on the surface of aerosols. During the last 10 years several rather astonishing observations have been made regarding Reaction (21): (a) a water vapor enhancement [15], (b) a large negative temperature dependence [16], and (c) a significant pressure dependence [17, 18]. In the last few months a series of independent studies in different laboratories have been made on Reaction (21) and at last a clear picture has emerged of the kinetics of this important reaction. The key study was made by Kircher and Sander [19] at the Jet Propulsion Laboratory. They used flash photolysis to generate HO<sub>2</sub> radicals and uv absorption to measure their concentration. They investigated the kinetics of Reaction (21) at temperatures between 230 and 420 K, at pressures between 100 and 700 torr, with H<sub>2</sub>O vapor at pressures between 0 and 10 torr, and for both the hydrogen and deuterium isotopes. The Kircher and Sander study provides data for the complete range of atmospheric conditions for which Reaction (21) is important.

Tests of their results are provided by several independent measurements. Table 1 summarizes the results of four recent studies of the

TABLE 1 - Summary of  $\text{HO}_2 + \text{HO}_2$  reaction temperature dependence studies at low pressure.

| k (T)                           | k (298)   |                             | Temperature<br>Range | Method | References                       |
|---------------------------------|---|-----------------------------|----------------------|--------|----------------------------------|
|                                 | (10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) |                             |                      |        |                                  |
| (2.0 ± 0.6) exp [(595 ± 120)/T] | 15  |                             | 253-390              | DF/LMR | This work <sup>20</sup>          |
| 2.25 exp [(610 ± 200)/T]        | 17  |                             | 240-417              | FP/UV  | Kircher and Sander <sup>19</sup> |
| 2.4 exp [(560 ± 200)/T]         | 16  |                             | 298-358              | FP/IR  | Thrush and Tyndall <sup>21</sup> |
| (2.6 ± 0.4) exp [(581 ± 44)/T]  | 18  |                             | 273-339              | MM/UV  | Cox and Burrows <sup>22</sup>    |
| DF = discharge flow             | MM = molecular modulation   | UV = ultraviolet absorption |                      |        |                                  |
| FP = flash photolysis           | LMR = laser magnetic resonance  | IR = infrared absorption    |                      |        |                                  |

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temperature dependence of  $k_{21}$  at low pressure. The pressure dependence of the reaction is small enough that it can be neglected at pressures less than about 10 torr, so in this region it may be considered purely bimolecular. The first line in Table 1 summarizes measurements made by G.A. Takacs in my laboratory [20]. He used laser magnetic resonance to detect  $\text{HO}_2$  radicals in a discharge-flow experiment. Several different methods were used to generate  $\text{HO}_2$ , including the reactions of F and Cl atoms with  $\text{H}_2\text{O}_2$  and the reaction of Cl with  $\text{CH}_3\text{OH}$  followed by the reaction of the  $\text{CH}_2\text{OH}$  product with  $\text{O}_2$ . The  $\text{HO}_2$  concentration was calibrated by using Reaction (9) to convert  $\text{HO}_2$  to  $\text{NO}_2$  or  $\text{OH}$  which were independently detected and calibrated. The low pressure value of  $k_{21}$  given by Kircher and Sander [19] was derived from the  $P = 0$  intercept of plots of  $k_{21}$  versus pressure. Thrush and Tyndall [21] used flash photolysis production of  $\text{HO}_2$  radicals and infrared absorption with a diode laser for their detection. The 1979 study by Cox and Burrows [22] used uv absorption for detection of  $\text{HO}_2$  in a molecular modulation experiment. The agreement of the results from these four studies is remarkable. All values of the rate coefficient at 298 K fall within the range  $k_{21} = (1.5 \text{ to } 1.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Similarly the temperature coefficients,  $E/R$ , are in excellent agreement among the data sets, although the Thrush and Tyndall and Cox and Burrows studies cover relatively small temperature ranges.

From the slope of plots of  $k_{21}$  versus pressure Kircher and Sander determined the termolecular rate coefficients and their temperature dependence for  $M = \text{Ar}$  and  $\text{N}_2$ . The values of these are  $k(\text{Ar}) = 8.4 \times 10^{-34} \exp(1100/T)$  and  $k(\text{N}_2) = 1.9 \times 10^{-33} \exp(980/T)$  in  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . Thus the termolecular rate coefficient in  $\text{N}_2$  is about  $5.1 \times 10^{-32}$  at 298 K. The effect of one atmosphere of  $\text{N}_2$  is to increase the effective bimolecular rate coefficient from about  $1.6 \times 10^{-12}$  to about  $2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . If water vapor is present, a further enhancement about 70% is found with 10 torr  $\text{H}_2\text{O}$  at 298 K. The recommended expression for modelling the  $\text{HO}_2 + \text{HO}_2$  reaction in air at high pressures and in the presence of water vapor is given by the expression:

$$k_{21} = (2.3 \times 10^{-13} \exp(590/T) + 1.7 \times 10^{-33} \exp(1000/T)[M])(1 + 1.4 \times 10^{-21} \exp(2200/T)[\text{H}_2\text{O}])$$

This equation, largely derived from Kircher and Sander [19], brings together the results from many different studies of this critical and complex reaction.

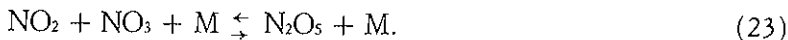
NO<sub>3</sub> CHEMISTRY

Several years ago Noxon *et al.* [23] first observed NO<sub>3</sub> radicals in the atmosphere by means of its absorption at 662 nm of lunar light. Many subsequent measurements [24, 25] have been made and the general conclusion can be drawn that the observed atmospheric concentrations of NO<sub>3</sub> are not accurately reproduced by attempts to model its chemistry with the available reaction rate data. This conclusion has stimulated a great deal of interest and activity involving NO<sub>3</sub> chemistry.

The nitrate radical is most abundant during the nighttime because it is very rapidly photolyzed by sunlight. Its source is the slow reaction of NO<sub>2</sub> with ozone:



It is known to react with NO<sub>2</sub>, forming N<sub>2</sub>O<sub>5</sub>:



These reactions demonstrate the key role that NO<sub>3</sub> plays in atmospheric chemistry. It is a critical intermediate in the formation of N<sub>2</sub>O<sub>5</sub>, a potential reservoir and sink for NO<sub>x</sub>. Since other NO<sub>x</sub> species, NO and NO<sub>2</sub>, have a dominant part in tropospheric and stratospheric chemistry, the possibility of a significant nighttime chemistry involving NO<sub>3</sub> must be investigated. Several groups including ours at NOAA are starting research on NO<sub>3</sub> kinetics.

Atkinson, Pitts, and coworkers at the University of California at Riverside are in the process of publishing a series of papers on NO<sub>3</sub> chemistry. I will briefly describe a few of their results. Their method involves the use of a smog chamber experiment with long path infrared absorption measurements of reactant concentrations [26]. Their kinetic measurements are based on the competition between two different reactants for the NO<sub>3</sub> radical. N<sub>2</sub>O<sub>5</sub> is used as a source of NO<sub>3</sub>. Table 2 summarizes some of their data for reactions of NO<sub>3</sub> with selected organic compounds. Most of these materials are present in significant concentrations only in polluted urban environments. For the alkene compounds the rate coefficients follow the general trend found for the addition reactions of O and OH. This supports the proposal that the mechanism involves addition to the double bond. A dramatic increase in reactivity is observed with the



TABLE 2. -  $\text{NO}_3$  radical reaction rate coefficients at 298 K (from Atkinson *et al.* [26], UC Riverside).

| Compound              | k ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) |
|-----------------------|--|
| ethene                | $(6.1 \pm 2.6) \times 10^{-17}$                          |
| propene               | $(4.2 \pm 0.9) \times 10^{-15}$                          |
| 1-butene              | $(5.4 \pm 1.2) \times 10^{-15}$                          |
| isobutene             | $(1.7 \pm 0.19) \times 10^{-13}$                         |
| cis-2-butene          | $(1.89 \pm 0.22) \times 10^{-13}$                        |
| trans-2-butene        | $(2.11 \pm 0.24) \times 10^{-13}$                        |
| 2-methyl-2-butene     | $(5.1 \pm 1.6) \times 10^{-12}$                          |
| 2,3-dimethyl-2-butene | $(3.1 \pm 1.0) \times 10^{-11}$                          |
| benzene               | $\leq 1.1 \times 10^{-17}$                               |
| toluene               | $(2.0 \pm 1.1) \times 10^{-17}$                          |
| m-xylene              | $(7.6 \pm 3.5) \times 10^{-17}$                          |
| napthalene            | $(6.4 \pm 2.5) \times 10^{-15}$                          |
| formaldehyde          | $(3.23 \pm 0.26) \times 10^{-16}$                        |
| acetaldehyde          | $(1.34 \pm 0.28) \times 10^{-15}$                        |

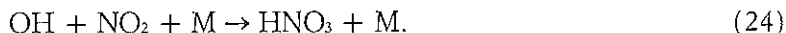
addition of methyl groups. The aldehydes apparently react mainly by H atom abstraction and the expected product,  $\text{HNO}_3$ , was observed. The reaction mechanism for the aromatic compounds is not known, but may involve abstraction also.

If one assumes a nitrate radical concentration of about 300 ppt [25] the lifetimes of these organic compounds range from about 1/3 year for materials with a rate coefficient of  $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to about 13 seconds for materials with a rate coefficient of  $10^{-11}$ . It is possible that the faster reactions play a significant role in defining the atmospheric lifetimes of both nitrogen oxides and some organic materials. Atkinson *et al.* [26] have raised the point that the addition reaction products of some of the compounds may be highly toxic, especially the dinitrate products. An additional interesting point is that the reactions may provide a nighttime source of other reactive radicals such as OH or  $\text{HO}_2$  or that a compound such as  $\text{HNO}_2$ , nitrous acid, may be formed.  $\text{HNO}_2$  is a source of OH and NO radicals as soon as the sun comes out.

## FUTURE STUDIES

The interest in atmospheric environmental problems has stimulated a great deal of laboratory research on chemical kinetics. New research tools, especially lasers, have aided in increasing the quantity and quality of data. A major problem that is limiting the development of this research area is that often the reactions that need to be studied are not easily identified. For example, it is not possible to assess the effect of a reaction on model calculations until one has an estimate of the rate coefficient. Also it is not possible to tell which previous studies may be in error. One must speculate on reactions to which model predictions are very sensitive or for which there are inconsistencies in the data.

There is one other topic which should be pursued. This is the study of reaction products. I believe much more emphasis should be placed on this part of laboratory kinetics. For example, the key termination reaction for nitrogen oxides is:



where it is assumed that  $\text{HNO}_3$  is nitric acid. It is possible that an isomer of this compound is formed, namely, peroxyxynitrous acid,  $\text{HOONO}$ . Two isomers are observed on the similar system of  $\text{Cl}$  addition to  $\text{NO}_2$ :  $\text{ClONO}$  and  $\text{ClNO}_2$ . Also it is known that  $\text{HOONO}$  is stable and that it is formed in solution. If this isomer is formed, its existence introduces a new species to the list of atmospheric trace constituents. I believe there are many similar "well known" reactions that must be investigated to confirm such details.

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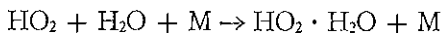
## DISCUSSION

ANDERSON

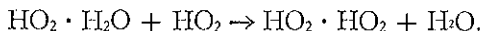
Could you briefly discuss the mechanism involved in the water vapor insertion into the  $\text{HO}_2 + \text{HO}_2$  reaction?

HOWARD

Yes. I deliberately omitted many such gory details because I had visions of finding a comatose audience when the lights were turned back on. Recall that the  $\text{HO}_2 + \text{HO}_2$  reaction has a pressure-dependent component, and so what is happening is that the water vapor molecule acts as a chaperon in the association reaction. The  $\text{HO}_2$  radical has a very large dipole moment, about 2.1 Debye. It is even larger than the dipole moment of water. This molecule associates with a water molecule through a hydrogen bond and forms a complex.



A second reaction occurs between the  $\text{HO}_2$  — water complex and  $\text{HO}_2$ :



Presumably this is a fast bimolecular reaction. It gives the same product,  $\text{HO}_2 \cdot \text{HO}_2$ , that is obtained by the thermolecular reaction in the absence of water vapor. This product must decompose to  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  quite rapidly. Kircher and Sander discuss some of the details of this mechanism in their paper and David Golden and coworkers at SRI International have also analyzed it in terms of kinetic theories. Both have papers coming out very soon in the Journal of Physical Chemistry.

ANDERSON

Have you estimated the bond strength in the first step, that is, between water and  $\text{HO}_2$ ?

HOWARD

Yes. In fact, in some of the studies of the water vapor effect there is a

measurement of that from the temperature dependence of the water vapor effect. The bond energy is somewhere around 7 or 8 kcal mol<sup>-1</sup>. It is a relatively strong hydrogen bond.

ANDERSON

Have you looked for the disappearance of HO<sub>2</sub> in the LMR experiment resulting from the attachment of water?

HOWARD

Yes. But there is a problem in that kind of experiment. What happens is that there is a pressure broadening of the HO<sub>2</sub> line on addition of H<sub>2</sub>O vapor. The sensitivity of the experiment is derived from the narrowness of the rotational line. In the presence of tiny amounts of water vapor, an enormous broadening of the HO<sub>2</sub> line develops, making it impossible to measure the HO<sub>2</sub> accurately. This is an indication perhaps of a strong interaction between the HO<sub>2</sub> molecule and the water vapor. So in our Laser Magnetic Resonant experiment we cannot study the association reaction. The previous work on these complexes has all been done at high pressure with uv absorption detection.

CRUTZEN

The reaction HO<sub>2</sub> + NO is of course a key question in the atmosphere. Are there similar problems there with water vapor adducts? And also the possibility that the HOONO molecule which you formed by OH + NO<sub>2</sub> may be formed there.

HOWARD

Yes. So far as I know, no one has investigated the effect of water vapor on the HO<sub>2</sub> + NO reaction. What you are suggesting is that in the presence of water vapor HO<sub>2</sub> + NO could lead to HOONO?

CRUTZEN

Yes, this would make the possibility greater that you end up with the HOONO molecule because the water vapor could carry off the excess energy, which otherwise would make it difficult for HOONO to form.

HOWARD

Yes. That is a possibility, and as far as I know, no one has ever looked for such a thing. That the  $\text{HO}_2 + \text{NO}$  reaction would form  $\text{HOONO}$  is unlikely otherwise, because there is too much energy to be removed before you can form stable  $\text{HOONO}$ . But you are correct that it would help to associate  $\text{HO}_2$  with water.

LIBERTY

There was a lot of discussion about the carbon monoxide in the atmosphere. You pointed out that through free radicals carbon monoxide is oxidized to carbon dioxide. Do you believe that this is the real sink for carbon monoxide, in other words, that the scheme you described is really representative for sink for carbon monoxide?

HOWARD

Yes, I do. I do not know of any other mechanism, certainly no other homogeneous mechanism that is significant.

ROWLAND

I would comment here that there is a related experiment that was carried out by Professor Ehhalt's group in Germany in which they were looking at the radioactive carbon monoxide, carbon 14, monoxide formed by cosmic ray produced carbon 14. They measured the concentration of carbon-14 monoxide in Germany and found that its concentration varied with the season and the concentration was higher in the winter and lower in the summer, as you would expect because the concentration of hydroxyl is lower in the winter and higher in the summer. And they were able to model the actual lifetime of the carbon 14 monoxide quite well with models of the hydroxyl concentration as a function of season. They then checked this by making one measurement in Florida, where the hydroxyl concentration would be even higher, and the concentration of carbon 14 monoxide was lower, as expected from that kind of modeling.

MALONE

If I read the table correctly, there was a difference of about six orders of magnitude in the rate constants for the  $\text{NO}_3$  reactions. Is this true? It must require an extraordinary measurement technique. Is it quite credible?

HOWARD

Yes, that's right, that the rate constant for ethylene was in the  $10^{-17}$  range and the one for the tetramethyl ethylene was around  $10^{-11}$ . So there is about a six-decade factor. There are different tricks for accomplishing the measurement of rate constants over this range. First one can vary the reactant concentration, in this case the hydrocarbon concentration, by quite a large factor, by probably about a factor of  $10^5$  or  $10^6$ . Also the reaction time can be varied by a factor of 10 to 100 in a chamber experiment. And finally, if they want to try to measure one very accurately — it is possible to put in another material whose rate coefficient is similar in magnitude and to look at the two reactants in competition.

KNABE

We have a steady increase in the exhaust of NO and transformation of NO<sub>2</sub> by the excessive automobile traffic. Is there any effect expected on the radical formation on this changing relation between NO, NO<sub>2</sub> and SO<sub>2</sub> in the atmosphere? In Europe we observed many unusual effects on the vegetation and so on. My question is: are any radicals formed maybe by that new conservation which were not there before?

HOWARD

Not that I know of. I think the complement of radicals that we have now is large enough to account for the chemistry that occurs.

ROWLAND

My impression is that he may have asked the question: Have you changed the concentrations of old radicals in such a way that it would have biological effects?

HOWARD

Oh, yes. In fact one of the things from the study that I described on nitrate radicals was that they observed some molecules that are toxic compounds. For example, some nitrate compounds which involve the addition of two nitrate radicals to an organic substrate. Apparently those are very toxic, so I would say the likelihood of forming such molecules would be increased as you increase

the concentration of nitrogen oxides, because you have to have attached to one organic substrate.

ROWLAND

The comment I would add to that — and it is especially downwind from places where you have sources of nitrogen oxide, that you would expect these effects.

CRUTZEN

This was something which was considered in the Academy report in the United States, an older paper which I was involved in, whether the nitrogen oxides actually would gobble up so much hydroxyl radicals that the oxidation of  $\text{SO}_2$  would be effected. There are some slight indications in Europe that may have occurred in the forest, but it does not seem to be right for the United States, so different regions may have different problems here.

CHAMEIDES

I have a question concerning the  $\text{SO}_2$  reaction which perhaps is somewhat speculative. The new mechanism for  $\text{SO}_2$  homogeneous oxidation, presumably converts an OH radical to an  $\text{HO}_2$  radical. Could that combined with the recent observation by Becker and his group that the  $\text{SO}_2 + \text{OH}$  reaction is dependent on oxygen concentrations and which imply that that reaction is practically five times faster in the lower troposphere than had been thought previously? And I wonder if perhaps this  $\text{SO}_2 + \text{OH}$  reaction, if this fast rate constant is correct and the mechanism is correct, could actually be a significant way of converting OH to  $\text{HO}_2$  and producing ozone and oxygen. Would you care to comment on that?

HOWARD

Sure. First, I am not familiar with the work of Becker. The little bit I have heard seems to be in general consistent with the observations of Calvert and Stockwell. That  $\text{SO}_2$  could be the source of an oxidant by such a mechanism is an interesting idea. It is something that could be very directly tested in a small chamber experiment or by modelling. It will depend upon the concentration of  $\text{SO}_2$  relative to other oxidant forming species such as CO or hydrocarbons. But it is something that in my opinion could be directly tested.



LIBERTI

Because of the importance of OH and the large amount of work you have done in this field, which analytical procedure do you suggest for atmospheric OH determination?

HOWARD

I think there is probably not a single method that one would want to trust in such an important measurement. Probably something like what Anderson, Davis, and Wang are trying to do with lasers to measure it in a direct way in one location, plus some kind of less direct measurements of the type that Ehhalt and Campbell use, looking at the oxidation of some species. I think we are going to have to have several methods to do it. It is such a difficult problem, and there is so much variability in the conditions under which you would like to measure it from the stratosphere down to the surface that one is really going to have to use several different methods.

ARNOLD

I should greatly like to comment on the homogeneous  $\text{SO}_2$  oxidation. You have pointed out that the problem is the fate of the  $\text{HSO}_3$  intermediate radical, and you have mentioned the recent suggestions including the  $\text{O}_2$  reaction. I assume that the kinetics is now known for this reaction. From our stratospheric and recent tropospheric observations of the  $\text{HSO}_3$  and  $\text{H}_2\text{SO}_4$  gases we can estimate the lifetime of  $\text{HSO}_3$  in the atmosphere, and it turns out to be much shorter than to be expected for instance for the hydroxyl radical reaction as a sink alone. It also turns out that the lifetime is such that we cannot exclude that heterogeneous removal may have a role. It is just of the order which you may expect for heterogeneous removal, assuming an efficient high sticking probability. And if you assume that the  $\text{O}_2$  reaction is the main sink, you may get an estimate on the effective rate coefficient for this process from such observations. And finally I should like to add that the fact that  $\text{HSO}_3$  clusters very efficiently to ionic clusters being composed of sulphuric acid and water, the same composition as is expected for the aerosols, implies that we should not forget about the possibility that  $\text{HSO}_3$  radicals may also undergo heterogeneous removal in the atmosphere.

HOWARD

I could comment on that. You may recall from yesterday that Professor

Arnold has observed chemical species in the stratosphere associated with negative ions, that he interpreted these as being  $\text{HOSO}_2$  — and if that were correct, then I think that the Stockwell and Calvert mechanism is not correct. I do not think there should be any  $\text{HOSO}_2$  in the atmosphere, if their mechanism occurs, according to the scheme that they have developed. If Arnold's identification is correct, then I think that the Stockwell and Calvert scheme is not significant. Maybe the observed ion cluster species is  $\text{SO}_3$  not  $\text{HOSO}_2$ .

ROWLAND

But what about at much lower pressures?

HOWARD

But you still have  $\text{O}_2$  present. One fifth of the air is  $\text{O}_2$  where Arnold makes his measurements. The  $\text{HOSO}_2$  should still convert to  $\text{HO}_2$  and  $\text{SO}_3$ .

CRUIZEN

It was not clear to me at what pressures were these Stockwell and Calvert measurements made.

HOWARD

At one atmosphere. I think the reason they do most of their work at one atmosphere is because their chamber probably leaks...

## II.

ATMOSPHERE AND THE SECONDARY PROCESSES:  
THE EFFECT OF GEOLOGICAL AND ANTHROPIC  
COMPONENTS

# THE PHOTOCHEMISTRY OF TROPOSPHERIC TRACE SPECIES: THE CENTRAL ROLE OF RADICALS AND THEIR POSSIBLE VARIABILITY

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## *Abstract*

In the presence of sunlight, reduced species emitted into the atmosphere from the earth's surface are oxidized, converted to soluble forms, and then returned to the biosphere-lithosphere-hydrosphere. The free radical OH, predicted to be present in the atmosphere at levels of about  $10^5$ - $10^6$  molecular  $\text{cm}^{-3}$ , is believed to be the primary species in initiating the oxidation of most of these reduced atmospheric compounds. The concentration of the OH radical in the remote troposphere is primarily controlled by the atmospheric levels of  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , CO,  $\text{CH}_4$  and  $\text{NO}_x$ . However, it appears that anthropogenic activities can significantly affect the atmospheric levels of  $\text{O}_3$ , CO,  $\text{CH}_4$ , and  $\text{NO}_x$  and thus may have conceivably caused a perturbation in OH levels on a global scale. A recent analysis of  $\text{CH}_4$  in ice cores which indicated that  $\text{CH}_4$  has increased significantly over the past 400 years suggests that OH levels have in fact undergone a secular variation in the recent past.

## *Introduction*

While scholars have speculated about the atmosphere's composition since the days of the pre-Socratic Greek philosophers, the first significant

scientific advances in atmospheric chemistry date back only to the 18th century studies of Joseph Priestley, Antoine-Laurent Lavoisier, and Henry Cavendish. It was these scientists who first established that the major constituents of Earth's atmosphere are nitrogen (79% by volume) and oxygen (20%), with lesser amounts of water and carbon dioxide.

During the 19th and early 20th centuries, many prominent chemists and physicists further advanced our knowledge in this area. Sir William Ramsey documented the presence of the noble gases argon, helium, krypton, neon, and xenon in the atmosphere. Other investigators found evidence for small quantities of methane, hydrogen, ozone, carbon monoxide, sulfur dioxide, and hydrogen sulfide in the air and nitrate, sulfate, chloride, and ammonium ions dissolved in rainwater. Thus by the middle of the 20th century, a good deal of qualitative information on the chemical composition of the atmosphere had been gathered.

Since the 1950s, rapid advancement in chemical analytical techniques and high-speed computers has led to an explosion of knowledge concerning atmospheric composition. The atmosphere has been found to be a reservoir for a myriad of trace gaseous and aerosol species with concentrations below 1 ppmv (1 part per million per volume of air). And, in spite of their relatively low concentrations, these atmospheric trace gas and aerosol species often can have a major impact on the environment. Some gases, for instance, because of their toxicity, can affect plant and animal life; others can affect climate via the "atmospheric greenhouse effect". Aerosols, on the other hand, can have a significant effect upon cloud formation and precipitation patterns.

Recognizing the potential of atmospheric trace species for altering or influencing the global environment, it may reasonably be asked: Why are these species present in the atmosphere? Can their presence, for example, be explained directly in terms of planetary thermodynamics? In fact, as indicated in Table 1, simple calculations show that most trace species are present in the atmosphere at much higher levels than would be predicted solely on the basis of thermodynamic equilibrium with nitrogen, oxygen, carbon dioxide, and water. Clearly, kinetic mechanisms involving a combination of chemical, physical, and biological processes are controlling the trace gas composition of the atmosphere. It is the identity of these kinetic mechanisms and their relationship to natural life cycles that have been of fundamental interest to atmospheric chemists in recent decades and are the subject of this work.

TABLE 1 - *Atmospheric Trace Gas Composition is Controlled by a Complex Combination of Processes.*

| Species                          | Thermodynamically equilibrated concentration <sup>a</sup> (Mole fraction) | Actual atmospheric concentration (Mole fraction)      | Reliability with which global distribution is known | Principal sources                       | Principal sinks       |
|----------------------------------|---|---|---|---|-----------------------|
| CH <sub>4</sub>                  | 10 <sup>-145</sup>  | 1.6 × 10 <sup>-6</sup>                                | High  | Biogenic                                | Photochemical         |
| CO                               | 6 × 10 <sup>-49</sup>   | (0.5 - 2) × 10 <sup>-7</sup>                          | Fair  | Photochemical, anthropogenic            | Photochemical         |
| O <sub>3</sub>                   | 3 × 10 <sup>-30</sup>   | 10 <sup>-8</sup> - 10 <sup>-7</sup>                   | Fair  | Photochemical                           | Photochemical         |
| NO + NO <sub>2</sub>             | 2 × 10 <sup>-10</sup>   | (10 <sup>-12</sup> - 10 <sup>-8</sup> ) <sup>b</sup>  | Low   | Lightning, anthropogenic, photochemical | Photochemical         |
| HNO <sub>3</sub>                 | 1 × 10 <sup>-9</sup>  | (10 <sup>-11</sup> - 10 <sup>-9</sup> ) <sup>b</sup>  | Low   | Photochemical                           | Rainout               |
| NH <sub>3</sub>                  | 2 × 10 <sup>-60</sup>   | (10 <sup>-10</sup> - 10 <sup>-9</sup> ) <sup>b</sup>  | Low   | Biogenic                                | Photochemical rainout |
| N <sub>2</sub> O                 | 2 × 10 <sup>-19</sup>   | 3 × 10 <sup>-7</sup>                                  | High  | Biogenic                                | Photochemical         |
| H <sub>2</sub>                   | 2 × 10 <sup>-42</sup>   | 5 × 10 <sup>-7</sup>                                  | High  | Biogenic, photochemical                 | Photochemical         |
| OH                               | 5 × 10 <sup>-28</sup>   | 10 <sup>-15</sup> - 10 <sup>-12</sup> <sup>c</sup>    | Very low  | Photochemical                           | Photochemical         |
| HO <sub>2</sub>                  | 4 × 10 <sup>-28</sup>   | 10 <sup>-13</sup> - 10 <sup>-11</sup> <sup>c</sup>    | Very low  | Photochemical                           | Photochemical         |
| H <sub>2</sub> O <sub>2</sub>    | 1 × 10 <sup>-24</sup>   | 10 <sup>-10</sup> - 10 <sup>-8</sup>                  | Very low  | Photochemical                           | Rainout               |
| H <sub>2</sub> CO                | 9 × 10 <sup>-96</sup>   | 10 <sup>-10</sup> - 10 <sup>-9</sup>                  | Low   | Photochemical                           | Photochemical         |
| SO <sub>2</sub>                  | 0   | (10 <sup>-11</sup> - 10 <sup>-10</sup> ) <sup>b</sup> | Fair  | Anthropogenic, photochemical volcanic   | Photochemical         |
| CS <sub>2</sub>                  | 0   | (10 <sup>-11</sup> - 10 <sup>-10</sup> ) <sup>b</sup> | Low   | Anthropogenic, biogenic                 | Photochemical         |
| OCS                              | 0   | 10 <sup>-10</sup>                                     | Fair  | Anthropogenic, biogenic, photochemical  | Photochemical         |
| CH <sub>3</sub> CCl <sub>3</sub> | 0   | (0.7 - 2) × 10 <sup>-10</sup>                         | Fair  | Anthropogenic                           | Photochemical         |

<sup>a</sup>) Thermodynamically equilibrated concentration is that calculated by assuming thermodynamic equilibrium with a gas mixture containing 0.78 atm N<sub>2</sub>, 0.21 atm O<sub>2</sub>, 0.01 atm H<sub>2</sub>O, and 3.3 × 10<sup>-4</sup> atm CO<sub>2</sub> at a temperature of 298 K. <sup>b</sup>) Lower concentration limits cited may not necessarily reflect actual minimum concentrations but rather the lower limit on detection sensitivity of current instrumentation. <sup>c</sup>) Concentrations of these transient species become much lower at night.

### *Solar Radiation*

One of the key components of these kinetic mechanisms is the presence of solar radiation. Chemical reactions between the major constituents of the troposphere occur at negligible rates. However, the formation of more chemically active species under the influence of light gives rise to rapid reaction chains that play a major role in controlling the trace composition of the atmosphere. Because it is driven by the absorption of photons, the chemistry of the lower atmosphere often is referred to as tropospheric photochemistry. Of course, all photons from the sun do not take part in tropospheric photochemistry. Most ultraviolet solar photons are absorbed in the upper levels of the atmosphere and never penetrate the tropopause (c.f. Leighton, 1961). Photons with wavelengths shorter than 240 nm are absorbed by oxygen and nitrogen molecules in the thermosphere, and ozone, found primarily in the stratosphere, is a key absorber of photons in the spectral region between 240 and 300 nm. Thus, for the troposphere we need consider only those chemical reactions that are activated by photons with wavelengths of 300 nm or longer, as illustrated in Fig. 1.

One of the key distinguishing features between the chemistry of the troposphere and that of the stratosphere is that ultraviolet photons sufficiently energetic to break an oxygen-oxygen bond are present in the stratosphere but not in the troposphere. As first noted by William J. Humphreys in 1910, this photodissociation of stratospheric oxygen molecules leads to the generation of ozone and, as a result, much higher concentrations of ozone are found in the stratosphere than in the troposphere.

### *The Earth-Atmosphere Interface*

A variety of biological and geological processes can result in the emission of gases from Earth's surface to the atmosphere. These surface emissions, which can have a major effect on atmospheric composition, appear to be highly variable in both the types of species released and the rates at which they are emitted into the atmosphere. Although data are quite limited, those available suggest that different biotic provinces, such as tropical evergreen forests, deciduous midlatitude forests, swamps and wetlands, alpine tundra, and deserts each emit a unique array of gases.

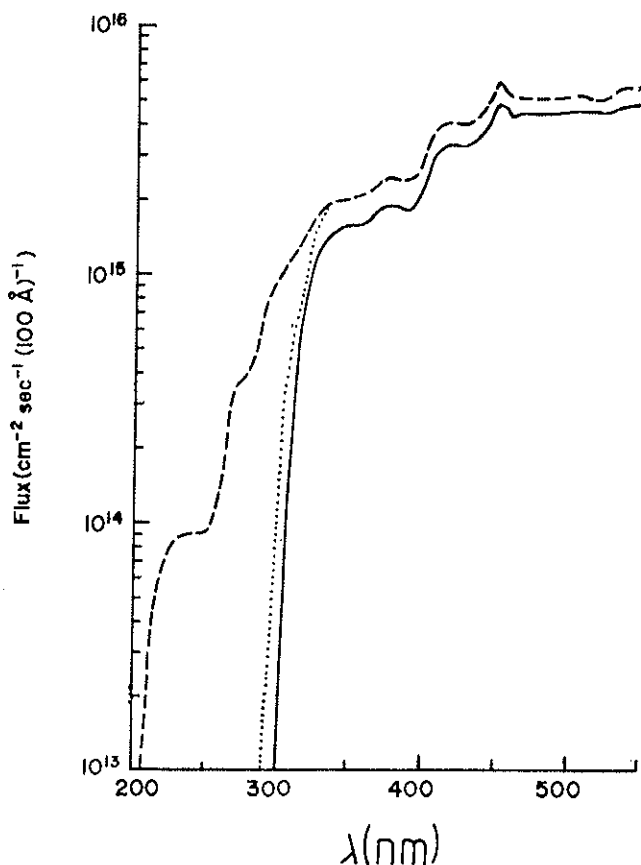


FIG. 1. The flux of solar radiation as a function of wavelength;  $\lambda$ . The broken line is the flux of solar radiation at the top of the atmosphere. The flux of solar radiation at the ground for solar zenith angles of  $0^\circ$  and  $45^\circ$  is represented by the dotted line and solid line respectively.

Even the oceans should not be looked upon as having a homogeneous interface with the atmosphere; there is growing evidence that the biological diversity of the oceans is quite large. Given the diversity of ecosystems on Earth it is quite likely that we will continue to find that the "natural" troposphere is highly inhomogeneous in its chemical composition.

In spite of the complexity of biogeospheric surface emissions, one generalization is in order: The vast majority of trace species emitted into the atmosphere are in reduced oxidation states (such as hydrogen sulfide,



ammonia, and methane). By contrast, materials returned to the surface from the atmosphere, usually by dissolution in rain drops or by dry deposition, are highly oxidized (such as sulfuric acid, nitric acid, and carbon dioxide). The link between these reduced and oxidized species is supplied by atmospheric photochemical reactions, thus giving rise to a chemical cycle whereby reduced gases are emitted into the atmosphere, photochemically oxidized, and then removed from the atmosphere.

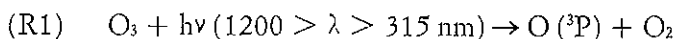
That reduced atmospheric gases are oxidized is not surprising; the large atmospheric abundance of oxygen thermodynamically favors their oxidation. However, molecular oxygen rarely is directly responsible for oxidizing these reduced gases. The oxygen-oxygen bond is relatively strong (120 kcal/mole) and thus molecular oxygen does not react readily with most reduced gases at atmospheric pressures and temperatures.

In the early 1900s, reduced atmospheric species were believed to be oxidized by ozone and hydrogen peroxide; today, highly reactive free radical species (present in the atmosphere at levels of 10 ppt per volume of air or less) are recognized as being responsible for a large part of this oxidation. The recognition of the importance of these free radical species has constituted the major scientific breakthrough in tropospheric photochemistry during the past decade.

### *Tropospheric OH Free-Radical Photochemistry*

Because free radicals have an unpaired electron in their outer shell, and thus an affinity for adding a second electron, they can act as strong oxidizers of atmospheric trace gases. Of the free radicals present in the atmosphere, OH, the hydroxyl species, appears to be the most pivotal in tropospheric chemistry. The chemical mechanism responsible for the presence of hydroxyl radicals in the troposphere was first proposed by Levy (1971) and further refined by Crutzen (1973), McConnell *et al.* (1971), and Wofsy *et al.* (1972).

As illustrated in Figure 2, the production of hydroxyl radicals is initiated by the photolysis of ozone. Ozone, present in the troposphere at concentrations ranging from 10 to 100 ppbv, has a bond energy of 26 kcal/mole. Solar photons having wavelengths between 315 and 1200 nm can dissociate ozone and produce an oxygen atom in its ground electronic state:



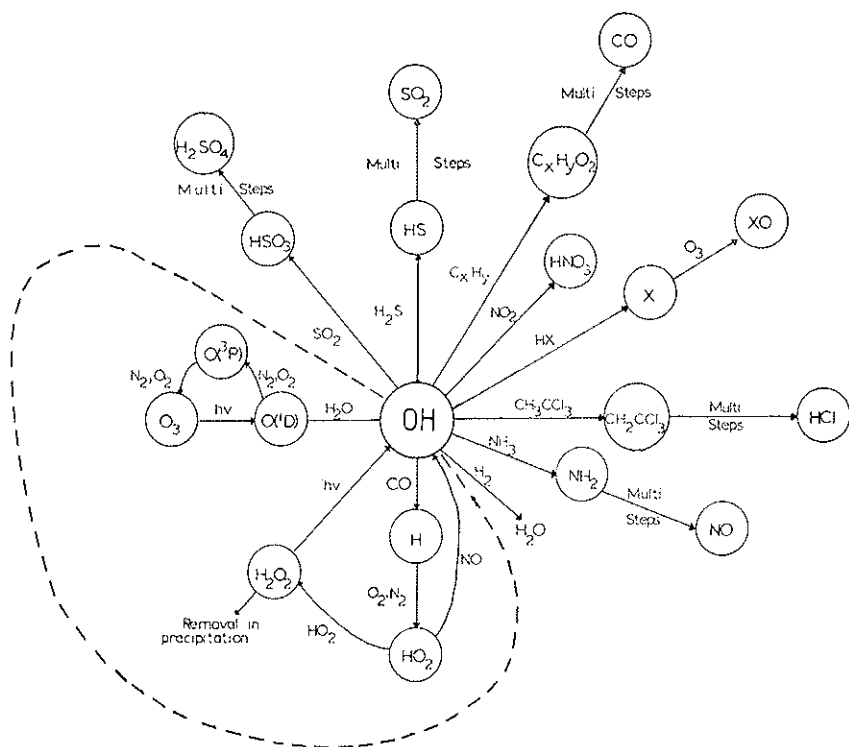
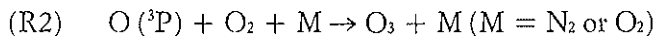


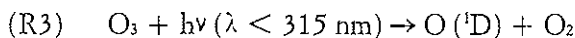
FIG. 2. The photochemistry of tropospheric OH. The reactions inside the dotted line play a major role in determining the concentration of OH.

The  $O(^3P)$  atom rapidly reforms ozone by combining with  $O_2$  in a three-body reaction:



Thus, the sequence of these two reactions is a null cycle with no net chemical effect.

When ozone absorbs a photon in the near-ultraviolet with a wavelength shorter than 315 nm, an electronically excited oxygen atom is produced:

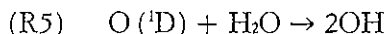


The  $O(^1D) \rightarrow O(^3P)$  transition is forbidden and therefore  $O(^1D)$  has a

relatively long radiative lifetime of 110 seconds. In the lower atmosphere, rather than relax radiatively,  $O(^1D)$  most often collides with nitrogen or oxygen molecules:



This ultimately leads to the regeneration of ozone by the three-body reaction (R2), resulting in another null cycle. Occasionally, however,  $O(^1D)$  collides with water to generate two hydroxyl radicals:

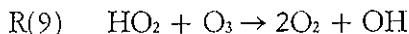


This reaction sequence is the primary source of tropospheric hydroxyl radicals.

The removal of hydroxyl from the atmosphere occurs most frequently as a result of reactions with carbon monoxide or methane:



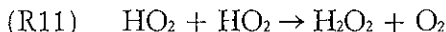
However, several complications arise in hydroxyl chemistry when one considers the ultimate fate of the hydrogen and methyl radicals formed in these two reactions. Both radicals combine rapidly with molecular oxygen to form hydroperoxyl radicals (i.e.  $HO_2$  and  $CH_3O_2$ ). But the hydroperoxyl radical can regenerate OH:



It also can lead to chain termination via the reactions



or



followed by the removal of hydrogen peroxide in rain.

The chemistry of the methylperoxyl radical ( $CH_3O_2$ ) and its products is quite complicated and the kinetics of many of the reactions still are quite tentative. A likely scheme for the degradation of  $CH_3O_2$  is presented

in Figure 3. The major features of this scheme are the production of  $\text{H}_2\text{CO}$ , then  $\text{CO}$ , and ultimately  $\text{CO}_2$  and the conversion of  $\text{OH}$  radicals to  $\text{HO}_2$  radicals in the process of oxidizing  $\text{CH}_3\text{O}_2$  to  $\text{CO}$ . As we shall see later, this production of  $\text{HO}_2$  plays a major role in the photochemistry of tropospheric ozone.

An order of magnitude estimate of the  $\text{OH}$  concentration in the remote troposphere may be obtained by considering  $\text{OH}$  to be in a photochemical equilibrium established by reactions (R3), (R4), (R5), (R6), (R7) and that no regeneration of  $\text{OH}$  from  $\text{HO}_2$  occurs. Under these assumptions,

$$n(\text{OH}) = 2F \frac{n(\text{O}_3) J_3}{n(\text{CO}) k_6 + n(\text{CH}_4) k_7} \quad (1)$$

where

$$F = \frac{n(\text{H}_2\text{O}) k_5}{n(\text{H}_2\text{O}) k_5 + n(\text{M}) k_4} \quad (2)$$

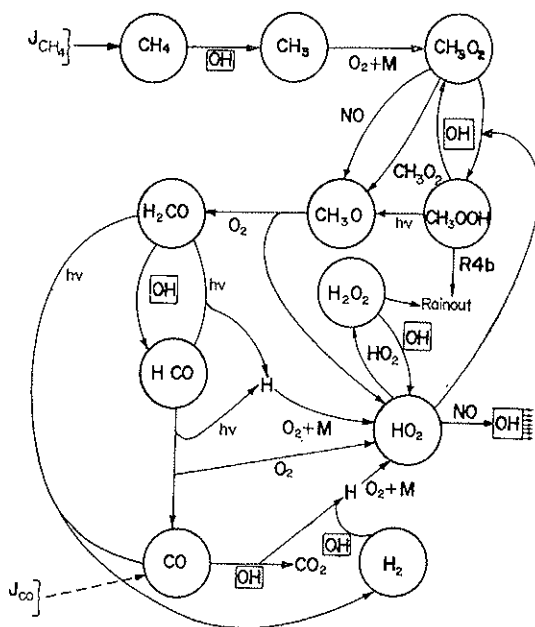


FIG. 3. A tentative scheme for methane oxidation reaction sequence.  $J_{\text{CH}_4}$  and  $J_{\text{CO}_3}$  represent non-photochemical sources of  $\text{CH}_4$  and  $\text{CO}$ .

is the fraction of O ( $^1\text{D}$ ) atoms which form OH,  $n(X)$  is the number density of the species X and  $J_m$  and  $k_m$  are the photolysis frequency and rate constant of the  $m^{\text{th}}$  reaction. Adopting the parameters listed in Table 2, which are appropriate for the remote marine troposphere, Eqn. (1) predicts a diurnally averaged OH level of about  $0.8 \times 10^6$  molecules  $\text{cm}^{-3}$ .

While Eqn. (1) predicts OH levels in the remote troposphere in reasonably good agreement with the predictions of more elaborate photochemical models which properly treat the  $\text{HO}_2/\text{OH}$  coupling, for conditions appropriate for less remote regions where enhanced  $\text{NO}_x$  levels are commonly encountered Eqn. (1) does not accurately calculate the OH concentrations. This is because as  $\text{NO}_x$  levels increase, a greater fraction of the  $\text{HO}_2$  radicals produced from the methane oxidation reaction sequence react with NO via (R8) to regenerate OH. Thus as illustrated in Figure 4, the levels of OH calculated in a complete photochemical model increase substantially as  $\text{NO}_x$  levels increase from the pptv level (typical of remote marine conditions) to the more polluted ppbv level. For  $\text{NO}_x$  levels in

TABLE 2 - *Parameters Used for Order-of-Magnitude Estimate of OH Levels in Remote Troposphere.*

| A. CONCENTRATIONS  |   |
|--|---|
| <i>Species</i>   | <i>Number Density, n (molecular <math>\text{cm}^{-3}</math>)</i>              |
| $\text{O}_3$   | $7 \times 10^{11}$  |
| CO   | $3 \times 10^{12}$  |
| $\text{CH}_4$  | $4 \times 10^{13}$  |
| $\text{H}_2\text{O}$   | $4.5 \times 10^{17}$  |
| $\text{M} = \text{N}_2 + \text{O}_2$   | $2.5 \times 10^{19}$  |
| B. RATE CONSTANT (for $T = 290^\circ \text{K}$ )                               |   |
| <i>Reactions</i>   | <i>Constant</i>   |
| (R3) $\text{O}_3 + h\nu \rightarrow \text{O}(\text{D}) + \text{O}_2$           | $J_3 = 4.5 \times 10^{-6} \text{ s}^{-1}$ (diurnal average)                   |
| (R4) $\text{O}(\text{D}) + \text{M} \rightarrow \text{O}(\text{P}) + \text{M}$ | $k_4 = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| (R5) $\text{O}(\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$          | $k_5 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| (R6) $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$                | $k_6 = 2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |
| (R7) $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$    | $k_7 = 6.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ |

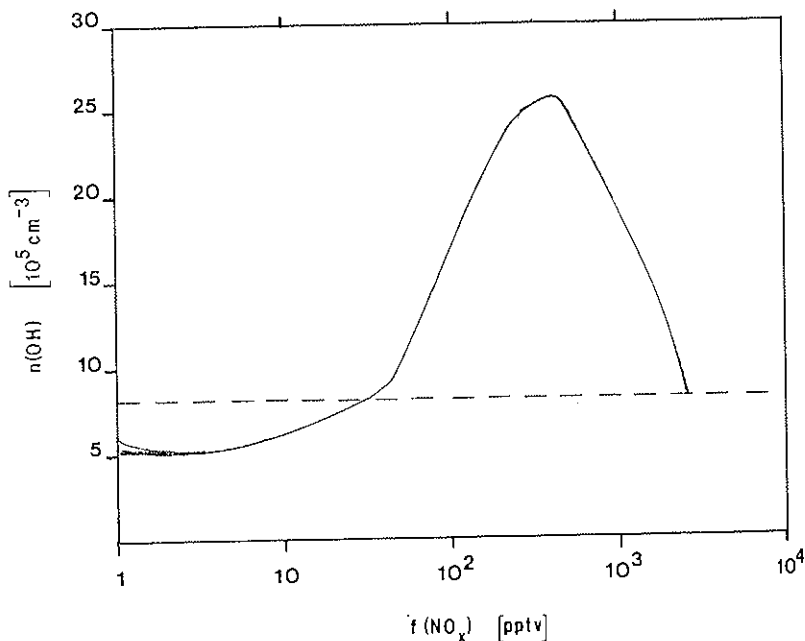
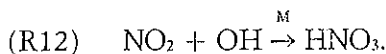


FIG. 4. Calculated diurnally averaged OH concentrations as a function of the assumed  $\text{NO}_x$  mixing ratio,  $f(\text{NO}_x)$ . The broken line is the OH concentration predicted from Eqn. (1) and the solid line is the concentration obtained from a complete photochemical model.

excess of a ppbv, however, OH is calculated to decrease as  $\text{NO}_x$  increases due to the growing importance of an alternate OH loss pathway.



Thus we find that in addition to  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CH}_4$ ,  $\text{NO}$  can play a major role in determining the concentration of tropospheric OH.

Figure 5 illustrates the OH levels calculated by a 2-dimensional diagnostic, photochemical model in which the observed levels of species such as  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{NO}_x$  were specified and the OH concentration was determined assuming photochemical equilibrium. The salient features of this predicted distribution are: 1) diurnally and seasonally averaged OH levels of the order of  $10^5$ - $10^6$  molecular  $\text{cm}^{-3}$ ; and 2) the highest OH levels are found in the tropics where high humidity and a large  $\text{O}(^1\text{D})$ -producing actinic flux cause a large rate of OH primary production.

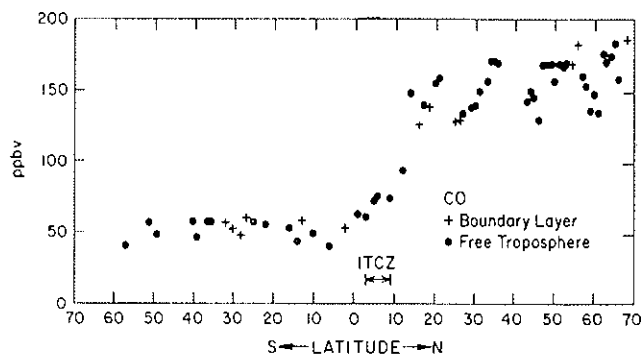


FIG. 5. Model calculated, diurnally and seasonally averaged OH concentrations as a function of altitude and latitude. The globally averaged OH concentration is predicted to be  $7 \times 10^5$  molecular  $\text{cm}^{-3}$ .

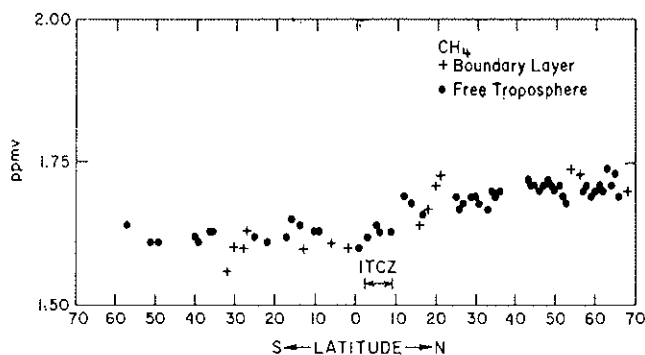


FIG. 6. Concentrations of atmospheric CO and  $\text{CH}_4$  observed by Heidt *et al.* (1980) during Project GAMETAG.

Model-predicted OH levels of the order of  $10^5$  to  $10^6$  molecules  $\text{cm}^{-3}$  in conjunction with laboratory data demonstrating the highly reactive nature of this radical (cf. Demore *et al.*, 1982) imply that OH controls the rate at which a large number of other atmospheric species are oxidized and removed from the atmosphere. Specifically, OH is believed to initiate the oxidation of  $\text{CH}_4$ , CO, non-methane hydrocarbons ( $\text{C}_x\text{H}_y$ ),  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ , and a variety of halogenated hydrocarbons (see Figure 2). It is for this reason that OH is currently viewed as the pivotal species in controlling the atmospheric component of the biogeochemical cycling of the elements. However, until model-predicted levels of OH are confirmed by direct atmospheric measurements the above conclusions must remain tentative.

Thus far, two approaches have been taken to verify the accuracy of the photochemical theory. One involves a direct comparison of measured OH levels with those predicted by a photochemical model. For this comparison to be meaningful, all parameters used in the model to calculate OH must be measured simultaneously with OH. These parameters include temperature and solar flux, as well as the concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_3$ , CO,  $\text{CH}_4$ , and NO. Unfortunately, performing this experiment has proved to be quite difficult. At this time, several of the above species either have not been measured at all, or, if they have been measured, serious questions remain about the accuracy of the measurements.

The measurement of OH itself has presented a major challenge to atmospheric chemists. Even though measurements have been reported in the literature that tend to be in qualitative agreement with model calculations, the accuracy of the data continues to be the subject of much scientific debate. Currently, at least seven independent groups in the U.S. and Europe are addressing this problem. Thus, direct comparison of measured OH levels with model-predicted values continues to be one of the challenging frontiers of global tropospheric chemistry.

An alternate, indirect test of OH photochemical theory, originally proposed by Singh (1977) involves the global distribution of methylchloroform ( $\text{CH}_3\text{CCl}_3$ ). This chemical currently is used as a cleaning and degreasing agent; its release into the troposphere is believed to be its only atmospheric source. Since methylchloroform is removed from the atmosphere by reaction with hydroxyl radicals, the concentration of hydroxyl determines its lifetime. Using the history of methylchloroform emissions and its present atmospheric distribution and abundance, it is possible to infer



its lifetime. This lifetime then can be compared to the lifetime obtained from model-calculated OH levels in the atmosphere. At present, the lifetime estimates from both methods agree within a factor of two or less. Model-calculated OH levels imply a  $\text{CH}_2\text{CCl}_3$  lifetime of about 5-8 years (Chameides and Tan, 1981; Logan *et al.*, 1981); note that the profile illustrated in Figure 5 yields a lifetime of 8 years. This lifetime agrees quite well with the values inferred from observational data by Singh (1977) and Rowland *et al.*, (1980) although it is somewhat smaller than the 11 year lifetime estimated by Prinn *et al.* (1983) from data gathered in the Atmospheric Lifetime Experiment. Thus it appears that free radical photochemical theory is at least qualitatively correct. However, large uncertainties are associated with both estimates and this qualitative agreement still could prove fortuitous.

Because tropospheric OH is photochemically controlled, a complete understanding of OH requires an understanding of the processes which control the distributions of the species which influence the OH photochemical equilibrium. Of these species the most important are  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ , CO, and  $\text{NO}_x$ . The levels of atmospheric  $\text{H}_2\text{O}$  are largely controlled by the processes of evaporation and condensation and are not discussed here; brief discussions of the atmospheric cycles of the other species are presented below.

### *Atmospheric $\text{CH}_4$ and CO*

The central role of hydroxyl radicals in atmospheric chemistry is well illustrated by examining the atmospheric cycles of methane and carbon monoxide. A quantitative assessment of both of these species was carried out in the 1920s in Belgium by Marcell Migeotte, who detected their absorption lines in the spectrum of infrared solar radiation reaching Earth's surface.

The major sources of atmospheric methane are biogenic. They include the anaerobic fermentation of organic material in swamps, tropical rain forests, paddies, and in the digestive systems of livestock as well as termites (Ehhalt, 1974; Zimmerman *et al.*, 1982). It is interesting to note that while virtually all the  $\text{CH}_4$  emitted to the atmosphere is biogenically produced, man's activities influence a large fraction of the production — specifically that produced by enteric fermentation in livestock and  $\text{CH}_4$

production in cultivated rice paddy fields. The major loss or sink process for  $\text{CH}_4$  is (R7), its reaction with OH. Calculations indicate that  $(200-300) \times 10^{12}$  g C as  $\text{CH}_4$  are cycled through the atmosphere in this manner.

Of the  $(200-300) \times 10^{12}$  g of C as  $\text{CH}_4$  oxidized annually by OH approximately  $(150-200) \times 10^{12}$  g C are converted to CO via the sequence of reactions illustrated in Figure 3. The remaining  $(50-100) \times 10^{12}$  g C are heterogeneously removed each year from the atmosphere via rainout and washout of  $\text{CH}_3\text{OOH}$  and  $\text{H}_2\text{CO}$ . In addition to the source from methane oxidation, carbon monoxide is produced from OH-initiated oxidation of non-methane hydrocarbons, incomplete combustion (principally automotive) of fossil fuels, and the burning of biomass, such as wood, agricultural wastes, and forests. A recent analysis of the carbon monoxide budget suggests that of the total CO source strength of about  $(600-1500) \times 10^{12}$  g C as CO produced annually, the burning of fossil fuels and biomass accounts for about 25-50% of the total (Logan *et al.*, 1981). As with methane the major sink for carbon monoxide is reaction with hydroxyl radicals.

It is interesting to note that the sources of both methane and carbon monoxide are mostly continental rather than oceanic. Because most of the world's land mass is in the northern hemisphere, the largest sources of both compounds are there. One might expect, therefore, to find an inter-hemispheric asymmetry for both methane and carbon monoxide. However, as can be seen in Figure 6, whereas considerably more carbon monoxide is found in the northern hemisphere, methane has a nearly constant mixing ratio of 1.65 ppmv with only a slight change in abundance across the ITCZ near the equator.

Differences in the latitudinal distributions of methane and carbon monoxide result from their respective atmospheric lifetimes. Based on the globally averaged hydroxyl radical concentration of about  $7 \times 10^5$  per cc and the appropriate rate constant, the atmospheric lifetime of methane is estimated to be about seven years and that of carbon monoxide about 65 days. Because long-lived species tend to be mixed uniformly throughout the troposphere by the winds, the uniform distribution of methane is consistent with its long lifetime. The lifetime of carbon monoxide is sufficiently short to prevent it from being mixed thoroughly throughout the troposphere. As a result, its distribution more closely resembles the distribution of its sources.

## Atmospheric Nitrogen Oxides

The principal reactive nitrogen oxide species found in the lower troposphere are NO, NO<sub>2</sub>, and HNO<sub>3</sub>, with nitric acid being more abundant by a factor of 2-10 in the remote troposphere. As illustrated in Figure 7, these three species are coupled chemically by a series of reactions that act to cycle them among each other. As with CO, large quantities of NO are produced as a by-product of burning fossil fuels and wood. Logan (1983) estimates, for instance, that fossil fuel burning produces about  $20 \times 10^{12}$  gN as NO yr<sup>-1</sup> and biomass burning another  $12 \times 10^{12}$  gN as NO yr<sup>-1</sup> out of total global NO source strength of about  $43 \times 10^{12}$  gN as NO yr<sup>-1</sup>. However, while measurements of tropospheric NO, NO<sub>2</sub>, and HNO<sub>3</sub>, are quite sparse, those that are available indicate that the distribution of nitrogen oxides is not so strongly affected by man-made urban sources as that of CO. The reason for this apparent difference is the relatively rapid rate at which nitrogen oxides are removed from the atmosphere. After being emitted into the atmosphere, NO is converted rapidly to NO<sub>2</sub> by reaction with ozone; NO<sub>2</sub> reacts with the critically important OH radical to form nitric acid. And nitric acid, which is highly soluble, is removed by such heterogeneous processes as dissolution in rain, attachment to aerosols and suspended particulates, and dry desposition on Earth's surface. In the lower troposphere, this process leads to a net nitrogen oxide lifetime of only a few days to a week — much shorter than that of CO. Thus, although NO and NO<sub>2</sub> may reach levels of 500 ppbv in urban centers and levels of

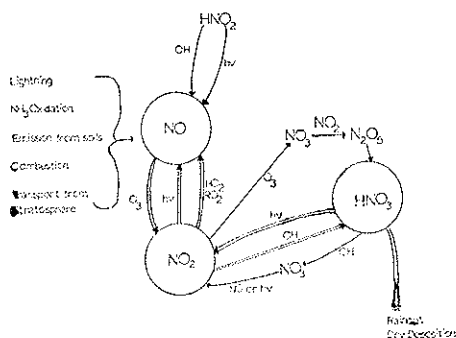


FIG. 7. The photochemistry of reactive nitrogen oxide species. Double-lined arrows represent primary reactive pathways and single-lined arrows represent secondary reactive pathways.

1 ppbv in much of the continental U.S., their removal is so rapid that little is transported to remote regions. For instance, observations by McFarland *et al.* (1979) indicate that NO levels in the remote Pacific are in the 1-20 pptv range.

It therefore appears that remote levels of tropospheric nitrogen oxides are dominated by natural rather than anthropogenic sources; these sources include the generation of NO by lightning, the direct release of NO and NO<sub>2</sub> from soils and marine waters, the OH oxidation of biogenically produced NH<sub>3</sub>, and the downward transport of stratospherically-produced nitrogen oxides. Of these, the lightning source, estimated to produce about  $4 \times 10^{12}$  gN yr<sup>-1</sup> by Barucki and Chameides (1983), looks to be quite significant. The stratospheric source which produces only about  $0.3 \times 10^{12}$  gN yr<sup>-1</sup> could be important in the mid and upper-troposphere (Kley *et al.*, 1981). The nitrogen oxide sources from soil emissions and NH<sub>3</sub> oxidation are still highly uncertain but the possibility that they contribute significantly to the nitrogen oxide budget cannot be ruled out.

### *Tropospheric Ozone*

Ozone is of major interest to tropospheric chemists for two reasons: It leads to the production of hydroxyl radicals, and it is a greenhouse gas. For many years, tropospheric ozone was believed to be chemically inert. Scientists held that the ozone present in the troposphere was formed initially in the stratosphere — where ultraviolet radiation is of high enough energy to dissociate oxygen — and mixed down into the troposphere. It was postulated further that ozone was removed from the atmosphere primarily by reacting with Earth's surface.

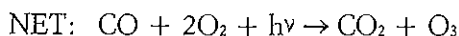
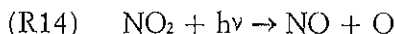
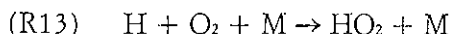
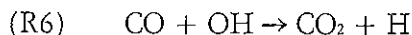
Several investigators have shown that several aspects of the global ozone distribution support this "*transport theory*" (c.f. Junge, 1962; Danielsen and Mohnen, 1977; Fabian and Pruchniewicz, 1977; Routhier and Davis, 1980). For one thing, tropospheric ozone concentrations increase with altitude, presumably indicating a stratospheric source. Positive correlations between ozone and species of stratospheric origin, such as the radionuclide <sup>7</sup>Be, also have been pointed to as evidence in support of the transport theory. Similarly, numerous observations showing that levels of tropospheric ozone above 1 km frequently are correlated negatively with water strongly suggest a stratospheric source for ozone.

However, growing awareness in the early 1970s that free radicals are

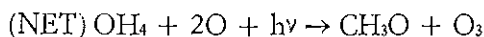
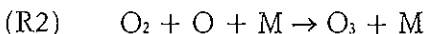
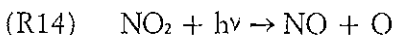
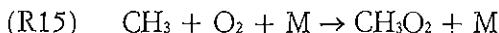
a ubiquitous component of the atmosphere led researchers to realize that ozone, rather than being chemically inert, is produced and destroyed by tropospheric photochemical processes and that these chemical processes could play a major role in the overall tropospheric ozone budget (Crutzen, 1973; Chameides and Walker, 1973).

In fact, evidence gathered by Seiler and Fishman (1981), appears to support the hypothesis that ozone can be produced photochemically in the remote troposphere. They found, for instance, that in several cases measurements in the free troposphere (the region above 1 km) show concentrations of ozone that are correlated positively with levels of carbon monoxide, a photochemical precursor of ozone.

The primary photochemical loss process for  $O_3$  arises from the sequence of reactions which produces OH, i.e. (R3) and (R5). Tropospheric ozone generation by photochemistry can arise from the oxidation CO and hydrocarbons via reaction sequences such as



and



Model calculations indicate that these photochemical sources and sinks for tropospheric  $O_3$  are quite large compared to downward transport from the stratosphere and loss at earth's surface. While about  $7 \times 10^{10}$   $O_3$  molecular  $cm^{-2} s^{-1}$  are transported across the tropopause (Mahlman *et al.*, 1980) and about  $8 \times 10^{10}$  molecular  $cm^{-2} s^{-1}$  are lost at the earth's surface,  $O_3$  is calculated to be produced photochemically at an average rate of  $1.6 \times 10^{11}$  molecular  $cm^{-2} s^{-1}$  and destroyed photochemically at a rate of  $1.5 \times 10^{11}$  molecular  $cm^{-2} s^{-1}$ .

While  $O_3$  is not directly affected by anthropogenic emissions, note that as emissions of hydrocarbons  $CH_4$ ,  $O$ , and  $NO_x$  increase they tend to enhance the rate of  $O_3$  production and could eventually enhance tropospheric  $O_3$  levels on a global scale as they already have on a local and regional scale. In fact Fishman *et al.* (1979) have argued on the basis of the observed asymmetry between northern and southern hemispheric ozone that  $CO$  and  $NO_x$  emissions primarily from fossil fuel burning have already led to an increase in  $O_3$  levels in much of the northern hemisphere.

That enhanced  $NO_x$  emissions could significantly affect  $O_3$  in the troposphere is illustrated in Figure 8. The  $O_3$  concentrations shown in Figure 8 were calculated with a one-dimensional, photochemical, eddy diffusion model for a "Low- $NO_x$  Case" and a "High- $NO_x$  Case". In the "Low- $NO_x$  Case", a vertically distributed lightning source of  $1.2 \times 10^9$   $cm^{-2} s^{-1}$ , a stratospheric  $HNO_3$  source of  $3 \times 10^8$   $cm^{-2} s^{-1}$ , and a small surface source of  $2.5 \times 10^8$   $cm^{-2} s^{-1}$ , were found to lead to surface  $NO_x$  mixing ratio of 25 pptv, the levels typically observed in the remote Pacific Ocean. In the "High- $NO_x$  Case", an additional anthropogenic  $NO_x$  surface source of  $2.5 \times 10^9$   $cm^{-2} s^{-1}$ , was included and this resulted in a surface  $NO_x$  mixing ratio of 100 pptv, a level more typical of rural North America, Europe and the north Atlantic. As illustrated in Figure 8, the enhanced  $NO_x$  levels in the "High- $NO_x$  Case" led to an approximate 30% rise in the calculated  $O_3$  levels in the lower and mid-troposphere.

### *Long-Term Variations in Tropospheric Composition*

Because of the central role of  $OH$  in tropospheric chemistry any variation in the concentration of  $OH$  in the troposphere is cause for concern. A change in  $OH$  levels would probably lead to changes in the concentration of a variety of greenhouse gases thereby causing a perturbation in the climate. The rates of formation of acids and atmospheric oxidants would

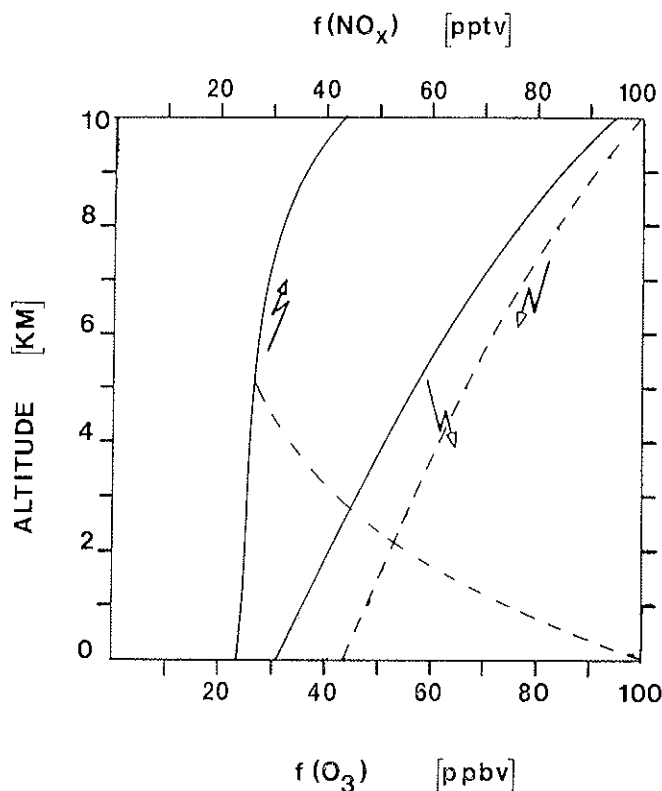


FIG. 8. The calculated  $\text{NO}_x$  and  $\text{O}_3$  mixing ratios,  $f$ , as a function of altitude for the "Low- $\text{NO}_x$  Case" (solid line) and "High- $\text{NO}_x$  Case" (broken line).

also change. Furthermore the rate of injection into the stratosphere of compounds such as  $\text{CH}_3\text{Cl}$ , which affect the levels of stratospheric ozone, would also be perturbed.

In fact evidence is beginning to mount that just such a perturbation in OH levels may have already occurred over the past few centuries and is continuing today. The fact that anthropogenic activities — through ever-rising cultivation of rice paddy fields, maintenance of livestock herds, and emissions of CO and  $\text{NO}_x$  from fossil fuel burning — have apparently begun to significantly rival the natural rates at which atmospheric  $\text{CH}_4$ , CO,  $\text{NO}_x$ , and  $\text{O}_3$  are produced would cause one to speculate that the levels of these species may be increasing and this in turn would imply a variation in OH as well.

Much stronger evidence suggesting that a significant perturbation in tropospheric chemistry has occurred has been uncovered in the record of  $\text{CH}_4$  levels in the atmosphere. In the past few year several investigators have reported that atmospheric  $\text{CH}_4$  levels are currently increasing at a rate of about 0.5-2% per year since at least 1965 (c.f. Rasmussen and Khalil, 1981; Ehhalt *et al.*, 1983; Blake *et al.*, 1982; Graedel and McRae, 1980). In an attempt to determine if this  $\text{CH}_4$  increase is a short-term fluctuation or part of a long-term trend, Craig and Chou (1982) analyzed air samples from polar ice cores which were trapped in polar ice far back as 27,000 BP. Their results shown in Figure 9 indicate that  $\text{CH}_4$  remained fairly constant from 27,000 BP to 1580 AD at 0.7 ppmv (parts per million by volume) — about half the present values of 1.65 ppmv. In 1580 methane levels began to rise, first at a rate of about 0.114 ppmv per century and then, from 1915, much more rapidly, at a rate of 2.5 ppmv

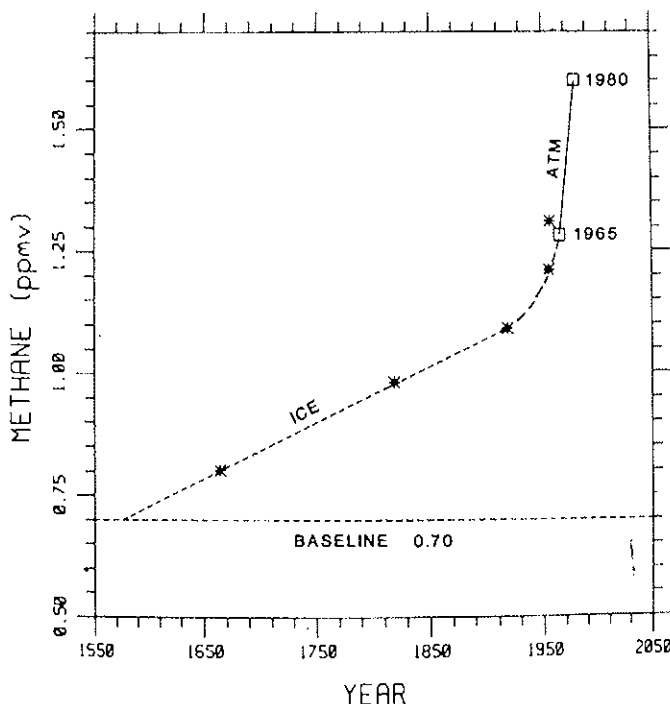


FIG. 9. The temporal variation in atmospheric  $\text{CH}_4$  as deduced from analysis of air bubbles trapped in polar ice cores (stars) and analysis of air samples (squares). After Craig and Chou (1983).



per century, roughly equivalent to the rate of 1.7 per cent per year inferred from present day measurements. Should the findings of Craig and Chou prove to be valid then their findings may have significant implications. An increase in methane from 0.7 ppmv to its present value of 1.66 ppmv is estimated to have caused an increase in global temperature of about 0.23°C due to the atmospheric greenhouse effect (Wang *et al.*, 1976). The temperature rise is roughly 38% of the increase calculated to have occurred as a result of the CO<sub>2</sub> increase. Furthermore, since methane interacts with OH the increase in CH<sub>4</sub> may have caused changes in the levels of OH and the myriad of species affected by OH.

There are two processes that could have led to a doubling in CH<sub>4</sub> over the past 400 years. The increasing CH<sub>4</sub> concentrations could be due to increasing biogenic production rates of CH<sub>4</sub>. It is known, for instance, that as the world's population demand for food has grown over the past centuries, the population of livestock and the total area of the world under rice paddy cultivation has also grown, implying a corresponding increase in methane production (Ehhalt, 1974). Alternatively increasing emissions of CO from wood and fossil fuel burning could have caused a decrease in OH and a corresponding increase in CH<sub>4</sub> (Sze, 1977; Chameides *et al.*, 1977). In the latter case, the effect of increased CO would be off-set to some extent by enhanced NO<sub>x</sub> emissions which would tend to increase OH (Liu, 1977).

What is the magnitude of the increase in CH<sub>4</sub> and/or CO emission rates that would be required to cause a doubling in the atmospheric CH<sub>4</sub> concentration? What does this change in CH<sub>4</sub> imply about the concentrations of OH and O<sub>3</sub>? These questions have been explored with the one-dimensional, photochemical model described earlier. For the "Low-NO<sub>x</sub> Case" and the "High-NO<sub>x</sub> Case" each, four model runs were carried out (i.e. Model O, Model A, Model B, Model C) as well as one additional model run (Model D) for the "High-NO<sub>x</sub> Case". Model O corresponds to present-day conditions (i.e.  $f(\text{CH}_4) = 1.65 \text{ ppmv}$ ) and was used to calculate the appropriate present-day OH and O<sub>3</sub> concentrations and the fluxes needed to support the observed levels of CH<sub>4</sub>, CO, and NO<sub>x</sub>. In the remaining model runs, we project back to the 16th century and assume CH<sub>4</sub> to have a concentration of half its present-day value. In Model A, the concentrations of CO and NO<sub>x</sub> were held fixed at their Model O values preventing any feedbacks between the CH<sub>4</sub>-H<sub>x</sub>O<sub>y</sub> and CO-H<sub>x</sub>O<sub>y</sub> or NO<sub>x</sub>-H<sub>x</sub>O<sub>y</sub> reactive systems. In Model B, these feedbacks are allowed to occur, as the fluxes of CO and NO<sub>x</sub> were held fixed but the levels of CO and NO<sub>x</sub> were allowed

to vary. Model C was like Model B but the CO surface flux was reduced by 1/3, the approximate fraction of the present-day CO emission rate estimated to be due to anthropogenic activities. In model D, run only for the "High-NO<sub>x</sub> Case", in addition to reducing the CO surface flux by 1/3, the NO<sub>x</sub> surface flux was reduced to the NO<sub>x</sub> surface flux used in the "Low-NO<sub>x</sub> Case". The "Low-NO<sub>x</sub> Case" and "High-NO<sub>x</sub> Case" results were then combined in a "Global Average Case" by taking a weighted average with 70% assigned to the "Low-NO<sub>x</sub> Case" and 30% to the "High-NO<sub>x</sub> Case".

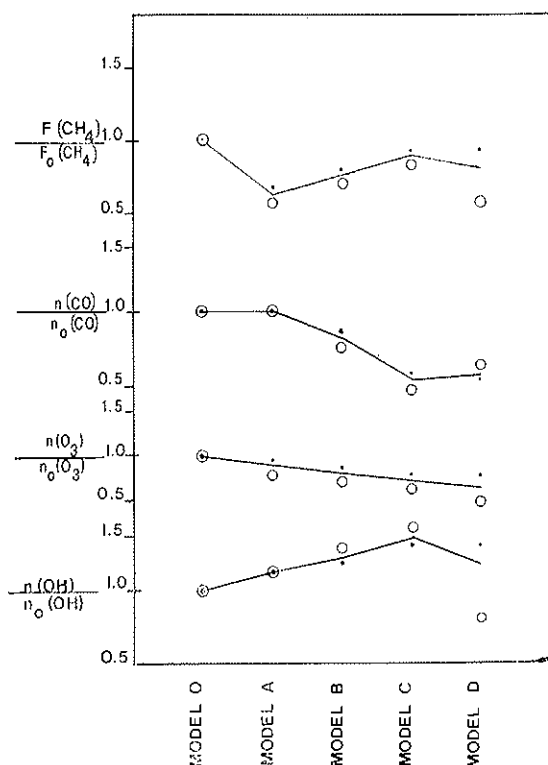


FIG. 10. The calculated relative variations in the CH<sub>4</sub> flux,  $F(\text{CH}_4)$ , and concentrations,  $n$ , at the surface in CO, O<sub>3</sub>, and OH from present-day conditions. Model O corresponds to present-day conditions; in Model A CH<sub>4</sub> is reduced by 1/2 and CO and NO<sub>x</sub> are held fixed; in Model B CH<sub>4</sub> is reduced by 1/2 and CO and NO<sub>x</sub> are allowed to vary; Model C is like Model B but the CO emission rate is reduced by 1/3; Model D is like Model C but the NO<sub>x</sub> emission rate is reduced to the "Low-NO<sub>x</sub> Case" value. The solid points represent the results for the "Low-NO<sub>x</sub> Case", the open circles the results for the "High-NO<sub>x</sub> Case", and the solid line an average of the two.

The results of the calculations are illustrated in Figure 10. We find that the  $\text{CH}_4$ -OH system is non-linear; an increase in  $\text{CH}_4$  leads to a decrease in OH and a further increase in  $\text{CH}_4$ . Thus, significantly less than a doubling in the  $\text{CH}_4$  emission rate is needed to cause a doubling in  $\text{CH}_4$ . If CO and  $\text{NO}_x$  emission rates were constant, the  $\text{CH}_4$  flux would have had to increase by only about 40% to have caused a doubling in  $\text{CH}_4$  according to the model calculations. Allowing for a corresponding increase in CO emissions in this time period, reduced the required increase in  $\text{CH}_4$  emissions to only 25%. However, as the results of Model D show, an increase in  $\text{NO}_x$  emissions as well as that of CO effectively offsets the impact of CO emission increases.

Another important result of our calculations concerns the concentrations of OH and  $\text{O}_3$ . It appears that the lower  $\text{CH}_4$  levels in the 16th century imply higher OH and lower  $\text{O}_3$  concentrations. In the case of OH the variation is predicted to have been quite significant, with about 20-50% more OH in the troposphere in the 16th century as compared to conditions typical of the present-day atmosphere. The change in  $\text{O}_3$  levels is predicted to be more modest — only about 10-15%.

Recognizing that the calculations presented here are based on a highly simplified model of tropospheric processes and that the ice core results of Craig and Chou (1982) have yet to be rigorously confirmed by independent investigators we must be cautious to not over-interpret the results of these calculations. Nevertheless, it does now appear quite possible that the troposphere may have undergone a significant chemical perturbation over the past 400 years and that this perturbation continues today. To better understand the character and magnitude of this perturbation a concerted campaign to elucidate the detailed trace gas composition of the troposphere and its temporal variations over the coming decades is needed.

### *Conclusion*

The tropospheric photochemical system consists of a highly complex chemical scheme in which free radical species and especially OH produced in the presence of solar radiation play a central role. The overall trend of this radical system is to oxidize reduced species emitted from earth's surface and cause their eventual return to the biosphere-lithosphere-hydrosphere in an oxidized valence state. This atmospheric chemical cycle is actually one component of a larger set of cycles. In these larger cycles

the key biological elements — carbon, oxygen, nitrogen, sulfur, and phosphorus — circulate through the biosphere, lithosphere, and oceans, as well as the atmosphere. By circulating these elements continuously, nature recycles and redistributes the chemicals needed to support life on Earth. And thus it is seen that tropospheric chemistry is closely coupled to biospheric processes.

Recent observations indicating that atmospheric  $\text{CH}_4$  is currently increasing and may have been steadily increasing since the 16th century coupled with the fact that anthropogenic activities appear to be a major component in the budgets of tropospheric  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}_x$ , and  $\text{O}_3$ , suggest that the free radical tropospheric system may be undergoing a significant perturbation on a global scale. The implications of such a perturbation have yet to be fully identified.

#### ACKNOWLEDGEMENT

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## DISCUSSION

MARINI-BETTÒLO

Could you give some figures about the CO sink in the soil?

CHAMEIDES

The loss of CO from the atmosphere to soils is roughly one-tenth that of the total CO budget, so it comprises a small fraction of the total. Measurements by Seiler and others show that CO can be emitted as well as absorbed by soils. However the net effect appears to be an uptake of atmospheric CO by soils. Presumably this uptake is being driven by microbial action in the soils.

MALONE

Another question: might it not have been more felicitous if Smith had coined the term "acidic deposition" rather than "acid rain"? What is the aggregate ratio of dry to moist?

CHAMEIDES

That ratio is unfortunately not well-known and it in all likelihood depends on where you are located, the closer you are to a source region generally the larger the dry deposition. My best guess right now is that on average the two processes — wet and dry deposition — are roughly of equal importance for acidic species like nitrates and sulfates. I would therefore have to agree with you that a more proper term for the environmental problem most commonly referred to as "acid rain" would be "acid deposition". It is also interesting to note that acid fog looks to be a potentially serious problem in many locations — this being a hybrid form of wet and dry deposition.

ROWLAND

I will comment briefly on the question Tom Malone just asked. I think the budgets for North America show that a number of the order of 20% of

the  $\text{SO}_2$  going into the atmosphere returns as wet deposition. This leaves 80% some place else. Some of that certainly goes across boundaries out over the ocean as well as across the land boundaries, but the measurements of the dry deposition of the experimental techniques are so far really very much open to question. So that uncertainties of a factor of 3 easily apply there. There was a detailed measurement at Hubbard Brook in New Hampshire, which shows that there the dry deposition was about one-half the wet deposition. But that is a long way from any source, so that probably is sort of the minimum value and the dry deposition close to sources can be probably several times the wet deposition.

WIESENFELD

Two quick questions about aqueous phase oxidation: in addition to oxidation in cloud drops can aqueous phase oxidation in aerosols be important?

CHAMEIDES

Aerosols may be important. The model tabulations I showed for  $\text{SO}_2$  oxidation did not include oxidation in aerosols and I am not aware of any calculations carried out by other investigators on this process. One problem is that such a calculation would be loaded with uncertainties. Nevertheless it is an intriguing possibility. For instance, in the marine environment where you have plenty of sea salt aerosol, whenever the humidity is above 78% those aerosols are wet and the humidity is very often above 78% in the marine boundary layer. When these aerosols are wet it is possible for  $\text{SO}_2$  to be dissolved in the aerosol along with atmospheric oxidants such as  $\text{H}_2\text{O}_2$  or  $\text{NO}_3$  and the  $\text{SO}_2$  can be oxidized to sulfates. Unfortunately because deliquescent aerosols are characterized by extremely high ionic strengths they cannot be treated as an ideal solution and as a result are very difficult to treat theoretically.

WIESENFELD

Can I follow up then with the second question, and that is related to one of your slides, which seemed to imply that it was indeed the free radicals which were undergoing phase transitions from the gas phase to the aqueous phase. There is an unfortunate problem here in nomenclature. People seem to talk about heterogeneous chemistry as occurring in the aqueous phase. In fact it is homogeneous.



CHAMEIDES

You are correct that technically speaking the key reactions occurring in the aqueous phase are homogeneous reactions — meaning aqueous phase homogeneous reactions. If for instance we take the oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$  in cloud droplets: there is the gas phase homogeneous reactions which produce  $\text{H}_2\text{O}_2$ ; there are the heterogeneous reactions involving the dissolution of  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$ ; and there are the aqueous-phase homogeneous reactions by which dissolved  $\text{SO}_2$  or  $\text{S}_{\text{IV}}$  is oxidized by dissolved  $\text{H}_2\text{O}_2$ . In this particular system even though there is a heterogeneous part to the overall reaction, the rate of oxidation is limited in most cases by the homogeneous aqueous-phase reaction.

WIESENFELD

But of course there can also be homogeneous aqueous phase photochemistry of ozone — that is well known.

CHAMEIDES

Yes there are reactions involving dissolved ozone, even photochemical reactions which can produce free radicals. However given the atmospheric abundance of ozone of about 20-40 ppbv and its very low solubility, it can be easily shown that the ozone concentration in cloudwater is low — about  $10^{-10}$  moles per liter — and therefore that homogeneous aqueous-phase ozone reactions have a negligible effect on cloud and precipitation chemistry.

CRUTZEN

In your analysis of methane and CO budget you have methane as one of the driving forces in changing the reactions in the atmosphere. However, there is so much more which has been changing in the biosphere. For instance, we know from our work in Brazil that the forests are sources of carbon monoxide, probably through reactive hydrocarbons as intermediates. And so this has to be folded in. I think for the carbon monoxide budget actually methane is not the main source but other hydrocarbons.

CHAMEIDES

In the calculations I presented here methane does not represent a major

source of carbon monoxide. Just as you stated, the major sources are non-methane hydrocarbon oxidation and anthropogenic production. And in fact if you accept the Craig and Chou measurements, then 400 years ago when methane was roughly one-half as abundant as it is today, methane oxidation had virtually no effect on the CO budget.

CRUTZEN

I think the whole scheme of reactions which is involved here is not yet well defined, especially if you take into account the possibility of heterogeneous reactions. For instance, the chemistry of methyl peroxide is very uncertain and depending on how you treat this species the methane oxidation chain could enhance OH rather than decrease it.

CHAMEIDES

Your point is certainly well taken; there are many aspects of tropospheric chemistry that are uncertain, and that involving methyl peroxide is without doubt a prime example. From my own estimation of how the methane system works in the atmosphere, I believe that a significant fraction of the methyl peroxide is removed by heterogeneous reactions before it has a chance to react. This terminates the chain making methane oxidation a net sink for OH regardless of the details of the chemistry of methyl peroxide and its daughter molecules. Nevertheless we certainly need to be aware of the many uncertainties in this chemistry.

REVELLE

What about methane from the ocean?

CHAMEIDES

That source appears to be quite small. While methane is certainly produced by microbes in oxygen-poor and anaerobic regions of the ocean, in order for the methane to escape to the atmosphere it must first pass through an overlying layer in the ocean with abundant oxygen. Probably the methane is oxidized by aerobic microbes in these layers before it can escape.

REVELLE

Is the atmospheric lifetime of  $\text{CH}_4$  increasing?

CHAMEIDES

There is no definitive answer to that question. All one can do at this point is speculate. If one accepts the measurements indicating that methane is increasing and one folds in the fact that anthropogenic sources of carbon monoxide are also increasing then the possibility that OH levels are decreasing seems to be a plausible conclusion. And if OH levels are decreasing then the methane lifetime is increasing. However one needs to be cautious since increases in the anthropogenic production of NO tend to cause OH to increase. At the present time a model does not exist that can definitively treat this system by folding in all the effects of pollutants on OH in a global context and determine if OH has in fact decreased over time and if so by how much. My own calculations that I have described here with a very simplistic model indicate that globally averaged OH levels have probably decreased and I would therefore speculate that the methane lifetime is probably increasing. But a good deal more work needs to be done in many different areas before this conclusion can be stated with any confidence.

ROWLAND

I think perhaps this is just a technical quibble on your use of homogeneous for the aqueous phase — there is an implication in the word "homogeneous" that the concentration is the same throughout, and it is my impression that when you are dealing with cloud drops, the concentrations are quite variable depending on how far into the drops you are. It is an inhomogeneous reaction in one phase.

CHAMEIDES

That is a good point; there are certainly large chemical inhomogeneities in the cloud system — inhomogeneities from drop to drop as well as within a single drop. For instance for a species like OH in the aqueous phase, the lifetime is about  $10^{-4}$  seconds. So that OH is destroyed chemically before it has a chance to really mix uniformly throughout most cloud drops. Studies of the effect of this non-uniformity have yet to be carried out, although I do

not think it will be overwhelming. Nevertheless the problem of non-uniformity is one that is going to have to be addressed.

#### WANDIGA

If you look at the distribution of CO along the latitudes, you find quite a big difference, which shows that in the southern and the northern and in the tropics there is a difference in the concentration of CO. However methane is uniformly distributed. What do you attribute this to?

#### CHAMEIDES

Because methane is long-lived with a lifetime approaching that of 10 years we would expect it to be fairly uniformly mixed in the troposphere even though its sources are not. CO on the other hand has a lifetime of the order of a month and therefore its distribution more closely reflects its source distribution. In this regard there has been an interesting study recently completed by Pinto et al at the Goddard Institute for Space Studies. They used a three-dimensional general circulation model and tried to reproduce the observed latitudinal distribution of CO. In order to do this they needed three sources: one was a well-distributed source and probably is that which arises from methane oxidation; another was a large northern hemispheric source and likely corresponds to the source from anthropogenic activities; and a third was another large source centered in the tropics. Presumably this tropical source of carbon monoxide is from biomass burning and/or oxidation of non-methane hydrocarbons. The important aspect of this work is that a large tropical source such as the one earlier suggested by Crutzen and co-workers is needed to explain the distribution of carbon monoxide.

# PERTURBATIONS OF THE ATMOSPHERE AND OF THE CLIMATE SYSTEM INDUCED BY VOLCANIC ERUPTIONS: RELEVANCE OF SOME SPECIFIC PROCESSES

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## *Abstract*

Progress in the understanding of those physical and chemical processes which preside over the perturbations induced by volcanic eruptions on the atmosphere, but whose effects may be felt by the entire climatic system, is reviewed in the light of current research related to the aftermath of the El Chichon eruption of 1982.

## *Introduction: Early Attempts to Characterize the System and Successive Developments in Identifying and Parameterizing the Effects of the Main Variables*

Large eruptions provide rare occasions to observe the transient response of the atmosphere to a quantifiable perturbation, whose amplitude and duration may be such that significant effects can be expected also on the other elements of the climate system.

The tenet that volcanic eruptions would affect the climate is neither new (Benjamin Franklin is credited with the original suggestion; for an early statement of the problem see Humphreys, 1940) nor basically disputed, but the state of knowledge was, and perhaps still is, such that the dynamic response of the system could not be reliably predicted.

The 1982 eruptions of the volcano El Chichon have occurred at a

time when the stage of development of climate models and the capability of carrying out measurements of a large number of variables on a global scale suggest that consistent checks of the theory are possible. Also, a great deal will be learned in detail from this concerted effort about interactive, atmospheric processes involving aerosols and their precursors, radiation, dynamics.

It may be of interest to outline relatively recent developments. On the basis of a comprehensive analysis of volcanic chronology since 1500 AD, Lamb (1970) had introduced a criterion, the Dust Veil Index (DVI), for relating empirically the climatic effects to the characteristics of the eruption. The DVI was expressed with three alternative formulae, claimed to be equivalent, each expression being the product of three quantities:

$$\text{DVI} = 0.97 \times R_{\text{Dmax}} \times E_{\text{max}} \times t_{\text{mo}}, \quad (1)$$

$$\text{DVI} = 52.5 \times T_{\text{Dmax}} \times E_{\text{max}} \times t_{\text{mo}}, \quad (2)$$

$$\text{DVI} = 4.4 \times q \times E_{\text{max}} \times t_{\text{mo}}, \quad (3)$$

where  $R_{\text{Dmax}}$  is the greatest percentage of depletion of direct radiation following the eruption,  $E_{\text{max}}$  is a coefficient related to the geographical extent of the veil (whole Earth = 1),  $t_{\text{mo}}$  is the duration in months,  $T_{\text{Dmax}}$  is the estimated lowering of avg. temperature in degrees Celsius over the middle latitude zone of the hemisphere,  $q$  is the estimated value in cubic kilometers of solid matter dispersed as dust in the atmosphere. The coefficients are set up so that for Krakatoa  $\text{DVI} = 1000$ . For El Chichon, assuming  $E_{\text{max}} = 1$ ,  $t_{\text{mo}} = 24$ ,  $q = 3$ , we obtain  $\text{DVI} = 320$ ,  $T_{\text{Dmax}} = 0.25^\circ \text{C}$ , and  $R_{\text{Dmax}} = 13\%$ .

The DVI does not take into account the detailed nature of the process and is based on a fair amount of estimation: it can be argued, for instance, that it is not the total amount of dust that matters, but rather the fraction that reaches the stratosphere, particularly as a sulfur compound, and how that content evolves in time; also, it is not just the change in direct radiation that has an effect, but the redistribution, in the entire spectrum, of the direct and diffuse radiation, etc. The DVI is an approach to identify and relate the relevant and measurable parameters; it gives a useful insight by associating volcanic and climatic chronologies. In the words of the author this is "about as far as one can go towards objectivity in the assessment of past eruptions". In this respect it reflects the state of knowledge on the problem in 1970.

Substantial climatic anomalies have been attributed to the large eruptions of the past, Krakatoa, Tambora, Katmai, etc. On the basis of a statistical analysis, Schneider and Mass (1975) have shown that there is an effect of volcanic dust on long term temperature records. Bryson and Goodman (1980), using available data and a simple model of dispersion and fallout, have made an historical analysis of the role of volcanic eruptions in modulating the direct beam radiation and have found that the resulting time series would explain about 77% of the radiation variance (see also Yamamoto, 1977; Taylor, 1980; Robock, 1981; Rampino *et al.*, 1979). In order to improve the value of estimates of historical volcanism, useful to assess its role on past climatic variations, Newhall and Self (1982) have proposed a composite indicator of the magnitude of past explosive eruptions termed the Volcanic Explosivity Index (VEI). The measured concentration of sulfur in ice cores collected in Greenland and Antarctica is a useful marker of past volcanic activity (Dansgaard and Hammer, 1978; Stothers and Rampino, 1983).

Measurements carried out in connection with the 1963 Mt. Agung eruption provided a data base useful for detailed analyses. Lidars, then in the first stages of development, showed the height-resolved structure and evolution of the stratospheric aerosol layer (Fiocco and Grams, 1964; Grams and Fiocco, 1967). Upper level sounding indicated that, as a consequence of the eruption, the temperature of the tropical lower stratosphere increased by several degrees (Newell, 1970, 1971; McInturff *et al.*, 1971). Tropical tropospheric temperatures decreased by about one-half a degree (Newell and Weare, 1976; Angell and Korshover, 1977); there was a depletion of the solar radiation received at the ground (Burdecki, 1964; Moreno *et al.*, 1965; Flowers and Viebrock, 1965; Volp, 1969) and the surface also appeared to have cooled (Angell and Korshover, 1977), although with some uncertainty due to the large fluctuations of the climatic signal. It is possible that the break in the quasi-biennial oscillation of the atmosphere observed in 1963 was related to the eruption (Sparrow, 1965, 1971; Berson, 1966; Ebdon, 1967; Newell, 1970, a, b). A long-term trend of the stratospheric water vapor concentration in the years following the eruption has also been tentatively associated with it (Mastenbrook, 1971; Newell *et al.*, 1974; Crescentini and Fiocco, 1983).

Hansen *et al.* (1978), with a one-dimensional radiative-convective model, simulated the thermal response of the atmosphere to the increased amount of aerosol at low latitudes. The resulting stratospheric temperature increase, which matches reasonably well the average heating observed, is

due mainly to the assumed stratospheric aerosol properties, but also to the tropospheric temperature, because of the absorption of upwelling infrared radiation; the simulation gave also an indication of tropospheric cooling. It was pointed out that the main limitation of the computation was the lack of an adequate treatment of atmospheric dynamics.

The heating pattern induced in the lower equatorial stratosphere by the Mt. Agung eruption was reproduced in a model calculation and associated to the changes in the albedo of the underlying system, thus providing also a measure of the absorption properties of the aerosols in the visible part of the spectrum (Fiocco *et al.*, 1976, 1977; Mugnai *et al.*, 1978). These authors have also investigated the changes in the photodissociation rates of ozone and other species resulting from the increased levels of the stratospheric diffuse radiation (Fiocco *et al.*, 1978; Petroncelli *et al.*, 1980).

Pollack, Toon, Turco and collaborators have extensively studied the characteristics of aerosols in the context of climate research (Pollack *et al.*, 1976; Toon and Pollack, 1975; Turco *et al.*, 1980, 1982). Relevant contributions in this field have been given by Reck (1974) and by Harshvardan and Cess (1976). Studies related to the nucleation and growth of sulfur stratospheric aerosols have been performed by Friend *et al.* (1980), by Hamill *et al.* (1977), and by Steele and Hamill (1981). Problems related to transport and dynamics of the volcanic clouds have been considered by Danielsen (1968, 1974), Dyer and Hicks (1968) and Cadle *et al.* (1976).

The 1980 eruption of Mount St. Helens was well documented: although the explosive force was large, the mass of sulfur injected into the stratosphere was small and did not cause a significant increase of its optical depth (Newell and Deepak, 1982; Deepak, 1982).

### *On the Microphysics of the Aerosols and Their Radiative and Thermodynamic Role*

A volcanic eruption releases in the atmosphere large quantities of solid and gaseous materials: depending on the explosive nature of the eruption and on the diffusive properties of the medium, a fraction of these materials arrives at stratospheric heights where the lack of water and precipitation as well as the high vertical stability favor substantially longer residence times than in the troposphere. The radiative field is modified by the presence of these constituents; because of the long times involved, the resulting perturbations may become climatologically effective. The



constituents that are of primary concern are the ash and the sulfur-bearing gases.

The ash has a comparatively short lifetime, depending on the relatively large size of the grains, and its radiative effects are dominant in the first few months following the eruption. The sulfur-bearing gases, through a series of imperfectly known reactions, undergo a conversion process which produces a population of aerosol particles consisting mainly of a mixture of sulfuric acid and water. Fine ash and impurities are also included in the mixture and may play a role in determining the nucleating and absorption properties of the particles.

After the initial nucleation phase, the physical and chemical evolution of the aerosol cloud, leading eventually to its disappearance, is dictated, on the long term, by the mechanisms of coagulation and sedimentation and, on the short term, by processes related to its radiative and thermal balance which may determine a variable  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$  ratio.

Coagulation leads slowly and irreversibly to bigger and heavier particles; gain or loss of water through evaporation and condensation may rapidly change their density and radius. In either case the sedimentation velocity is affected. Of particular interest are these adaptive processes in those regions (e.g. the Hadley cell) where the existence of updraughts may essentially sustain the particles for a very long time.

Aerosols are not a passively transported species and cannot be regarded strictly as tracers of motion. If present in large quantities their radiative properties may contribute to the heating and cooling of air to the extent of having a significant effect on atmospheric dynamics. In the 15-20 km region the heating rates attributed to the atmospheric gases are very small and the aerosol contribution may prevail.

The modifications of the radiative field induced by the presence of aerosols, if sufficiently large, may have a detectable effect on the climate system. Aerosols absorb and scatter solar radiation: as a result there is an attenuation of the direct solar field, on whose basis it is generally assumed that the energetic input to the underlying system is reduced.

Since however a large fraction of the scattering is in the forward direction, the depletion of solar radiation reaching the ground is not as large as expected merely on the basis of extinction. In addition the presence of the absorbing aerosol modifies the infrared characteristics of the atmosphere. The net effect depends on the size and refractive index of the particles.

Specific aspects of the problem, related to the individual as well as

to the collective properties of the aerosols, their spatial variation and temporal evolution, can be identified as follows:

- a) the size distribution,
- b) the composition and the complex refractive index,
- c) the radiative field,
- d) the heating rates,
- e) the thermodynamic properties, stability and lifetime of the aerosol layers,
- f) diffusion and transport by large scale atmospheric motions.

### *An Overview of Observational Results Related to the El Chichon Eruptions of 1982*

In 1982 the stratosphere was characterized by a very large increase of the aerosol content, consequence of large injections of volcanic material. At the beginning of the year a volcanic explosion at an as yet uncertain location manifested itself in the so-called mystery cloud (De Luisi, 1982). Subsequently, the eruptions of El Chichon, Mexico (17 N, 93 W), which occurred on 28 March and 3-4 April, have determined what is possibly the most intense stratospheric perturbation of the century, likely to have its effects felt on climatic conditions for a few years.

Several lidar stations detected the initial spreading of the cloud and followed its subsequent evolution. In the northern hemisphere (and in order of both increasing latitude and delay in the time of first arrival of the cloud overhead) these lidars are located in Hawaii (19.5 N: De Luisi *et al.*, 1982), in Japan (33.7 N: Hirono and Shibata, 1982. 35 N: Iwasaka *et al.*, 1983), in Italy (41.8 N: Adriani *et al.*, 1983. 42.3 N: D'Altorio and Visconti, 1983), in Germany (47.5 N: Reiter *et al.*, 1983); in the Southern hemisphere the only reporting station is located in Brazil (23 S: Clemesha and Simonich, 1983). Fig. 1 gives a sequence of the lidar observations in Frascati, Italy.

Airborne lidar observations have secured meridional cross sections of the cloud (McCormick, 1982). Balloon sightings of the El Chichon cloud were obtained (Ackerman and Lippens, 1983) one month after the eruption.

Data from the environmental satellites NOAA-7 and GOES showed that the eruptions had penetrated the tropopause and injected material into the stratosphere. The cloud produced by the April 4 eruption was tracked

by visible band imagery in its westward march, filling the latitude band 10 N to 30 N in about three weeks (Robock and Matson, 1983).

Measurements of the gaseous sulfur dioxide released were obtained with the Total Ozone Mapping Spectrometer (TOMS; Krueger, 1983) and with the Solar Backscatter Ultraviolet Spectrometer (SBUV; Heath *et al.*, 1983), both carried on the Nimbus 7 satellite. Three instruments on board the Solar Mesosphere Explorer (SME) also revealed features of the cloud: the Infrared Radiometer measured the thermal emission from the aerosols, while the Visible and Near Infrared Spectrometers measured the backscattered solar radiation. The three instruments are limb-scanning and view the atmosphere along the track of the sun-synchronous polar orbit (Barth *et al.*, 1983; Thomas *et al.*, 1983). Ground based and airborne spectrophotometric measurements of sulfur dioxide have also been carried out (Evans and Kerr, 1983).

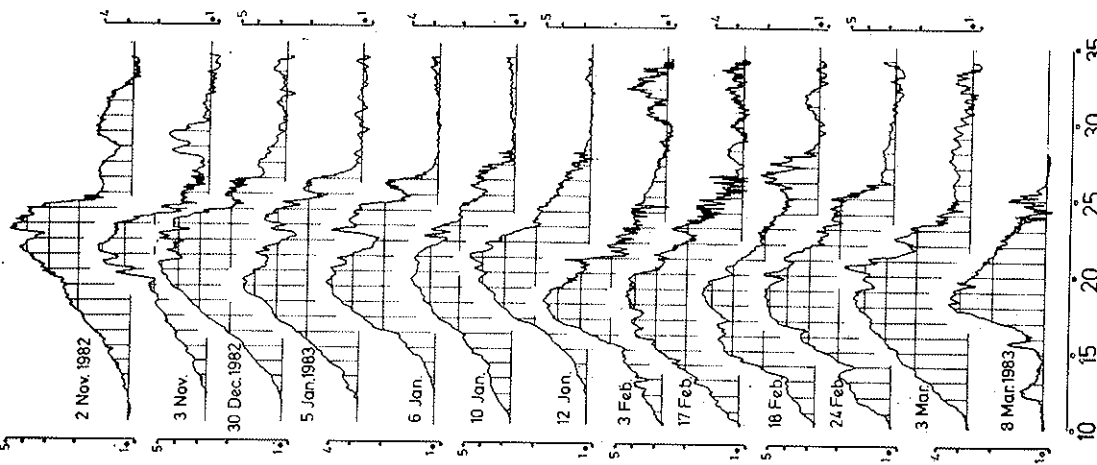
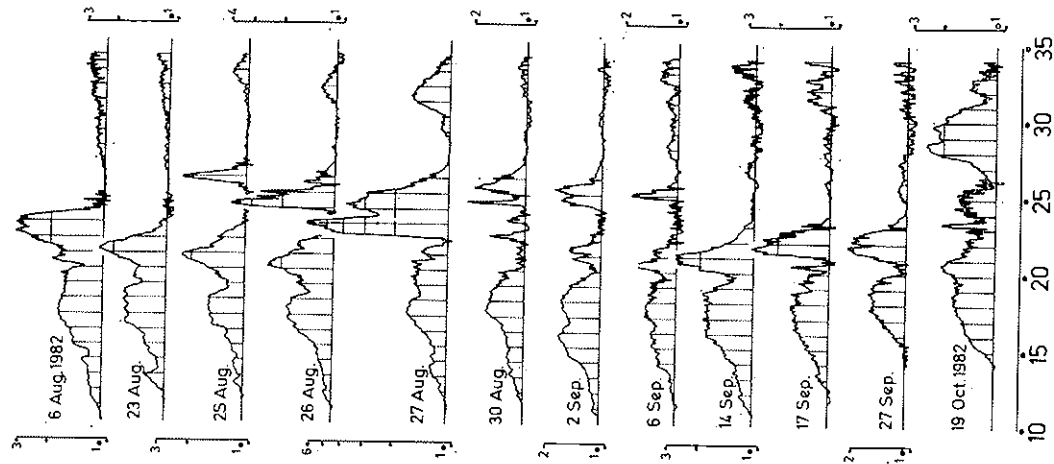
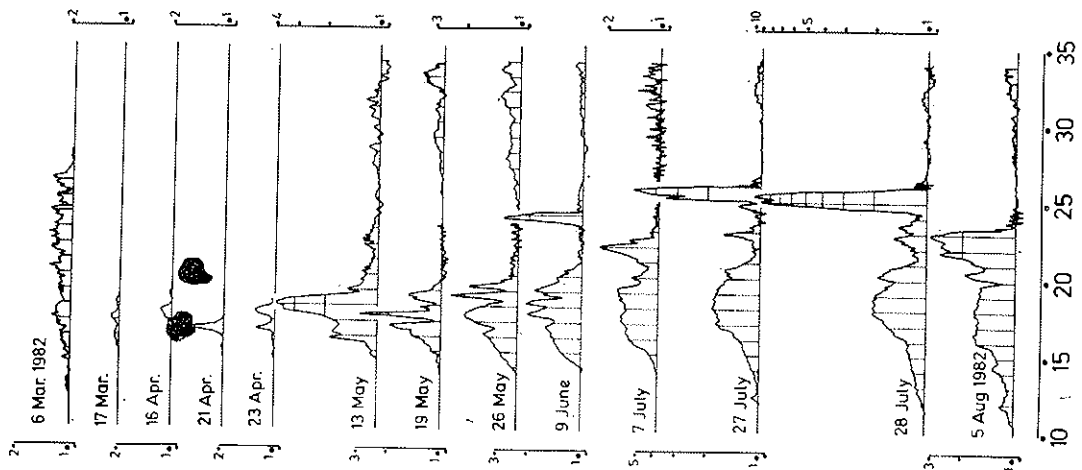
High latitude aerosol observations have been secured by the Stratospheric Aerosol Measurement (SAM II) satellite system: these have shown that the aerosol extinction profiles measured within the northern polar vortex differ significantly above 18 km from those measured outside the vortex (Mc Cormick *et al.*, 1983).

Particle sampling devices have been flown on balloons (Hofmann and Rosen, 1983) and on high-altitude aircraft (Oberbeck *et al.*, 1983; Knollenberg and Huffman, 1983; Wilson *et al.*, 1983; Gooding *et al.*, 1983; Woods and Chuan, 1983).

Stratospheric sulfate and other gases were collected by high altitude aircraft and balloons (Gandrud *et al.*, 1983; Mroz *et al.*, 1983; Vedder *et al.*, 1983). These measurements indicated an injection of about 7.6 Tg of sulfate into the global stratosphere. Ground and airborne extinction measurements were also carried out (Clarke *et al.*, 1983; Coulson, 1983; Dutton and De Luisi, 1983; Spinhirne, 1983; Witteborn *et al.*, 1983) as well as comparisons with Lidar measurements (Swissler *et al.*, 1983). Other reports on the initial phases of this phenomenon and attempts at drawing preliminary conclusions have by now appeared: some will be mentioned in the following section.

### *Some Specific Aspects*

Determining the size distribution and composition of the stratospheric aerosols and their evolution have been among the main questions posed since the discovery of the layer (Junge *et al.*, 1960). The steady state



background is considerably altered in the aftermath of an eruption, and a large change in the aerosol characteristics, relatively fast in the initial phase, occurs over a time interval of a few years.

The inversion of the results for the zonally-averaged infrared extinction, obtained with the SME Infrared Radiometer, has given an indication of the rapidity of the gas-to-particle conversion: the aerosol increased in mass to a maximum of 8 Tg about 15 weeks after the eruption (Thomas *et al.*, 1983).

Different functional expressions have been adopted to fit the available size distribution measurements and provide a base for analytic modeling. Mainly used at present are the log normal and the equivalent zeroth order logarithmic distribution (ZOLD), bell-shaped, monomodal curves characterised by a maximum and a width parameter.

Hofmann and Rosen have investigated the question of size distributions through the use of balloon-borne dust sondes. Data obtained shortly after the eruption showed the difficulty of fitting standard distributions (Hofmann and Rosen, 1983). In a recent study of the temporal evolution of the cloud they obtained log-normal fits, after approx. 200 days with mean radii around  $0.15\ \mu\text{m}$  in the 17-20 km region and around  $0.27\ \mu\text{m}$  in the 20-25 km region, and around  $0.22\ \mu\text{m}$  after approx. 400 days (Hofmann and Rosen, 1984).

Size distributions obtained in the height region from 15 to 20 km by different airborne techniques, 8 to 10 months after the El Chichon eruption, show the tendency of secondary modes with larger particle radii to develop and eventually take over, indicative of the importance of sedimentation at this stage in the evolution of the cloud.

Knollenberg and Huffman (1983), using laser-based size spectrometers, find a large-particle sedimentation mode with modal radius of about  $1.8\ \mu\text{m}$  at 15 km and about  $1.3\ \mu\text{m}$  at 20 km. This fact is in agreement with the assumption that the amount of  $\text{H}_2\text{SO}_4$  in the particles remains relatively constant and that particles at the two heights are characterized by a different dilution. In that case, if particles at 20 km had a 75%  $\text{H}_2\text{SO}_4$  concentration, the concentration at 15 km would be around 30%.

Oberbeck *et al.* (1983), using a wire impactor, also find evidence for bimodality, their large-particle sedimentation mode having a modal radius around  $0.6\ \mu\text{m}$  with a geometric standard deviation of 1.5 at 20.7 km.

In fact it may appear that the recently observed monomodal dis-

tributions lack those properties of symmetry implied by the use of a log-normal distribution function and that on the larger-radii side the slope of the function is sharper: the recognition of this fact has important consequences in calculations of the optical cross section where the large particles weigh a lot more than the smaller ones.

Two-wavelength lidar observations (Gobbi *et al.*, 1984) indicate a change in the ratio of the aerosol cross sections respectively at 1.064  $\mu\text{m}$  and 0.532  $\mu\text{m}$  which can be attributed to the existence of a narrow mode in the size distribution, or, possibly, to marked differences in the imaginary part of the refractive index at the two wavelengths.

Patterson *et al.* (1982) have studied the optical properties of the ash from the El Chichon in the wavelength region 300-700 nm. The samples were collected on the ground at various distances from the volcano. In the absence of in-situ data the refractive index for the stratospheric silicate was given as  $\tilde{n} = 1.53 - 0.001j$ .

Less is known at this time about the complex refractive index of the sulfur aerosol, and its variation with height, in view of the role that dilution and impurities may have, particularly in determining the imaginary part  $\tilde{n}''$ . Knowledge of the refractive index is essential in determining heating effects, and would help in assessing the aerosol composition.

As regards the worldwide spreading of the cloud, in a first approximation, models start by considering the effect of an undisturbed circulation on the motion of a conservative tracer. More intriguing is to ascertain to what extent aerosols can be considered conservative tracers and the possible effects of the heating induced by the cloud on the circulation.

Satellite observations, although lacking the resolution and sensitivity of other methods, give a global view of the phenomenon. Partial conclusions to be drawn from the satellites' observations are: the high altitude cloud took twenty one days to first circle the Earth moving from East to West; its maximum density occurred about eight weeks after the eruption. After the first week in June the aerosol completely encircled the Earth in the latitude band from the Equator to 30 N.

The subsequent spreading of the cloud towards higher latitudes in the Northern hemisphere can be followed through the sequence of ground-based lidar observations. On April 18 Hirono and Shibata (1983) reported intense layers at 16, 25.5 and 26 km. Fig. 1 shows the sequence of observations at Frascati: the profiles give the ratio of the total backscattering cross section of air (aerosols and molecules) to the molecular backscattering cross section as a function of altitude.

On April 21 a relatively weak layer appears around 16 km, possibly the first sign of arrival of the cloud. It is not until June that upper stratifications can be seen at that site. The intensity of the echoes reported is by an order-of-magnitude weaker than those observed at Fukuoka by Hirono and Shibata (1983). The latitude of the two stations differs by about 8°. The May-June data show, in the 16-20 km region, complex sets of stratifications, a few hundred meters thick separated by less than 1 km, which disappear by July. From now on, the 16-20 km region appears characterised by a relative homogeneity. After June 9th conspicuous stratifications are visible above 20 km, with particularly large R values obtained in July around 25 km and in August at various heights in the 21-27 km interval. At the end of summer the aerosol load shows a decrease and is down to early summer values. A consistent increase begins at the end of October: by now the layers have lost most of the small scale features and the lower stratosphere appears continuously filled from 10 to 25 km. After the beginning of the year a decreasing trend in the optical thickness is evident from these and subsequent unpublished data.

The thin stratifications appearing on the Frascati lidar data for several months after the eruption cannot be accounted for on the basis of simple models of turbulent vertical diffusion acting on inert particles. As already mentioned, their long lifetime is related to a balance between the different and variable mechanisms which affect the vertical transport of sulfur and water substance, in particulate and gaseous form. Particulates are acted upon by sedimentation, by vertical advection where that exists, e.g. in the Hadley cell, and by turbulent diffusion; they may gain or lose water. Gases move under the action of vertical advection and molecular or turbulent diffusion. Conditions existing in the upgoing branch of the Hadley cell may favor the formation of thin layers.

There is evidence that polar air masses, one and half years after the eruption, carry a good deal less aerosols indicating that meridional mixing is incomplete. In an analysis of the SAM II data satellite extinction data for the Northern hemisphere winter of 1982, supplemented by airborne lidar observations, McCormick *et al.* (1983) found the polar vortex to be an area of substantially low aerosol content where the El Chichon cloud does not seem to have penetrated and that either an aerosol sink or a supply of clean air exists in the polar winter vortex.

This observation is an additional indication that large horizontal and vertical inhomogeneities may arise as a result of the circulation, long after the eruption. These effects were noticed also after the Mt. Agung

eruption and were a basis to explain, in part, correlations found between ozone and aerosol content (Grams and Fiocco, 1967).

Modeling efforts aimed at simulating the worldwide diffusion of the cloud begin to appear: preliminary results gave rather faster transit times than have actually been observed (Capone *et al.*, 1983; Pitari *et al.*, 1984). While these results may be due to the scarce resolution of the circulation models, they may also point to the rather complex nature of the aerosol dynamics (see e.g. Crescentini and Fiocco, 1983). Related anomalies were found by us in utilising the meridional distribution model of Cadle *et al.* (1976), in efforts to simulate the effects of Mt. Agung (Fiocco *et al.*, 1977).

Essential in establishing the heating induced by El Chichon is the separation of other concurrent effects due to El Niño and to the quasi biennial oscillation.

Labitzke *et al.* (1983) have presented preliminary results, obtained almost in "real time", of a comparison between monthly mean stratospheric temperatures between 10° and 30° N for the years 1964-1982 with those of 1982: definite differences appear for the months of July and August with + 5 °C above the 18 year average at the 30 mbar level over 10° N.

Having examined the various periodic and quasi-periodic causes of fluctuation, Quiroz (1983) concludes that the amount of warming in the summer of 1962 due to the El Chichon at 30 mbar is 1 – 3 °C at latitudes between 35 N and the Equator, and that effects related to a volcanic modulation of the QBO would be of secondary importance.

Pollack and Ackerman (1983) have reported the results of calculation with a one-dimensional radiative-convective model which predict the El Chichon cloud to have caused an increase of planetary albedo of 10%, a decrease in total radiation at the ground of 2-3%, and an increase in temperature of 3.5 degrees at the 30 mbar level. The GCM of the European Center for Medium Range Forecast was utilised to model the perturbation introduced by a fixed layer with an optical thickness of 0.15 added to the background: a stratospheric warming of 3.5 °C in the stratosphere and a cooling of about 0.1 °C near the surface was obtained (Tanre and Geleyn, 1984).

In conclusion, the present intense research effort triggered by the El Chichon eruption should have a significant impact on aerosol science and on dynamic climatology. It is fair to expect that a detailed description of the spatial and temporal variation of the radiative field, of the fluxes



reaching the surface, of the heating rates, should be obtained by the measurements and by the use of radiation codes. These values will be used as inputs to general circulation models, to check their ability to simulate the spreading of the aerosol clouds, and to recognize expected feedback effects.

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## DISCUSSION

MARINI-BETTÒLO

I would like to know if there are figures about the average sulphur emissions by volcanoes per year.

FIOTTO

I can refer to two recent papers, one by Sedlacek *et al.*, the other by Berresheim and Jaeschke. The global volcanic sulphur release averaged between 1961-79, is estimated to be around  $1.5 \times 10^7$  t(SO<sub>2</sub>)/a: of this the contribution due to volcanic eruptions appears to be around 7% of the non-eruptive emissions. At least 58% of the sulfate aerosol present in the lower stratosphere between 1971-78 was of volcanic origin.

ARNOLD

A brief comment concerning your mechanism which stabilizes the dense layer in your suggestion. Your mechanism would apply only to condensed matter, to particles. However, the sulphuric acid vapor which we have measured is also concentrated in a very thin cloud, and here it should be kept in mind that the vapor is formed *in situ* probably from SO<sub>2</sub> precursor gas and that the lifetime of the sulphuric acid molecule is much less than one day. In the undisturbed stratosphere it is about one day. Under these conditions, where there is more aerosol, the vapor has an even shorter lifetime. And this would tell us that also the gas, and that means the precursor gas, the SO<sub>2</sub> is concentrated in such a thin layer. So this does not necessarily apply only to the aerosols which are formed from the condensable gas formed in turn from the precursor.

CRUTZEN

On the question of confinement in thin layers, since in the initial cloud which gets into the stratosphere the SO<sub>2</sub> concentration is very high, SO<sub>2</sub> being a strong absorber of ultraviolet radiation, one can think of reaction chains in which SO<sub>2</sub> oxidation leads to ozone formation. I once did calculations on the heating rates one gets there, and it is on the order of 10 to 30 degrees

per day, which is very large for the stratosphere. So I cannot see why these layers under such conditions can stay that confined; maybe what we are looking at is two phases really of the volcanic eruption: first, one has the initial eruption and then maybe a fast spread vertically, and then the  $\text{SO}_2$  is oxidized and starts spreading horizontally in sheets.



## NATURAL AND ANTHROPOGENIC AEROSOLS: A COMPARATIVE ANALYSIS

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Despite an imperfection of the present-day climate theory, the conclusion about an important climate-forming role of the atmospheric aerosol can be considered as quite reliable [1, 5, 24, 34]. The role of aerosol as a climatic system element is at least dual: (i) it directly affects the radiation transfer conditions in the atmosphere, and (ii) it changes the extent, size, distribution and radiative properties of cloudiness.

A purely scattering aerosol raises the albedo of the atmosphere, thereby decreasing the amount of radiation which reaches the Earth's surface. In the presence of aerosol absorption, a direct "energy-feeding" of the atmosphere takes place. Thus the anti-greenhouse effect appears when the atmosphere is excessively heated and the surface is cooled. However, since the absorbing aerosol is, at the same time, a heat source, simultaneously the atmospheric greenhouse effect grows. The total radiative effect of the atmospheric aerosols, which both absorb and scatter radiation, depends on the ratio between the absorption coefficients in the shortwave and IR regions, as well as on the surface albedo, sun elevation and cloud conditions.

The effect of aerosol on cloudiness consists in the following: (i) a certain part of aerosols acts as condensation nuclei, causing an increase in the amount of suspended small droplets, and (ii) aerosol particles, caught by clouds, change the radiative properties of clouds and, consequently, the vertical temperature profile. In its turn, this affects the conditions of the formation of cloudiness and of its subsequent transformation.

Since in real conditions the aerosol gets to the atmosphere through

both natural and anthropogenic mechanisms, and a relative contribution of the latter is constantly increasing, keen interest in a search for techniques for adequate evaluation of the disturbing effect of aerosols (anthropogenic, in particular) on climate is justified. Quite recently this interest has grown in connection with a discussion of possible climatic implications of nuclear explosions in the atmosphere, as a manifestation of an extreme anthropogenic impact on the ecological system of the planet [38].

The first stage of the consideration of the effect of aerosol on climate is the modeling of aerosol properties. The models (based on statistically reliable field-measurements data) are to parameterize such characteristics as complex refractive index of particles ( $m = n - ki$ ), their shape and size distribution, vertical profile of aerosol concentrations, as well as variability of these parameters in time and due to humidity.

With regard to the ever-increasing content of anthropogenic aerosols in the atmosphere and to its increasing role as a climate-forming factor, as well as in the light of the above-mentioned discussion, of interest is a comparative analysis of the physico-chemical properties of the natural and anthropogenic aerosols, which together define the term "atmospheric aerosol".

The composition and concentration of the atmospheric aerosol for each localization in space and time can be represented as a superposition of some background and "disturbing" aerosols. The parameters of the latter depend on the character, power, and distance of one source or several sources of "disturbance", and on the effectiveness of the mechanisms of sink. The regions of aerosol-generating mechanisms, both natural and anthropogenic, can serve as sources of disturbance.

Due to the considerably different nature of aerosols and their living conditions in different layers of the atmosphere (which are nearly isolated in the sense of energy- and mass-exchange), the atmospheric aerosol is subdivided into tropospheric, stratospheric, mesospheric, etc., aerosols. Its background and "disturbing" components are, accordingly, differentiated.

The natural mechanisms of atmospheric aerosol generation are as follows: soil-wind erosion, ejections to the atmosphere of salt particles from sea and ocean surfaces, emission of gases and vapors by photosynthesizing plants and by decay products, ejections of the products (soot aerosol, first of all) of natural fires of forests, steppes, peat bogs, and also volcanic eruptions.

The anthropogenic mechanisms are the following: ejections to the atmosphere of solid particles and gases resulting from engine fuel com-

bustion, functioning of industrial enterprises, agriculture (soil plowing, use of chemical fertilizers, herbicides and poisonous fertilizers, planned burning out of forests, prairies, etc.), as well as surface explosions of atomic and thermonuclear systems.

Thus, in general, the anthropogenic aerosol is not only the aerosol, whose chemical composition and other parameters differ from those of natural particles, but also natural particulate matter generated by non-natural mechanisms. For instance, the aerosols, both injected into the atmosphere and formed *in situ* as a result of nuclear explosions in the atmosphere.

There are also "ready" aerosols, which get to the atmosphere in the form of either solid particles (both hygroscopic and hydrophobic) or aqueous droplets, and aerosols formed *in situ*, directly in the atmosphere, as a result of dark and photochemical heterogeneous reactions.

For such a planet as the Earth, whose surface is mostly covered by oceans and seas (70%), the aerosol, genetically determined by water surface — salt and organic (largely bacterial) —, as well as formed *in situ* (due to emission of respective gases and vapors by oceans and seas) should have been considered as a true global background aerosol in the lower troposphere. Of great importance are, however, dust aerosol outbreaks from the continents, which sometimes practically "suppress" the marine aerosol. In the upper troposphere, as a result of the "cloud filter" effect, the true background aerosol should be practically completely void of salt components, and the concentrations of two other components should be considerably lowered. True background aerosols in the stratosphere are exclusively the particles, formed *in situ*. Of course, the above considerations are no more than a rather simplified scheme.

The existence of the continents and of developed meridional and zonal transports of air masses and their intensive vertical eddy mixing necessitates an inclusion of the continent-generated particles into real global background aerosols. Such an enrichment of the background aerosol at all the levels in the lower, and especially in the upper troposphere, as well as in the stratosphere, rather complicates both the general pattern and the notion of the global background aerosol.

Present knowledge of the atmospheric aerosol and the limits of this review do not permit a detailed comparative analysis of the available variety and types of atmospheric particles, whose mechanisms of generation are both natural and anthropogenic. Therefore, proceeding from comparative data on the power of the sources of different kinds of aerosols

and their contribution to the total aerosol optical activity [2, 4, 6, 20, 24], we shall confine ourselves to a discussion of the properties of such aerosols as soil, sea salt, sulfate, formed *in situ*, organic and (as a separate group) soot aerosols.

## 1. SOIL-DERIVED AEROSOL (SDA)

Estimates of the power of natural sources of SDA injected in to the atmosphere through wind erosion mechanism vary within  $(1-5) 10^8$  t/year [2, 15, 40]. However, as is noted by Ivlev [4], these figures are probably very much underestimated, and should be considered as the amount of the SDA contribution to the background global concentration of the atmospheric aerosol.

The SDA dispersiveness in the air surface layer is determined by natural dispersiveness of soil as a source of aerosol, and by effectiveness of the sand-jet effect of saltating particles. The formation of the real size distribution of SDA in this atmospheric layer is determined by the processes of sedimentation, impingement, condensation and adsorption of gases and vapors, capture and sedimentation on obstacles and surfaces [6]. Real size distributions of soil-erosion aerosols (SEA) can be described by the power law:

$$\frac{dN}{d \lg r} = \alpha \cdot r^{-\gamma}$$

where  $\gamma = 2 \div 3$  [4, 6, 24]. However, in some cases the real number density of SEA is characterized with due regard to several components, for which  $\gamma$  varies from 2 to 4. These cases either refer to the conditions of residence of the aerosols that have not reached a relative equilibrium, or reflect the fact that a given aerosol ensemble is produced by several independent sources. The size distribution of such ensembles of aerosols can be described by the log-normal law. A study of log-normal distributions has revealed two modes in SEA: A-mode ( $1 \mu\text{m} < r < 10 \mu\text{m}$ ) and B-mode ( $10 \mu\text{m} < r < 100 \mu\text{m}$ ). The A-mode is present in the SEA size spectra at any amount of dust-loads in the atmospheric surface layer. These particles are mostly of clay. The B-mode is typical of the conditions of increased dust-loads: these are quartz grains, whose surface is covered with a thin layer of clay dust. Since the B-mode particles have a shorter lifetime as compared to A-particles, the optical properties of remote-area

SEA should be determined, mainly, by the A-mode aerosol. The latter is characterized by substantially constant size distributions: for weak dust loads  $r_m < 0.4 \mu\text{m}$ ,  $\sigma = 2.2$ ; for moderate and heavy dust loads  $r_m = 0.45 \mu\text{m}$ ,  $\sigma = 2.1$  ( $r_m$  is the mean radius of particles in the number log-normal distribution;  $\sigma^2$  the dispersion of distribution).

The B-mode characteristics are more variable:  $r_s$  and  $r_v$  vary from 15-20 to 30-35  $\mu\text{m}$ , and  $\sigma$  from 1.4 to 2.0 ( $r_v$ ,  $r_s$  are mean radii, respectively, by volume and surface distribution). With increasing height over the surface the mean radius of particles,  $r_m$ , decreases: it decreases for large particles, and the spectrum of aerosol sizes is formed into a rather narrow distribution, with a maximum for middle troposphere conditions at  $r = 0.2\text{-}0.5 \mu\text{m}$ .

The concentration field and chemical composition of SEA differ as to considerable space/time variety in the lower atmospheric layers, which is, no doubt, determined by specific features of the SEA-generating mechanism, by non-uniform geographical distribution of aerosol sources, and by complicated atmospheric general circulation. In the regions of dust storms the SEA mass concentration ( $C_m$  SEA) may constitute  $(10^{-1} - 10^{-2}) \text{ g/m}^3$ . In the region of a powerful advection  $C_m$  averages  $(2\text{-}3) 10^{-4} \text{ g/m}^3$ . In the areas with a low level of soil erosion  $C_m$  SEA varies from  $2 \times 10^{-5}$  to  $4 \times 10^{-5} \text{ g/m}^3$ . In the off-shore regions of the Northern Hemisphere Atlantic  $C_m$  SEA constitutes  $(0.5\text{-}0.1) 10^{-6} \text{ g/m}^3$ . In deep regions of the Antarctic  $C_m$  SEA appears to be far less.

The SEA number density field ( $C_N$  SEA) is also rather variable. From data of complex observational programmes GAAREX and CAENEX [6, 9]  $C_N$  SEA in the air surface layer of the Karakum desert (for particles with  $r > 0.2 \mu\text{m}$ ) constitutes  $8\text{-}270 \text{ cm}^{-3}$ . In the air surface layer ( $0.5\text{-}2 \text{ m}$ ) of north-eastern Kazakhstan (for particles with  $r > 0.2 \mu\text{m}$ )  $C_N$  averages  $50\text{-}80 \text{ cm}^{-3}$  [11]. During the Saharan aerosol outbreak across the Atlantic the values of  $C_N$  near the sea surface reached  $6\text{-}40 \text{ cm}^{-3}$  (for particles with  $0.3 \mu\text{m} < r < 10 \mu\text{m}$ ).

Vertical profiles of  $C_m$  and  $C_N$  SEA are, as a rule, characterized by an exponential decrease. However, a stratified structure is often observed; it is most characteristic of the summer period and afternoon hours.

In most cases the mineral composition of SEA is represented by quartz, different kinds of clayey soil, carbonates, calcites, and gypsum. For some regions the content of iron oxide (hematite) turns out to be considerable.

An analysis of the mechanisms for SDA generation by nuclear ex-

plosions in the atmosphere [38] shows that in such conditions soil particles can get to the atmosphere as a result of soil loosening and blowing away of soil dust from the surface by a shock wave, as well as of the thermal heating of soil in the epicentre of the explosion, with subsequent repeated nucleation of the *in situ* aerosol particles in the form of smallest glass-like spheroids [28]. From the data obtained during nuclear tests, the atmosphere receives  $(1-6) 10^5$  tons of dust per 1 Mt charge equivalent exploded either on the surface or immediately over it [16]. The dust thus generated is preserved in the form of a persistent cloud, confined from above ( $Z_{\text{top}}$ , km) and from beneath ( $Z_{\text{bot}}$ , km). The values of the latter are functions of the height of the tropopause ( $Z_t$ , km) and of the yield of explosion ( $\xi$ , Mt):

$$Z_{\text{top}} = (Z_t - 13) + 21 \xi^{0.2}$$

$$Z_{\text{bot}} = (Z_t - 13) + 13 \xi^{0.2}$$

Inside this cloud the size distribution of particles can be characterized by normal-logarithmic distribution with  $r_m = 0.25 \mu\text{m}$ ,  $\sigma = 2.0$  (for particles with  $r < 3 \mu\text{m}$ ) and the power law ( $\gamma = 4.0$ ), to describe the "trail" of distribution in the range of particle sizes  $3 - 1,000 \mu\text{m}$ .  $C_N$  values in such clouds are greatest for the submicron fraction. About 8% of the total SDA mass in the cloud are assumed to be particles with  $r < 1 \mu\text{m}$ . The complex refractive index,  $m$  of dust particles in clouds is assumed to be  $1.5-0.001i$  [38]. Figure 1 shows model temporal dependences of the vertical optical thickness,  $\tau$ , of a post-nuclear dust cloud, calculated for the Northern Hemisphere [38]. As is seen,  $\tau$  values ( $0.55 \mu\text{m}$ ), immediately upon the formation of the cloud, can vary from  $\sim 0.25$  to  $\sim 3$ , depending on the SDA mass concentration in the cloud and on its size distribution.

Coming back to the soil-erosion type of SDA, note that a review of the estimates of  $m$ -values for SEA has been given in [6, 24]. The value of the refractive index,  $n$ , for a dry SEA sample varies within relatively narrow limits  $1.50 - 1.558$ . In the near UV region a trend to an increase of  $n$  is observed (at  $\lambda = 400 \text{ nm}$   $n \cong 1.59$ ). The values of the imaginary part,  $k$ , of the complex refractive index are greatly variable. In the visible the value of  $k$  varies from 0.007 to 0.0163, which, no doubt, reflects an increased sensitivity of  $k$  to the SEA chemical composition variability. In the near UV region the  $k$ -value can reach 0.025. In the near IR region a minimum of absorption by the SEA substance at  $\lambda = 1 \mu\text{m}$  and a

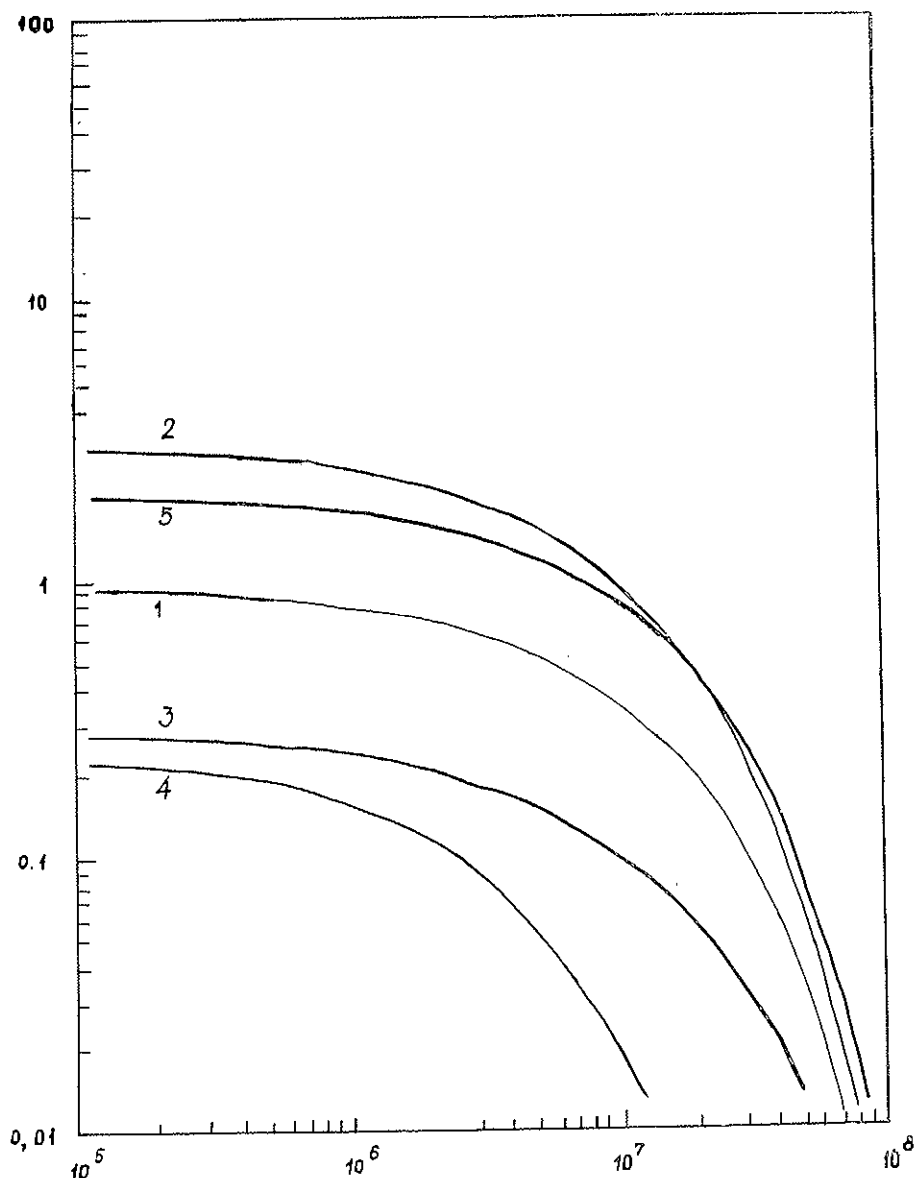


FIG. 1. Model calculations of the temporal dependence of the vertical optical thickness of a "nuclear" dust cloud, averaged over the Northern Hemisphere ( $\lambda = 550$  nm). The mass concentration of dust particles in the cloud corresponds to the injection to the atmosphere of  $3.3 \times 10^5$  (1),  $1 \times 10^6$  (2), and  $1 \times 10^5$  (3) tons of particulate matter per Mt of an equivalent charge. Particles' size distribution is log-normal and parameterized by the power law (see the text); 4,5 — calculations on the assumption of the prevailing content in the cloud of large ( $r_m = 1.0 \mu\text{m}$ ) and small ( $r_m = 0.1 \mu\text{m}$ ) particles.

maximum at  $\lambda = 10 \mu\text{m}$  are observed (the latter is determined by the effect of the  $\text{SiO}_2$  absorption band). The presence in SEA of considerable amounts of aluminum and/or iron oxides intensifies the above spectral dependence of  $k$ . Note that in the visible the  $k$ -value for hematite is rather high: 0.0165 ( $\lambda = 0.5 \mu\text{m}$ ), 0.154 ( $\lambda = 0.55 \mu\text{m}$ ) and 0.135 ( $\lambda = 0.6 \mu\text{m}$ ).

## 2. MARINE SALT AEROSOL (MSA)

Estimates of the annual amounts of MSA injected to the atmosphere vary within  $(1-2) 10^9$  ton. Sea-surface generated salt particles, due to specific character of the bubble mechanism, should be characterized by two considerably overlapping ranges of dispersion [6]. The smallest particles lie within  $r \geq 0.1 \mu\text{m}$ . The upper limit depends considerably on the speed of surface winds and on air humidity: in corresponding conditions, particles with  $r > 100 \mu\text{m}$  can be detected in the lower 10-m layer of the maritime air [21].

Measured size distributions of salt particles are monomodal and can be parameterized by the power law, with the index varying within 0.97-4.2 (average 2.3-2.6). The density of MSA particles is close to 2.35 - 2.40  $\text{g/m}^3$ . The spatial distribution of  $C_N$  MSA ( $r > 1 \mu\text{m}$ ) for different regions of the world ocean can be illustrated by the following values: in the Pacific Ocean  $C_N = (1.2-1.5) \text{ cm}^{-3}$ ; in the Indian Ocean  $(0.9-1.0) \text{ cm}^{-3}$ ; near the Australian coastline  $0.4 \text{ cm}^{-3}$ ; near the boundaries of the Antarctic ice sheet  $(1.8-2.1) \text{ cm}^{-3}$ , and near the Black Sea coastline  $(0.32-1.93) \text{ cm}^{-3}$  [8]. The vertical distribution of  $C_N$  MSA has some specific features. A maximum of  $C_N$  distribution is often observed at altitudes of several hundred meters (apparently, because of a decrease in the  $C_N$  MSA near the water surface, resulting from the capture of salt particles by sea waves). At altitudes 2-3 km the value of  $C_N$  MSA constitutes  $\leq 1\%$  of the total  $C_N$  value, which is explained by the "cloud filter". However, over land, near the coastline, at an altitude of 3 km,  $C_N$  MSA is somewhat higher than at the same level over the sea surface. This is connected with a more intensive turbulence over land. In general, sea-salt aerosol particles have to be chemically composed of dried sea water: 88.7% chlorides, 70.8% sulfates, 0.3% carbonates, and 0.2% other salts.

In fact, *in situ* measurements revealed deviations in the chemical composition of MSA, manifested in a relative enrichment of MSA (by a



factor of 1.5-2.5) with some microelements (for instance, K, Ca, Mg, I, Sr, Ba, F), as compared to the composition of sea water.

Observational data suggest an explanation to this fact: there is a surface layer  $\leq 150 \mu\text{m}$  thick, enriched with the above-mentioned elements, as compared to the layers beneath. The enrichment is most manifested in MSA particles with  $r \leq 0.5 \mu\text{m}$  and  $r \geq 10 \mu\text{m}$ . The hypotheses explaining this fact have been discussed in detail in [6].

Studies of MSA in the Atlantic [32] have shown that values of  $n$  of the refractive index at  $\lambda = 550 \text{ nm}$  and  $589 \text{ nm}$  constitute, respectively,  $1.548 \pm 0.002$  and  $1.544 \pm 0.002$ . The imaginary part,  $k$ , of the complex refractive index ( $\lambda = 480\text{-}520 \text{ nm}$ ) is estimated at  $10^{-3}$ , and in the region  $\lambda = 550\text{-}670 \text{ nm}$  it is almost half an order of magnitude as much. Data on  $n$  and  $k$  for  $\text{H}_2\text{O}$  and  $\text{NaCl}$  [37, 39] give an idea about the chemical properties of MSA in the IR spectral region. Note that in the region  $\lambda \geq 1.5 \mu\text{m}$  the role of the contribution of  $\text{H}_2\text{O}$  in the absorption of MSA increases. In this connection, of great importance is the problem of the effect of humidity on the values of  $n$  and  $k$ . So, for instance, at a relative humidity of  $f = 0.2$   $n = 1.546$  ( $\lambda = 0.5 \mu\text{m}$ ), and at  $n = 0.9$   $f = 1.345$  (which is very close to  $n_{\text{H}_2\text{O}}$ ). The imaginary part of the complex refractive index varies in this case from 0.054 to 0.003-0.001.

Summing up the discussion of the properties of this kind of aerosol, note that, to our knowledge, there is no quantitative evaluation in literature of salt aerosols in the upper troposphere and lower stratosphere, resulting from near-water nuclear explosions. Nevertheless, there are estimates [38], according to which an explosion of the 1 Mt yield immediately over the sea surface, should lift up about  $1.0 \times 10^6$  tons of water. Thus, for the case of multiple nuclear explosions over (or beneath) the surface of oceans and seas, the problem of mass injection of salt aerosols to the upper troposphere and lower stratosphere requires thorough investigation.

### 3. SOOT AEROSOL (StA)

Forest, steppe and peat bog fires are one of the sources of StA. The extrapolation of data on the global-scale contribution of the atmospheric aerosol of solid products of forest fires in the USA has given a value of  $(0.3\text{-}3.6) 10^8 \text{ ton/year}$  [2,7]. A substantial amount of soot

particles comes from anthropogenic sources: the amount of solid-phase anthropogenic aerosol, containing elemental carbon (EC), is estimated at  $(0.3-1.3) 10^8$  ton/year. The EC percentage in this aerosol varies, according to different data, from 27 to 48% (by weight). The StA number density in natural conditions varies from several particles/cm<sup>3</sup> to, probably,  $10^6$ /cm<sup>3</sup> (on the output of the source).

In case of multiple nuclear explosions in the atmosphere about  $1.8 \times 10^8$  t of aerosols are supposed to be injected into the atmosphere, with  $7.6 \times 10^7$  t StA, resulting from burning of industrial enterprises, wooden constructions, oil supplies, asphalt, and polymers. The supposed scale of forest fires (over an area of about  $10^6$  km<sup>2</sup>) should lead to the  $1.6 \times 10^8$  t load of the atmosphere, with about  $1.3 \times 10^7$  t StA [12]. Thus, on the whole, the atmosphere should be loaded with about  $8.9 \times 10^7$  t of the pure soot (EC) aerosol. The mean bulk density of StA in these conditions is supposed to be  $2 \times 10^4$  cm<sup>-3</sup>. The StA estimates substantially depend on data on EC percentage in the fuel-combustion derived aerosol. From laboratory data [12], the EC percentage from burning of wooden constructions varies from 8 to 50% (20% on the average); oil products from 2 to 90% (25% on the average); polymers from 12 to 50% (25% on the average); forest fires give from 3 to 27% (8% on the average).

The major mechanism of generation of both the natural and anthropogenic StA is a pyrolysis in the gas- or condensed-phase of the carbon-containing material. The microphysical characteristics of the resulting StA depend on the specific nature of the source: so, for instance, the particles produced by oil combustion have a coral-like structure and an effective spherical shape; the pyrolysis of coal gives particles in the form of spheres, with a great amount of smaller, randomly oriented spheroids inside them [11].

The way of burning governs the character of resulting StA. A smouldering source gives large flakes of soot (since in this case the coagulative growth of small, embryo particles is quite possible). In case of fast burning, small particles with  $r \leq 0.1$  μm are mostly formed. Also, the environment characteristics strongly affect the StA size distribution [27]. Initially-formed particles have a radius of 0.01-0.1 μm. As a result of coagulation, these "embryo" particles rapidly recombine. Therefore, the atmosphere residence-time of the embryo particles should be rather short (less than several days). Particles with  $r > 3$  μm, formed both in most favourable conditions for coagulation, and due to eddy "mechanical" lifting of large particles (from the sites of burnt houses, coal working,

weathered carbon-containing rocks, etc.) are rapidly removed from the atmosphere by gravitational sedimentation. Particles with  $r = 0.1\text{--}3\text{ }\mu\text{m}$  (particles of accumulative mode) in the atmosphere can be rather long-lived, being limited from above with effective sink mechanisms. Globally-averaged estimates [30] have led to the following residence times of particles: 1 week in the lower troposphere (up to 1.5 km), 1 month in the upper troposphere, and more than a year in the stratosphere. In estimation of the life-time of the accumulative mode StA particles of great importance is the external and internal mixing of aerosol particles. The external mixing gives larger particles due to recombination of EC homogeneous particles ("young" StA); in case of internal mixing, EC is in physical contact with aerosol particles of different chemical composition ("old" StA). The external mixing generates hydrophobic aerosols, while the internal mixing leads, as a rule, to the formation of hygroscopic particles. As a result, the mechanisms for washing out of these two types of merged aerosols are quite different. Electronmicroscope studies of EC particles have shown that "embryo" particles are, as a rule, spheroids; often these are agglomerates in the form of chains and clusters. Their specific surface is about  $1,000\text{ m}^2/\text{g}$  [30].

Depending on the character of the inflaming material, the conditions of the pyrolysis process and the properties of the EC- residence medium, their surface can be covered with adsorbed substances. Often these are hydrophobic, incompletely burnt, hydrocarbons. However, the cover may happen to be hydroscopic (due to adsorption of atmospheric gases), ready to form hydrogen and coordinate bonds. Pure EC is absolutely inert at usual temperatures. This is an hydrophobic, insoluble substance (it may be oxidized at about  $600\text{ }^\circ\text{C}$  or in the atmosphere of  $\text{F}_2$ , but such conditions do not occur in the real atmosphere). EC is capable of reacting with radicals, which may be essential from the viewpoint of the chemical reactions taking place in the atmosphere. The EC catalytic activity in reactions of atmospheric  $\text{SO}_2$  oxidation has been reported in [29]. These reactions can be driven by two mechanisms: "dry" (in the presence of water) and "moist", when an EC particle is filmed with water. The "moist" mechanism is more effective [10].

As has been mentioned above, the StA size distribution depends both on specific inflaming material and on the way of its pyrolysis, and on the properties of the environment, into which the StA particles are injected [42]. The size distribution of StA from urban and forest fires has been suggested to be parameterized by log-normal distribution [38]

(in the first case  $r_m = 0.1 \mu\text{m}$ ,  $\sigma = 2.0$ ; in the second case  $r_m = 0.05 \mu\text{m}$ ,  $\sigma = 2.0$ ). A study of the laboratory-generated StA size distribution (propane pyrolysis, undertaken by E. Hindman *et al.* [24]) has shown that the size distribution is a 3-mode one (Fig. 2):  $r_m^I = 5 \times 10^{-3} \mu\text{m}$ ,  $r_m^{II} = 5 \times 10^{-2} \mu\text{m}$ ,  $r_m^{III} = 0.3-0.4 \mu\text{m}$ . For the accumulative mode, as a most long-lived one in the atmosphere, a representation of the size distribution by the power law can be characterised, after A. Boden [24],

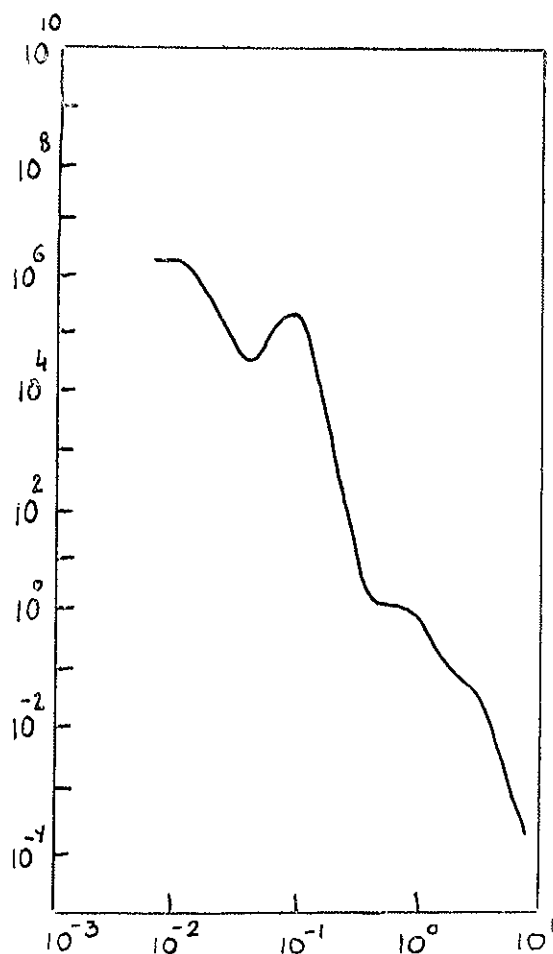


FIG. 2. Size distributions of laboratory-produced soot particles (propane soot).  $d_g$  — mean geometrical diameter.

in the following way:  $\gamma = 4.9$  ( $r < 0.25 \mu\text{m}$ );  $\gamma = 4.6$  ( $r \leq 0.35 \mu\text{m}$ );  $\gamma = 5.1$ - $5.2$  ( $r > 0.4 \mu\text{m}$ ).

The specific weight of StA is estimated at  $1.9$ - $2.0 \text{ g/cm}^3$  [24, 38], depending on porosity of the particles (the density of graphite is  $2.21$ - $2.25 \text{ g/cm}^3$ ).

Rather meagre and contradictory are data on vertical profiles of the StA distribution in the atmosphere. This problem requires thorough investigation. The following heights have been proposed [28] for the top ( $Z_{\text{top}}$ ) and bottom ( $Z_{\text{bot}}$ ) levels of smoke clouds: urban fires  $Z_{\text{bot}} = 1 \text{ km}$ ,  $Z_{\text{top}} = 7 \text{ km}$ ; accidental forest fires  $Z_{\text{bot}} = 1 \text{ km}$ ,  $Z_{\text{top}} = 5 \text{ km}$ ; vast post-nuclear fires (a 10% contribution from urban fires):

$$Z_{\text{top}} = 1.5 (4A_f/\pi)^{3/2}$$

$$Z_{\text{bot}} = 1/3 Z_i$$

where  $Z_i$  is the height of the tropopause,  $A_f$  the area under fire.

Inside carbonaceous-smoke clouds, the  $C_N$  value is considered as unvariable, which is too rough an approximation. The problem of the optical characteristics of StA, with due regard to its porosity, has been considered in [11]. If  $\phi$  is the solid-phase part (EC) of the particle's volume, and  $m_1$  and  $m_2$  complex refractive indices for EC and air, then the complex refractive index for a soot particle,  $m_p$  is expressed by the formula:

$$\begin{aligned} m_p &= n_p - k_p i = [\phi n_1 + (1 - \phi) k_1] - [\phi k_1 + (1 - \phi) k_2] i = \\ &= 1 + \phi (n_1 - 1) - \phi k_1 i \end{aligned}$$

and, thus, is a function of the  $\phi$ -parameter.

The problem of the optical characteristics of the aerosols, soot particles included, was discussed at the First International Workshop on Light Absorption by Aerosol Particles (IWLAAP) [24]. The real part,  $n$ , of the StA complex refractive index in the visible ( $0.3$ - $0.7 \mu\text{m}$ ), according to V. Egan [24], varies from  $1.665$  to  $1.775$  ( $m_{\text{ec}} = 2.0$ - $1i$ , for the visible).

An estimate of the imaginary part,  $k$ , (for the same spectral region) from data of the IWLAAP participants, varies from  $0.4$  to  $1.04$ . In model calculations [38],  $m$  was taken to be  $1.75$ - $0.38i$ . In the IR spectral region (from  $2$  to  $40 \mu\text{m}$ ), from data of F. Voltz [24], the  $k$ -value

increases with increased wavelength: at  $\lambda = 3 \mu\text{m}$   $k = 0.35$ ; at  $\lambda = 40 \mu\text{m}$   $k = 1$  (a technique of embedding in KBr pills was used).

The scattering index of StA,  $\sigma_s$ , was estimated by the IWLAAP participants at  $(1.3.5) 10^{-4} \text{ m}^{-1}$  (average  $\sigma_s = 2.41 \times 10^{-4} \text{ m}^{-1}$ ), and the StA absorption index,  $\sigma_a$ , at  $(3.8) 10^{-4} \text{ m}^{-1}$ . The specific index of scattering for soot particles,  $B_s$ , is assumed in [12] to be  $4 \text{ m}^2/\text{gC}$ , and the specific absorption index,  $B_a$ ,  $6 \text{ m}^2/\text{gC}$ .  $B_s$  estimates by the IWLAAP participants were within  $4.11 \text{ m}^2/\text{gC}$  (on the average,  $7.14 \text{ m}^2/\text{gC}$ ). The single scattering albedo,  $\tilde{\omega}$ , from the same estimates, varied within  $0.090\text{--}0.292$  (StA average  $0.171$ ).

The IWLAAP participants have also undertaken a study of the dependence of the optical properties of StA on the percentage of ammonium sulfate in the particles, as a model of interior mixing of aerosols (Table 1).

These data, apart from being of purely practical interest, are also important from the viewpoint of understanding the laws of formation of the optical properties of the internally mixed atmospheric aerosol.

And finally, studies of the phase function,  $P(\Theta)$ , of StA, undertaken by G. Grams within the framework of IWLAAP [24], have made it possible to estimate the asymmetry coefficient  $g = \langle \cos \Theta \rangle = \frac{1}{2} \int_{-1}^{+1} \cos \Theta P(\Theta) d \cos \Theta$ , of the phase function of soot particles. It turned out to be  $0.48$ . For the particles with equal amount of EC and ammonium sulfate,  $g = 0.58$ .

Summing up the discussion of the optical properties of StA, an importance should be emphasized of consideration of not only the inner structure but also the shape of soot particles. Model calculations made in

TABLE 1 - *The Dependence of Averaged Optical Characteristics of the Soot Aerosol on the Percentage of Ammonium Sulfate in It [24].*

| Parameter        | EC percentage in aerosols |             |              |
|------------------|---------------------------|-------------|--------------|
|                  | 100                       | 50          | 4            |
| $B_a$            | 7.14                      | 2.20 -2.38  | 0.394-0.761  |
| $\tilde{\omega}$ | 0.171                     | 0.549-0.618 | 0.761-0.939  |
| $k$              | 0.581                     | 0.132-0.179 | 0.027-0.0541 |

[33] for an ensemble of randomly oriented particles, have shown that in the "Rayleigh" region of aerosol sizes the substitution of spheroids by ellipsoids (with the axis lengths ratio 3:1) leads to a 40% increase of the specific absorption by such an ensemble. For large soot particles with  $r \gg \lambda$  ( $\lambda$  is the length of the incident wave) the ratio of the specific light extinction by an ellipsoidal particle to that by a spheroid depends on the factor  $Z = a/b$ , where  $a$  and  $b$  are the lengths of ellipsoid's axes; in case of a flattened StA particle this ratio is  $Z^{1/3}/4$ , and in case of an extended one  $Z^{2/3}/2$ .

There is no doubt that in view of high optical activity of StA, further specification is needed of its microphysical properties, optical constants and of the distribution of concentrations in space and time.

#### 4. SULFATE AEROSOL, FORMED "IN SITU"

From the estimates available, the annual amount of particles formed in the atmosphere as a result of chemical heterogeneous reactions constitutes 840-1,400 Mt, 20-30% falling on anthropogenic particles.

The tropospheric air always contains a considerable amount of small submicron particles, the so-called Aitken particles (AP), which are widely spread. Experimental data show that, on the average, not less than 50-75% of the total mass concentration of AP fall on sulfates [43]. The average percentage of the mass concentration of organic and nitrate components in the aerosol of the sub-micron range is estimated at 20-25% [2, 22]. Undoubtedly, nuclear explosions (with a yield of about  $10^{32}$  NO molecules per 1 Mt of trinitrotoluene equivalent [12] should generate great amounts of nitrate and sulfate aerosols, but there are no estimates so far.

Natural and anthropogenic emissions of  $H_2S$ ,  $SO_2$ ,  $CH_3SH$ ,  $(CH_3)_2S$ ,  $CS_2$ ,  $CH_2(CH_2)_2SH$ , and some other compounds are sources of sulfate aerosols [6]. In the rich-in-oxygen atmosphere of the earth and in the presence of such strong oxidizers as  $O_3$ ,  $OH$ ,  $O$ ,  $NO$ ,  $NO_2$ , the oxidation reactions take place, giving first  $SO$  and then  $SO_2$ . The latter, through the mechanism of homogeneous gas-phase reactions (apparently, with participation of  $OH$  and  $HO_2$  radicals), is oxidized into  $SO_3$ , after which the last, very fast stage of the oxidation process starts — the formation of  $H_2SO_4$ .  $H_2SO_4$  is rapidly hydrated in the moist atmosphere and reacts with  $NH_3$ , giving ammonium sulfate and such semi-neutralized compounds as  $NH_4HSO_4$  and  $(NH_4)_3H(SO_4)_2$ .

The concentration field of sulfate aerosols is characterized by changes in  $C_N$  from several particles to hundreds of thousands of particles per  $\text{cm}^3$ . Relatively low mean values of  $C_N$  are observed over the oceans, and high values over the continents (except for high latitudes). In the northern Pacific and Atlantic Oceans the value of  $C_N$  AP often decreases to  $5 \text{ cm}^{-3}$  [21]; over the ice sheet of Greenland it constitutes  $150\text{--}950 \text{ cm}^{-3}$ ; in the tropics and at midlatitudes over the oceans  $C_N$  AP averages about  $300 \text{ cm}^{-3}$ ; over the continents by an order of magnitude higher. In the air over large industrial centers  $C_N$  AP can reach  $10^5 \text{ cm}^{-3}$  near the surface and  $10^3\text{--}10^{-1}$  at an altitude of  $3,000 \text{ m}$  [26].

The anthropogenically-induced AP can be transported to other regions. The insolation regime markedly influences the content of these aerosol particles, and therefore both seasonal and diurnal changes are observed [25].

The values  $4 \times 10^{-6} \text{ g/m}^3$  (the lower troposphere over the continents) and  $0.1 \times 10^{-6} \text{ g/m}^3$  (the middle and upper troposphere) are proposed as an averaged characteristic of the mass concentration of sulfate aerosols [40]. The *in situ* produced aerosol has a characteristic bimodal distribution  $dS/dlgr$ . The first mode is determined by Aitken particles themselves ( $r \leq 0.1 \mu\text{m}$ ). The second, coagulative mode ( $0.1 \mu\text{m} < r < 1 \mu\text{m}$ ) is constantly supplied with heterogeneously coagulating Aitken particles and, for these particles, it is the last form of existence before the aerosol particles in question leave the atmosphere. The parameters of the coagulative mode are:  $d_g$  (mean geometrical diameter) =  $0.37 \mu\text{m}$ ,  $\sigma = 2.00$  [41]. The relative air humidity,  $f$ , substantially affects the size distribution of particles: with it increasing, the maximum of the spectrum is shifted to the region of large radii.

The hygroscopic properties of sulfate aerosols largely determine their specific weight. Depending on size, it varies from 1 to  $2 \text{ g/cm}^3$ . So, for instance, the mean bulk density of submicron particles substance is estimated in [41] at  $1.37 \text{ g/cm}^3$  and in [17] at  $(1.82\text{--}1.93) \text{ g/cm}^3$ .

The optical constants of sulfate aerosols greatly depend on the value of  $f$ . Since at  $525 \text{ nm}$  the refractive index,  $n$ , for water,  $\text{H}_2\text{SO}_4$  ( $f = 0.5$ ), and  $(\text{NH}_4)_2\text{SO}_4$  ( $f < 0.8$ ) are, respectively, 1.33, 1.4, and 1.52, one may believe that in the visible the refractive index,  $n$ , of real sulfate aerosols varies within 1.4–1.52 at  $f < 80\%$ , and at  $f > 80\%$   $n \rightarrow 1.33$ .

The imaginary part,  $k$ , of the complex refractive index for sulfate aerosols in the visible, from the estimates of the IWLAAP participants [24], varies within  $8.1 \times 10^{-6} \text{ -- } 5 \times 10^{-3}$ . These estimates (the upper



limit, in particular) are overestimated by several orders of magnitude, since in this spectral interval the  $k$ -value for ammonium sulfate does not reach even  $10^{-7}$ . The specific absorption index averages  $0.139 \text{ m}^2/\text{g}$  [24]. The single scattering albedo for this kind of particles is 0.971.

## 5. ORGANIC AEROSOL (OA) \*

### 5.1 Organic aerosols, formed *in situ*

There is an opinion about the global spreading and substantial role of organic aerosol in the formation of the properties of the atmospheric aerosol. However, information about this component is very meagre and fragmentary. From the estimates available, the atmosphere obtains annually from 90 to 600 million tons of organic vapors, then formed *in situ* into organic aerosol. Of this amount, 15-20% fall on anthropogenic aerosols [2, 4].

At the initial stage of the *in situ* formation of organic aerosol, an aqua-chemical interaction of hydrocarbon molecules is supposed to take place with such atmospheric oxidizers as  $\text{O}_3$ ,  $\text{OH}$ ,  $\text{NO}_x$  [31].

It has been stated in [2] that the OA content over western Europe at an altitude of 3-4 km constitutes  $1 \times 10^{-6} \text{ g/m}^3$ . This, apparently, means that up to the mid-troposphere, OA is well mixed. This is confirmed by chemical analysis data. OA in the lower and middle troposphere has the following characteristics: the concentration of neutral aliphatic, aromatic, and polar hydrocarbons varies, respectively, within:  $(6.2-0.8) \cdot 10^{-6}$ ,  $(0.12-0.52) \cdot 10^{-6}$ , and  $(0.1-0.35) \cdot 10^{-6} \text{ g/m}^3$ . The concentrations of organic acids constitute, respectively,  $(0.15-0.70) \cdot 10^{-6}$  and  $(0.03-0.2) \cdot 10^{-6} \text{ g/m}^3$ . As has been mentioned above, the average percentage (by mass) of the organic component in the submicron range is estimated at 20-25%. The specific weight of this aerosol (based on the above-given data on the chemical composition, on the whole) constitutes about  $1 \text{ g/m}^3$ .

### 5.2 Rough-disperse OA

Organic particles are also observed in the rough-disperse fraction of

\* The notion does not include soot particles.

the atmospheric aerosol. Studies of the chemical composition of SEA testify to the presence in it of 1-2% of rough-disperse organic particles [6]. Besides, organic matter is present in SEA in the form of "cementing" agents, considerably governing the size distribution of the SEA itself. In soils the organic component is a mass with a very complicated composition, containing living organisms, fragments of dead organisms, biologically synthesized compounds, as well as decay products and their derivatives. In the aerosol samples taken over Repetek and Ankata (the Kara-Kum desert) [9], the mass concentration of the organic component in the SEA rough-disperse fraction constituted about  $2 \text{ mg/m}^3$  [4].

The organic component is also present in marine aerosol. It is also characterized by a complicated chemical composition. Over remote oceanic regions the concentration of organic matter in the rough-disperse aerosol fraction can reach  $2\text{-}4 \text{ mg/m}^3$  [41], but in other cases it does not exceed  $0.15\text{-}0.47 \text{ mg/m}^3$  [18].

Most characteristic sizes of organic particles of marine aerosols do not exceed  $10 \text{ }\mu\text{m}$ . Data on organic aerosol are rather inadequate and do not even permit one to draw, in general terms, a reliable pattern of its optical properties. No doubt much effort is required before real possibilities appear to consider this component in a general model of aerosol.

## 6. GLOBAL BACKGROUND AEROSOL (GBA) IN THE LOWER TROPOSPHERE

The problem of the global background aerosol has been briefly discussed above. The sophisticated nature and substantial uncertainty of this notion have been mentioned. Apparently, of all the global regions most favourable for studies of GBA the Antarctic continent is the best.

Systematic studies of the atmospheric aerosol in the Antarctic revealed a strong annual change in Mirny and at the South Pole, with summer-season values of aerosol concentrations exceeding tenfold those in winter, which points to a substantial effect of meteorological conditions on the values of  $C_{\text{GBA}}$ .

From data of measurements at the South Polar Plateau the mean bulk aerosol density varies from  $15 \text{ particles/cm}^3$  (in winter) to  $100\text{-}150 \text{ particles/cm}^3$  (in summer). A prevailing size of particles lies within  $0.02\text{-}0.2 \text{ }\mu\text{m}$ . In summer, at the expense of downward air fluxes, the values  $C_N = 500\text{-}1,500 \text{ cm}^{-3}$  were registered. This jump attributed to the appearance in the Antarctic air of considerable concentrations of particles

with  $r \leq 0.01 \mu\text{m}$  (and in some cases  $r \leq 0.005 \mu\text{m}$ ). With moist air advection from the Wedell Sea toward the South Polar Plateau, and in strong surface winds, the number density of aerosol reached 250-600 particles/cm<sup>3</sup> [19].

The size distribution of the Antarctic aerosol is described in [35] by a two-mode model (Fig. 3, Table 2).

As for submicron particles (AP) consisting, as has been mentioned above, of transformed minor gaseous components nucleation products, it is assumed that their lifetime does not exceed 2-3 days and they are locally formed over ice caps at a rate of about  $4 \times 10^{-21} \text{ g/cm}^3 \text{ s}$ .

The concentration of rough-disperse particles with  $r \geq 0.14 \mu\text{m}$  constituted about  $0.5 \text{ cm}^{-3}$ . These particles contribute most to the aerosol mass. Undoubtedly, they are driven from remote regions. Covering the surface, these particles form aerosol insertions into polar ice. Their long-term concentration variations can serve as indicators of paleoclimate changes.

A major chemical component of this mode during the Antarctic summer was sulfate (80-90% by mass), which probably appeared due to

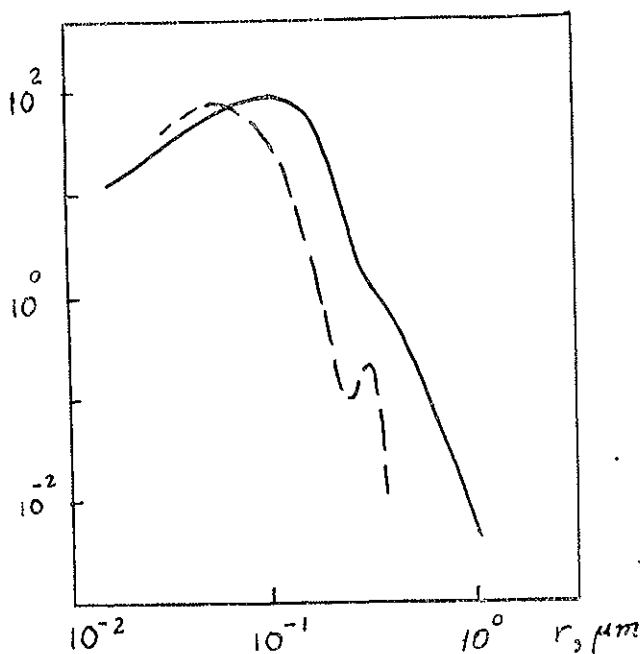


FIG. 3. Number density of polar aerosol. a) South Pole; b) Barrow, Alaska.

TABLE 2 - *Characteristic Values of the Parameters of a Two-Mode Arctic Aerosol Model.*

| Parameters  | Rough disperse mode    | Aitken mode            |
|---|------------------------|------------------------|
| Average radius, $\mu\text{m}$                           | 0.4                    | 0.005                  |
| Number density, $\text{cm}^{-3}$                        | 0.5                    | 1000                   |
| Particles density, $\text{g}/\text{cm}^3$               | 2.16 (NaCl)            | 1.0                    |
| Mass of particles, g                                    | $5.78 \times 10^{-13}$ | $5.23 \times 10^{-19}$ |
| Mean mass concentration, $\text{ng}/\text{m}^3$         | 288                    | 0.78                   |
| Mixing ratio (with respect to air), $\text{mld}^{-1}$   | 0.37                   | 0.001                  |
| Thickness of layer, km                                  | 10                     | 10                     |
| Total content in the atmosphere, $\text{g}/\text{cm}^2$ | $2.88 \times 10^{-7}$  | $7.84 \times 10^{-10}$ |
| Optical thickness (at $\lambda = 500 \text{ nm}$ )      | 0.010                  | $4.01 \times 10^{-9}$  |
| Stox rate of sedimentation, $\text{cm}/\text{s}$        | $4.7 \times 10^{-3}$   | $3.4 \times 10^{-7}$   |
| Coefficient of diffusion, $\text{cm}^2/\text{s}$        | $8 \times 10^{-7}$     | $2 \times 10^{-3}$     |

transport in the lower stratosphere or in the upper troposphere. In winter, the portion of sulfates drops to about 60%. In summer, the contribution of dust from the Southern Hemisphere arid zones (Australia, Kalahari and Atacama deserts), as well as of sea salts does not exceed several per cent. In winter the portion of dust decreases, and that of particles grows to 30-40% (by mass).

In summer, surface inversions over the ice cap are weaker, which stimulates aerosol mixing in the troposphere and its motion to the surface. A relative spreading of the tropopause favours the air transport from the lower stratosphere to the upper one. The transport takes place, apparently, near the boundaries of the continent, but it may also take place over its interiors. As a result, rather a homogeneous distribution of aerosol concentrations and composition over the Antarctic continent is observed [36].

In winter the surface inversion layer is almost isolated from the above atmosphere and only a small part of dust and, largely, salt particles, reaches the South Pole. It is this that determines an increase in the winter-season concentrations of sodium but a decrease in the content of other components (Table 3) [13].

Estimations of the aerosol optical thickness in the Antarctic [36] gave values (for  $\lambda = 500 \text{ nm}$ ), ranging from  $(0.012 \pm 0.005)$  to  $(0.025 \pm$

TABLE 3 - Mean Concentrations (ng/m<sup>3</sup>) of Various Elements in the Antarctic Aerosol in the Summer and Winter Seasons.

| Element | Concentration, ng/m <sup>3</sup> |             |
|---------|----------------------------------|-------------|
|         | summer                           | winter      |
| S       | 76 ± 24                          | 29 ± 10     |
| Na      | 5.1 ± 1.17                       | 40 ± 31     |
| Al      | 0.83 ± 0.41                      | 0.30        |
| Fe      | 0.63 ± 0.25                      | 0.25 ± 0.12 |

0.010). Note that, so far, no anthropogenic impact on the composition of the Antarctic aerosol has been detected.

## CONCLUSION

Summing up the discussion of the microphysical and optical properties of the atmospheric natural and anthropogenic aerosols, again it is important to emphasize the fact that to construct adequate optical atmospheric models, reliable, well-substantiated models of aerosol properties are needed. Unfortunately, present knowledge in this field is quite inadequate. It concerns all the types of aerosols, but, first of all, those formed *in situ* (here organic aerosol is studied least of all), soot aerosol, and solid-phase industrial aerosol. Of great importance are representative sets of parameters obtained from synchronous complex observations, needed for numerical simulation of the atmospheric processes, which characterize each of the main types of the atmospheric aerosol. Along with substantiation of parameterization of the properties of cloudiness as a stochastic system, the above-mentioned problem has been and still is one of the most urgent problems in the physics and chemistry of the atmosphere.

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# INCREASING CONCENTRATIONS OF PERHALOCARBONS, METHYLCHLOROFORM AND METHANE IN THE ATMOSPHERE

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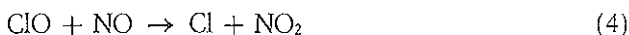
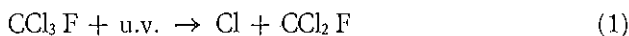
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## *Introduction*

The total concentration of organically-bound chlorine in the troposphere now exceeds 3,000 parts per trillion by volume ( $1 \text{ pptv} = 10^{-12}$ ), an increase of at least a factor of two during the time period from 1970-1983. The major components include  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_3\text{Cl}$ , with lesser contributions from numerous other chlorinated chemical species. The potential environmental importance of ultraviolet photodissociation in the stratosphere of the chlorofluoromethanes  $\text{CCl}_3\text{F}$  (Fluorocarbon-11) and  $\text{CCl}_2\text{F}_2$  (Fluorocarbon-12) [Molina and Rowland, 1974a; Cicerone *et al.*, 1974; Crutzen, 1974; Rowland and Molina, 1975a; W.M.O.-N.A.S.A., 1982; N.A.S., 1976, 1979, 1982, 1984] was recognized soon after the detection of  $\text{CCl}_3\text{F}$  in tropospheric air in both the northern and southern hemispheres [Lovelock *et al.*, 1973]. Atomic chlorine released by photolysis of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ , as shown in (1) for the former, initiates the ozone-depleting  $\text{ClO}_x$  stratospheric chain of (2) and (3) [Stolarski and Cicerone, 1974; Crutzen, 1974]. The most effective altitudes for  $\text{ClO}_x$ -chain removal of ozone lie between 30-45 km because the O atoms required for (3) are much less abundant in the lower stratosphere and below 30 km the alternative reaction of (4) becomes dominant in completing the cycle returning  $\text{ClO}$  to  $\text{Cl}$ .

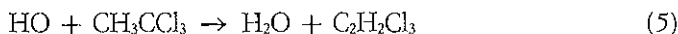
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Compounds released in the troposphere are usually removed by rain-out, by solar photolysis in the visible or near ultraviolet wavelengths, or through chemical attack by reactive species such as HO radicals. These processes are not important for perhalo fluorocarbons such as  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  because they lack solubility in water droplets, are transparent to solar radiation with wavelengths longer than 295 nm, and have no available chemical reaction channels with common atmospheric reactants such as HO and atomic O [Rowland and Molina, 1975a]. Without tropospheric removal, the atmospheric lifetimes for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  were estimated to be 40-150 years, as controlled by stratospheric decomposition processes [Molina and Rowland, 1974a]. For similar reasons, the atmospheric lifetime for carbon tetrachloride,  $\text{CCl}_4$ , was calculated to be 30-50 years and assumed to be controlled by stratospheric processes as well [Molina and Rowland, 1974b].

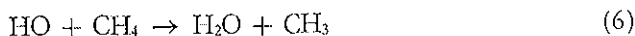
Some of the common anthropogenic chlorinated molecules such as  $\text{CH}_3\text{CCl}_3$  (Methylchloroform) and  $\text{CHClF}_2$  (Fluorocarbon-22) are not fully halogenated, and contain C-H bonds which are susceptible to reaction with tropospheric HO radicals. The most abundant of these in its present atmospheric concentration is  $\text{CH}_3\text{CCl}_3$  which is decomposed by reaction (5).



The high concentration of  $\text{CH}_3\text{CCl}_3$  makes it useful as a monitor for the rate of removal of similar molecules from the atmosphere [Rowland and Molina, 1975b; Singh, 1977; McConnell and Schiff, 1978; Singh *et al.*, 1979; Makide and Rowland, 1981; W.M.O.-N.A.S.A., 1982]. We have estimated an atmospheric lifetime of 6 to 7 years for  $\text{CH}_3\text{CCl}_3$  from a comparison of its measured absolute concentrations versus total emissions [Makide and Rowland, 1981] and from its observed hemispheric concentration gradient [Rowland *et al.*, 1984a]. The measured laboratory reaction rate of  $\text{CHClF}_2$  with HO is less than half as large as  $k_5$ , leading

to an estimated atmospheric lifetime more than twice as long (17 years) as for  $\text{CH}_3\text{CCl}_3$ .

Methane is found throughout the troposphere in concentrations now exceeding 1.6 parts per million by volume ( $1 \text{ ppmv} = 10^{-6}$ ), and is the most abundant source of C-H bonds in the atmosphere. Its primary atmospheric removal process is also reaction with HO radicals, as in (6). The atmospheric lifetimes for  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  can be connected through the relative rates of reactions (5) and (6), and the value observed in the laboratory



for  $k_5/k_6$  of 1.5 leads to an estimate of 9 to 10 years for the lifetime of methane [Mayer *et al.*, 1982]. The major sources of methane in the atmosphere involve anaerobic biological processes occurring in swamps, rice paddies, ruminant mammals, etc. [Ehhalt, 1978]. With an atmospheric burden of about 4500 megatons and a ten-year lifetime, the emissions of methane to the atmosphere must be in the range of 450-500 megatons per year. The world-wide concentration of methane has been observed to be increasing from 1978-1981 at a rate of about 0.02 ppmv per year [Rasmussen and Khalil, 1981; Blake *et al.*, 1982; Khalil and Rasmussen, 1983; Rowland *et al.*, 1984b], implying a current imbalance between sources and sinks for methane of about 50 megatons per year.

Methyl chloride is now present in the atmosphere at about 600 pptv, and was probably also there in comparable concentrations in the year 1900 and before. Very likely  $\text{CH}_3\text{Cl}$  was then the only major organochlorine compound because all of the others now present in large concentrations have been introduced in 20th century technological uses. Although the emission sources for  $\text{CH}_3\text{Cl}$  have not been quantitatively established, the major current release to the atmosphere is believed to come from natural sources such as the oceanic chlorination of methyl iodide released from kelp beds [Watson *et al.*, 1980; Singh *et al.*, 1983]. From the inverse ratio of HO reaction rates vs.  $\text{CH}_3\text{CCl}_3$ , we have estimated the atmospheric lifetime of  $\text{CH}_3\text{Cl}$  as 1.6 years [Makide and Rowland, 1981].

The first anthropogenic compound to be released to the atmosphere in important quantities was  $\text{CCl}_4$  which began to be manufactured industrially about 70 years ago. Although  $\text{CCl}_4$  was formerly used in major quantities as a cleaning agent, its major current use on a world-wide basis is as

the synthetic precursor of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ . The perhalo fluorocarbons were developed about fifty years ago as a class of chemical compounds suitable for use as refrigerants, and  $\text{CCl}_2\text{F}_2$  has been for many years the standard refrigerant gas in most applications. Home air-conditioning, however, has been developed with  $\text{CHClF}_2$  as the working fluid.

The same properties of chemical inertness and volatility make these chlorofluorocarbons useful for many other purposes, including the major one as propellant gases for aerosol spray devices. Other important uses are found as solvents and as the expansion gas in the blowing of polyurethane foams. Manufacture of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  doubled every 5 to 7 years through the 1950s and 1960s, reaching in 1974 world-wide yearly production levels of about 370 kilotons for  $\text{CCl}_3\text{F}$  and 470 kilotons for  $\text{CCl}_2\text{F}_2$  as tabulated by the Chemical Manufacturers Association [C.M.A., 1982, 1983]. Methylchloroform is widely applied as a solvent, especially for grease removal, and is currently at a world-wide level of about 500 kilotons per year.

The exponential increases in yearly production for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  continued until the scientific connection to potential ozone depletion became apparent in the mid-1970s. These environmental concerns have led to consideration of national and/or international regulations for the production and release of these compounds to the atmosphere. A ban on the usage of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  as propellant gases for aerosol sprays was announced in late 1976 by three U.S. government agencies, and similar prohibitions are in effect in Canada and several Scandinavian countries. No regulations are in effect in most other countries, although a voluntary reduction in use as aerosol propellants has been agreed upon in several European countries. No regulations applicable to other important uses are in force in any country, and some of the production formerly intended for aerosol propellant use has been shifted to other end uses.

Most of the applications for all of these compounds, except that of  $\text{CCl}_4$  as synthetic precursor for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ , involve eventual release to the atmosphere unchanged, usually within a few months. Analysis of the data on the yearly production and atmospheric release for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  shows that the cumulative release of each to the atmosphere has at all times in the past two decades exceeded 85% of its cumulative manufacture [C.M.A., 1983]. Most of the residual amount not yet emitted to the atmosphere is held either in refrigerators or in "closed-cell" polyurethane foams.

### *Possible tropospheric sinks for chlorofluoromethanes*

As the importance of atmospheric accumulation of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  was realized, many suggestions were offered of possible alternative reactions which might result in the removal of these compounds from the atmosphere. Such searches for "tropospheric sinks" for chlorofluoromethane compounds can be carried out by testing individually proposed removal mechanisms, or by looking for changes caused by the combined effects of all such processes [Rowland and Molina, 1975a, 1976; N.A.S., 1976, 1979, 1982, 1984; Cunnold *et al.*, 1978]. All specifically identified removal mechanisms (e.g. freezing out into Antarctic snow [N.A.S., 1976]; decomposition on desert sand [Alyea *et al.*, 1978; Lovelock and Simmonds, 1980; Lovelock, 1982]) have been judged to be unimportant relative to stratospheric removal [N.A.S., 1976, 1979, 1982, 1984; W.M.O.-N.A.S.A., 1982].

The other possibility for the discovery of such tropospheric sinks, either singly or in combination, lies through comparisons of the total amounts of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  found in the atmosphere with the amounts expected still to be there if stratospheric photodecomposition is the only important removal process [Rowland and Molina, 1976]. An alternative to this integral approach is the differential, "trend analysis" method in which incremental changes in atmospheric burden are compared with incremental emissions to the atmosphere over a particular period of time. The most complete application of the trend analysis procedure has been carried out through the Atmospheric Lifetime Experiment (ALE) sponsored for its first several years by C.M.A. and now by N.A.S.A. [Cunnold *et al.*, 1978, 1983a,b; Prinn *et al.*, 1983; Simmonds *et al.*, 1983].

In the past, the atmospheric accumulations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  have been frequently stated to be much smaller than expected for stratospheric loss alone, indicative of tropospheric sinks capable of removing  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in time periods as short as 10 years [Jesson *et al.*, 1977; Jesson, 1980, 1982; Miller *et al.*, 1981]. The basis for the estimate of chlorofluoromethane atmospheric lifetimes as short as ten years has usually been the claim that a substantial fraction of the  $\text{CCl}_3\text{F}$  or  $\text{CCl}_2\text{F}_2$  emitted to the atmosphere is no longer there, and by inference must have been removed by some not yet identified atmospheric process. The calculation of such "missing"  $\text{CCl}_3\text{F}$  has often been based upon tropospheric concentrations measured in the north temperate region, e.g. at  $52^\circ\text{N}$ , together with a "weighting factor" determined from the north/

south concentration gradient of a factor of two reported for 1971-2 by Lovelock *et al.* [1973]. Other measurements made in 1972 failed to confirm these large latitudinal gradients in  $\text{CCl}_3\text{F}$  [Wilkniss *et al.*, 1973, 1975], and extensive measurements during the past few years have shown  $\text{CCl}_3\text{F}$  gradients no larger than 15% between the northern and southern temperate zones [N.A.S. 1979, 1982; Cunnold *et al.*, 1983a]. The measured atmospheric burdens are then approximately in agreement with the amounts expected to remain if stratospheric losses represent the only important sink for  $\text{CCl}_3\text{F}$ . The atmospheric lifetime for  $\text{CCl}_3\text{F}$  has been estimated as 78 years from its observed concentrations during 1978-1981 in the ALE program [Cunnold *et al.*, 1983a], while that for  $\text{CCl}_2\text{F}_2$  has been given as  $> 80$  years [Cunnold *et al.*, 1983b]. Both lifetimes are consistent with negligible loss to all tropospheric sinks combined, and stratospheric decomposition is now confirmed as the only important sink for either molecule.

### *Increasing tropospheric concentrations of chlorinated compounds*

The tropospheric concentrations of  $\text{CCl}_3\text{F}$  in 1971 as reported by Lovelock *et al.* [1973] ranged from 80 pptv at 50°N latitude to about 40 pptv in the southern temperate zone. Since that time, measurements have been made by several research groups with increasing frequency over the past decade, including the multiple assays made since mid-1978 by the several stations in the ALE program [Cunnold *et al.*, 1983a,b]. Our own measurements have been taken during various seasons by collecting air samples in remote locations and returning them to the laboratory for analysis. Our data collected around July 1979 are illustrated in Figure 1, and in January 1980 in Figure 2. These distributions show varying latitudinal gradients in different seasons, while clearly demonstrating that  $\text{CCl}_3\text{F}$  is present in approximately equivalent concentrations in all remote locations throughout the world. In 1984 the tropospheric concentration of  $\text{CCl}_3\text{F}$  is about 200 pptv, an increase of a factor of 3 over that reported by Lovelock for 1971. The input of  $\text{CCl}_3\text{F}$  to the atmosphere continues at approximately 270 kilotons per year, and the observed concentrations continue to rise steadily [Cunnold *et al.*, 1983a; N.A.S., 1984]. If its atmospheric lifetime is 78 years and atmospheric release continues at the yearly rate of 270 kilotons, the eventual steady-state amount  $\text{CCl}_3\text{F}$  can be expected to increase by another factor of 4.7 to approximately 1000 pptv.

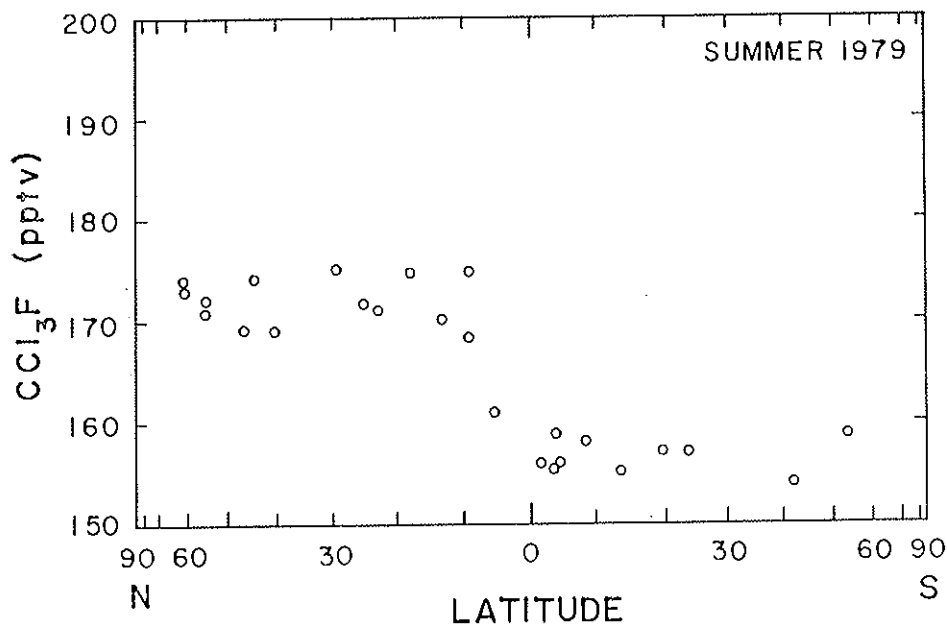


FIG. 1. Tropospheric Concentrations of  $\text{CCl}_3\text{F}$  Measured in Remote Locations during Summer 1979.

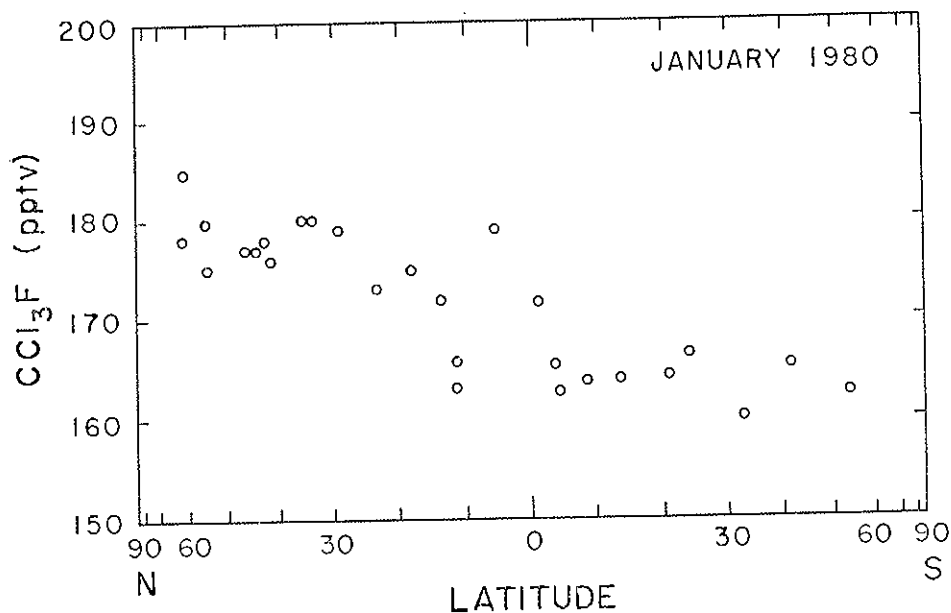


FIG. 2. Tropospheric Concentrations of  $\text{CCl}_3\text{F}$  Measured in Remote Locations during January 1980.

The tropospheric concentrations of  $\text{CCl}_2\text{F}_2$  have also been increasing steadily during the entire period of its measurements, and are now approaching 400 pptv in the northern hemisphere. These concentrations are also about three times larger than those present in 1970. The emissions estimates for  $\text{CCl}_2\text{F}_2$  made earlier by the Chemical Manufacturers Association [1981] showed a consistent decrease from 1974 through 1980, but the atmospheric measurements of  $\text{CCl}_2\text{F}_2$  were not in agreement with these estimates [Rowland *et al.*, 1982; Gidel *et al.*, 1983]. Most of this discrepancy has now been removed with the substantial increase in the revised C.M.A. estimates [1982, 1983], which now show  $\text{CCl}_2\text{F}_2$  emissions of 392.5, 412.2, and 422.8 kilotons per year estimated for 1980-1982, in contrast to the earlier value of 333.7 kilotons per year for 1980 [C.M.A., 1981]. A major uncertainty remains in the origin of these increased emissions of  $\text{CCl}_2\text{F}_2$  because much of the expressed basis for the revised calculations has been the attribution by C.M.A. of an 18% yearly growth in releases from the Soviet Union and other eastern European countries from 1975 onward. No direct estimates of  $\text{CCl}_3\text{F}$  or  $\text{CCl}_2\text{F}_2$  releases in these countries have been published for any year after 1975 [Borisenkov and Kazakov, 1977], and an 18% yearly increase amounts to a factor of 4 increase in less than 9 years. Such a rapid production increase clearly requires a very large development of manufacturing capacity, and the assumption now attributes more than 20% of the world production of  $\text{CCl}_2\text{F}_2$  to the Soviet Union. Despite the uncertainty in the actual origins of the  $\text{CCl}_2\text{F}_2$  now being released to the atmosphere, the concentrations definitely are rising steadily, consistent with the very long atmospheric lifetimes calculated from current atmospheric models, now as long as 150-200 years [Cunnold *et al.*, 1983b]. The atmospheric concentration of  $\text{CCl}_2\text{F}_2$  at steady-state with yearly emissions of 422 kilotons can be expected to increase by a factor of 7 for an atmospheric lifetime of 120 years and a factor of 11 if the lifetime is 200 years. The expected eventual accumulation of  $\text{CCl}_2\text{F}_2$  at current emission rates would then be 3000-4000 pptv.

Measurements made in our laboratory have shown slowly increasing concentrations of  $\text{CCl}_4$  versus time to the present level of about 115-120 pptv in the northern hemisphere, with concentrations only a few pptv lower in the southern hemisphere. The latitudinal distribution in December 1980 is shown in Figure 3. This gradient in concentration is substantially smaller than that found with  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$ , consistent with the fact that widespread industrial use of  $\text{CCl}_4$  began much earlier

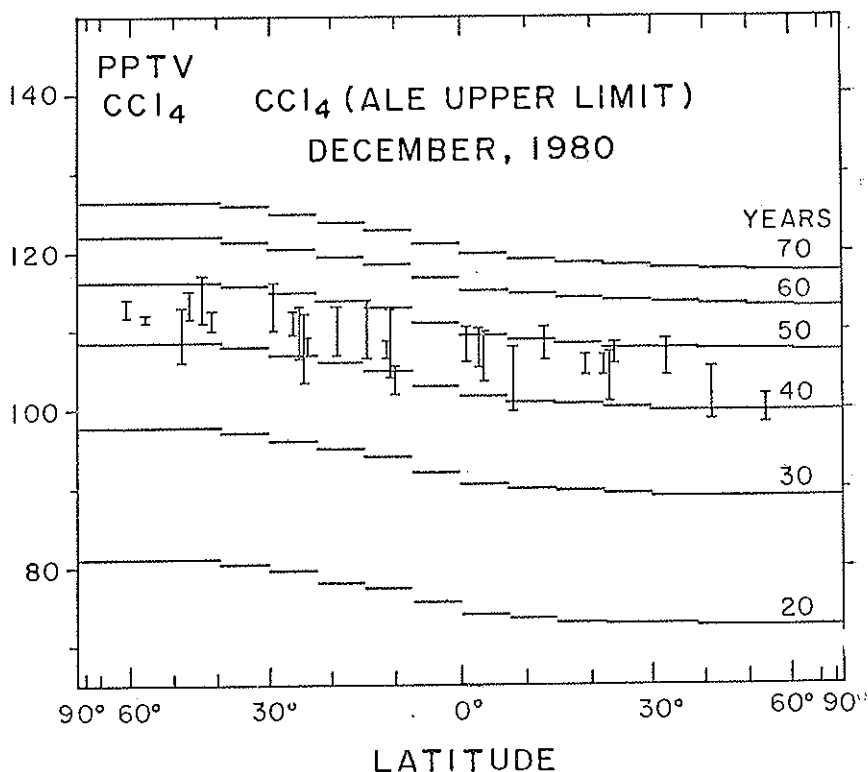


FIG. 3. Tropospheric Concentrations of  $\text{CCl}_4$  Measured in Remote Locations during December 1980. Calculated concentrations for various postulated atmospheric lifetimes in combination with the upper limit estimated for atmospheric emissions by Simmonds *et al.* (1983).

than for the chlorofluorocarbon compounds. All of the anthropogenic halocarbons are produced and used almost entirely (about 95%) in the northern hemisphere, and consequently are found in higher concentrations in the north. We have evaluated north/south transport parameters from the observed gradient in concentrations for  $\text{CCl}_3\text{F}$ , as in Figures 1 and 2, and have then applied them with a plausible emission pattern versus time for  $\text{CCl}_4$  [Simmonds *et al.*, 1983]. The amounts of  $\text{CCl}_4$  and the latitudinal gradient in concentrations is quite satisfactorily reproduced, as shown in Figure 3, lending plausibility to the assumption that all of the  $\text{CCl}_4$  in the atmosphere can be satisfactorily attributed to anthropogenic origins. Some previous evaluations of tropospheric concentrations for  $\text{CCl}_4$  have indicated levels as high as 150-160 pptv [N.A.S.,



1982; W.M.O.-N.A.S.A., 1982]. However, new absolute calibrations for measurements made by some of the research groups involved have resulted in downward revisions [Simmonds *et al.*, 1983] in the estimated tropospheric concentrations until the remaining disagreement with the data of Figure 3 is probably within the respective experimental accuracies.

Our measurements and those of others indicate a slow increase (about 2% per year) in the tropospheric concentrations of  $\text{CCl}_4$ , consistent with a yearly emission rate of 100-150 kilotons/year and an atmospheric lifetime of 45-70 years. Such an atmospheric emission rate is higher than expected from the frequent statement that the current major use as precursor molecule for the production of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  accounts for about 95% of the total  $\text{CCl}_4$  production. On the other hand, experimental observations of tropospheric concentrations of  $\text{CCl}_4$  in some urban locations routinely show excess amounts relative to simultaneous measurements in remote locations at the same latitude, indicating that urban releases of  $\text{CCl}_4$  are occurring in substantial quantities during the 1980s. The present magnitude of estimated releases for  $\text{CCl}_4$ , 100-150 kilotons/year, corresponds to about half as much chlorine being added to the troposphere in the form of  $\text{CCl}_4$  as in being added for  $\text{CCl}_3\text{F}$ . An atmospheric lifetime of 70 years for  $\text{CCl}_4$  and continued emissions at 150 kilotons/year would result in a further increase in  $\text{CCl}_4$  concentration by a factor of about 3, toward a steady state concentration of about 350 pptv.

Concentrations exceeding 100 pptv in the northern hemisphere have also been observed for methylchloroform, with an excess of 35-40% in the north temperate zone relative to the south temperate zone, as shown in Figure 4. As with  $\text{CCl}_4$ , substantially higher concentrations have also been reported earlier for  $\text{CH}_3\text{CCl}_3$  by other research groups [W.M.O.-N.A.S.A., 1982; N.A.S., 1982; Prinn *et al.*, 1983] but new absolute calibrations have lowered most of these measurements into reasonable consistency with the data of Figure 4. Comparisons of the amounts remaining in the atmosphere with the estimates of total release to date show that only about  $50 \pm 5\%$  still remains there, indicative of appreciable loss already through tropospheric decomposition processes.

The only important contributor to these processes is reaction (5) with HO radicals. Comparison of the integrated emissions with the observed atmospheric concentrations led to an estimate of  $6.9 \pm 1.2$  years for the atmospheric lifetime of  $\text{CH}_3\text{CCl}_3$  [Makide and Rowland, 1981]. Although atmospheric concentration data are now available for

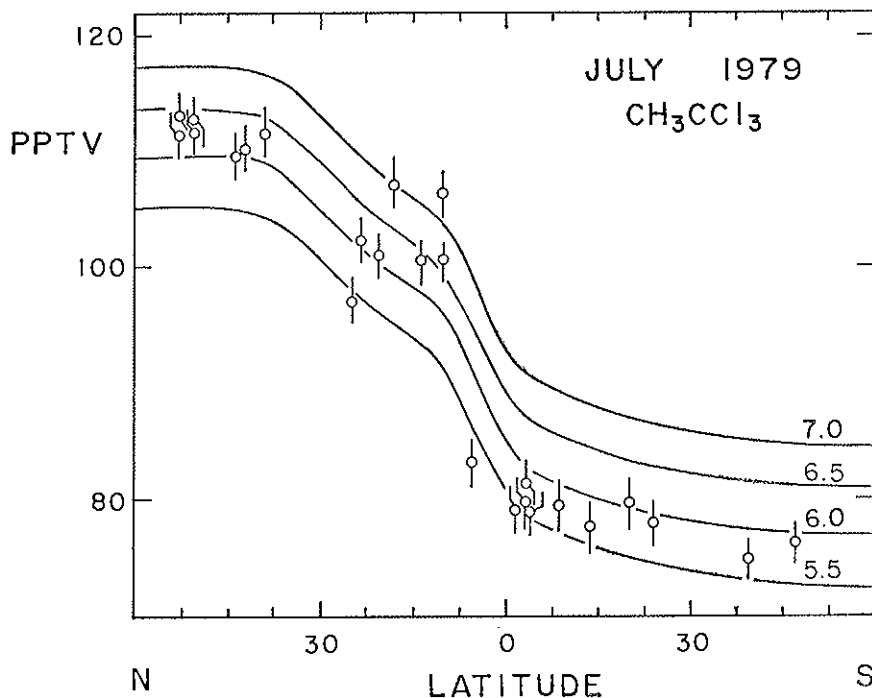


FIG. 4. Tropospheric Concentrations of  $\text{CH}_3\text{CCl}_3$  Measured in Remote Locations during Summer 1979. Calculated concentrations for various postulated atmospheric lifetimes. Assumed hydroxyl sinks of equal magnitude in both hemispheres; primary losses in tropics.

an additional five years, there has been no appreciable improvement in the estimates of environmental release and therefore no better check on the actual atmospheric lifetime for  $\text{CH}_3\text{CCl}_3$ . The world-wide production has not been rising during the last several years, and the atmospheric concentrations appear to be leveling off as would be expected with nearly-constant emission and an atmospheric lifetime of only about 7 years. The expected latitudinal dependence of  $\text{CH}_3\text{CCl}_3$  concentrations has been simulated with transport parameters fitted to the  $\text{CCl}_3\text{F}$  gradient, and various assumed atmospheric lifetimes for loss by reaction (5). The results are shown in Figure 4 and demonstrate reasonable agreement both in absolute magnitude and in latitudinal gradient for lifetimes of about  $6 \pm 1$  years. The simulation in Figure 4 has assumed equal losses in the northern and southern hemispheres, with 80% of all losses by HO radical reaction occurring between  $30^\circ\text{N}$  and  $30^\circ\text{S}$ .

The five most abundant organochlorine compounds in the troposphere in 1984 are  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_3\text{Cl}$ . The organochlorine content in the troposphere includes approximately 600 pptv from  $\text{CCl}_3\text{F}$  ( $3 \times 200$  pptv), 700 pptv from  $\text{CCl}_2\text{F}_2$  ( $2 \times 350$  pptv), 480 pptv from  $\text{CCl}_4$  ( $4 \times 120$  pptv), 420 pptv from  $\text{CH}_3\text{CCl}_3$  ( $3 \times 140$  pptv) and 600 pptv from  $\text{CH}_3\text{Cl}$ , for a total of 2800 pptv. Other chlorocarbon molecules such as  $\text{CHClF}_2$ ,  $\text{CCl}_2\text{FCClF}_2$ ,  $\text{CClF}_2\text{CClF}_2$ ,  $\text{CH}_2=\text{CHCl}$  and  $\text{CCl}_2=\text{CCl}_2$  contribute another 300 pptv or more in the northern hemisphere for a present total in excess of 3000 pptv Cl. Methyl chloride is the only one of these molecules not almost entirely of anthropogenic origin, and was probably therefore the chief contributor of organochlorine content in the atmosphere in the year 1900 and earlier. If its concentration at the beginning of the century was about equal to its present value, the total organochlorine content in 1900 was probably around 600-700 pptv.

The atmospheric concentrations of anthropogenic molecules such as  $\text{CCl}_4$  first became appreciable in the 1940s, and the concentrations of the other chlorofluorocarbons in the 1950s and 1960s. The total concentration of organochlorine compounds probably reached 1500 pptv about 1970, and 3000 pptv early in the 1980s. The concentrations of chlorine in the stratosphere must inevitably follow these tropospheric concentrations, with allowance for the time delay in upward transport. One clear implication of these estimated increases in the tropospheric concentrations of organochlorine compounds during the 20th century is that a change in stratospheric inorganic chlorine concentrations must already have occurred relative to that which existed during the 19th century [Wuebbles, 1983]. However, because full equilibration of the chlorine concentration up to the stratopause lags behind tropospheric concentrations by a decade or more, the present upper stratosphere does not yet accurately reflect the changes in tropospheric organochlorine content which have already occurred during the 1970s.

Estimates of future concentrations of organochlorine compounds in the troposphere are basically dependent upon the projected yearly anthropogenic releases to the atmosphere, coupled with the individual atmospheric lifetimes of the chemical species involved. The concentration of relatively short-lived  $\text{CH}_3\text{CCl}_3$  will probably not increase too much beyond the present values unless there are substantial increases in the yearly production and release. However, the increases in  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  observed during the past ten years are likely to be repeated in the next decade and longer because the observed atmospheric lifetimes are in the

range of many decades to centuries. A total organochlorine content of about 4000 pptv Cl in the troposphere is a reasonable prediction for 1990, with continued increases of about 1000 pptv Cl per decade into the 21st century unless there is a major change in the release patterns for the perhalo chlorofluorocarbons.

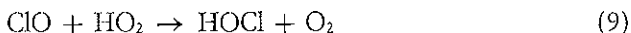
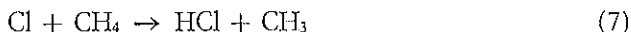
Some indication of concentrations of organochlorine compounds to be expected in the more distant future can be calculated from the extrapolations to steady state described above. With 1000 pptv of  $\text{CCl}_3\text{F}$ , 3000-4000 pptv of  $\text{CCl}_2\text{F}_2$ , 350 pptv of  $\text{CCl}_4$ , 150 pptv of  $\text{CH}_3\text{CCl}_3$  and 600 pptv of  $\text{CH}_3\text{Cl}$ , plus an estimated 800 pptv in now-minor compounds, a tropospheric organochlorine concentration of 12,000-14,000 pptv can be reached. These steady-state concentrations are only approached for the longer-lived compounds over a period of several centuries, and a more directly pertinent indication of future concentrations can be found from a projection to 2084 A.D. With atmospheric lifetimes of 120, 80, 70 and 7 years for  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_4$  and  $\text{CH}_3\text{CCl}_3$ , respectively, the factors of concentration growth over the next 100 years at present emission rates will be about 4.4, 3.5, 2.6 and 1.3, to about 3000, 2000, 1300 and 500 pptv of Cl, and a total of 6800 pptv Cl bound in these four organochlorine compounds. With the addition of 600 pptv for  $\text{CH}_3\text{Cl}$  and 600 pptv for the minor compounds, the total Cl content of the troposphere would then be 8000 pptv in carbon containing compounds alone. Of course, an increase in yearly emissions for the longer-lived compounds would result in substantially greater total atmospheric burdens of organochlorine compounds. A relatively small  $\text{CCl}_2\text{F}_2$  increase of 12 kilotons per year, comparable to the CMA estimated [1983] increases for 1981 and 1982 of 19.7 and 10.6 kilotons would cause  $\text{CCl}_2\text{F}_2$  with a 120-year lifetime to reach the factor of 4.4 increase in about 45 years, and a factor of about 11 by 2084 A.D. If the lifetime were actually 200 years, then the concentration increases by 2084 A.D. would be considerably higher for either steady emissions at 422 kilotons per year or for a linear increment of 12 additional kilotons per year.

### *Environmental consequences from increasing chlorocarbon concentrations*

The growths in the tropospheric concentrations of several organochlorine compounds, and in the stratospheric release of atomic Cl from their decomposition has a variety of potential environmental consequences. One of these is the direct physicochemical effect of Cl upon the ozone

content of the stratosphere; others arise as indirect responses because of the importance of (a) the heating effect in the upper stratosphere from the absorption of u.v. radiation by ozone; and (b) the partial absorption by  $O_3$  of u.v. radiation with wavelengths between 290-320 nm, and thereby the prevention of its transmission to biological species at the earth's surface.

Molecules with atmospheric lifetimes exceeding one year generally exhibit a negligible vertical gradient in mixing ratio within the troposphere. Ultimately, the stratospheric mixing ratios are controlled by these mixing ratios at the tropopause, and an increase in average tropospheric concentration for organochlorine compounds is followed inexorably by an increase in their stratospheric concentrations. Furthermore, stratospheric decomposition then inevitably causes increases in the concentrations of the chlorinated compounds formed following photodecomposition of the organic species. These include not only Cl and ClO, but also HCl, ClONO<sub>2</sub> and HOCl formed by reactions such as (7) to (9). The



measured growth in the tropospheric organochlorine content is necessarily followed by an increase in Cl/ClO content at 40 km, and the chain reaction of (2) and (3) then leads directly from photochemical theory to a diminished average concentration of ozone at that altitude.

The concerns for changes in atmospheric ozone can be divided into two major categories: changes in total column of ozone, and changes in the concentrations at particular altitudes. The penetration of ultraviolet radiation to the surface of the earth is determined almost entirely by the total amount of ozone in the atmospheric column, with very little dependence on the altitude distribution of this ozone. However, if the prime concern is with processes such as the conversion of ultraviolet energy into heat after absorption by ozone (i.e. with the temperature structure of the stratosphere), then a redistribution of ozone to different altitudes is extremely important.

Measurements of the total amounts of ozone in a vertical column of the atmosphere can be made with a Dobson spectrometer from the penetration of 300-320 nm ultraviolet radiation to the earth's surface.

An alternate technique uses the back-scattered solar ultraviolet (BUV) radiation reflected into space and measured outside the atmosphere from an orbiting satellite. The vertical distribution of ozone within this total column can be measured with the ground-based Dobson instrument through the "umkehr" technique, which depends upon the variation in ultraviolet penetration versus solar zenith angle over a period of several hours. The vertical distribution of ozone can also be determined from the wavelength dependence of the BUV signal.

Statistical analysis of the world-wide umkehr data has shown significant loss (about 3%) of ozone at 40 km over the past decade in amounts consistent with the expectations from photochemical theory [Reinsel *et al.*, 1984]. This conclusion is contrary to that stated in an earlier paper in which no such diminution was found [Reinsel *et al.*, 1983], but which had no corrections for the well-known perturbation of umkehr results by light-scattering from volcanic particulates. Angell and Korshover [1983a] have also interpreted the umkehr data to indicate ozone depletion in the upper stratosphere over the past decade. They avoided any correction for light-scattering from volcanic dust by choosing an overall time interval straddling the large volcanic eruption of Fuego in 1974. Analysis of the BUV data from the satellites Nimbus-4 and Nimbus-7 has likewise shown evidence for ozone depletion at 40 km over the decade of the 1970s [Heath, 1981].

Calculations of the aeronomic consequences of the depletion of ozone at 40 km altitude indicate an expected decrease in atmospheric temperatures between 40-50 km [N.A.S., 1979]. Separate evaluations of the atmospheric effects from increasing concentrations of CO<sub>2</sub> have also predicted a decrease in upper stratospheric temperatures. An approximate 5°C decrease in average temperature at the stratopause has been reported during the 1970s [Angell and Korshover, 1983b], but the observed decrease is larger than that generally calculated for the combined effects from ClO<sub>x</sub>-induced ozone decreases at 40 km plus increased CO<sub>2</sub> concentrations throughout the stratosphere. One recent report, however, has indicated calculated temperature changes of the same magnitude as actually observed over the past decade when the two effects are considered together [Brasseur *et al.*, 1983]. Close comparisons between this calculation and others indicating lesser temperature changes have not yet been carried out to determine the origin of these discrepancies among atmospheric models.

The predictions of the extent of future diminution with increasing

atmospheric chlorine content of the total vertical column content of ozone have fluctuated considerably over the past decade as further information has become available about the chemistry of the troposphere and lower stratosphere [N.A.S., 1976, 1979, 1982, 1984]. The current estimates are substantially lower than the  $15 \pm 5\%$  depletions calculated about five years ago [N.A.S., 1979]. Some of these re-evaluations have been caused by improved accuracy in measurements of chemical or photochemical reaction rates, or by the inclusion as very important to the overall calculation of additional chemical reactions and reactants (e.g.  $\text{ClONO}_2$ ,  $\text{HOCl}$ ,  $\text{HO}_2\text{NO}_2$ ). Other changes have been brought about by the recognition that the concentrations of many trace species are increasing significantly with time, in addition to the well-established increases for  $\text{CO}_2$  and the chlorofluoromethanes. Among the other species which are changing are  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and tropospheric  $\text{O}_3$  [N.A.S., 1982, 1984], while an increase has been postulated for  $\text{NO}_x$  which has not yet been confirmed in the atmosphere itself. Predictions of future changes in the concentrations of  $\text{O}_3$  and other stratospheric species now require simultaneous inclusion of future growth rates for many molecules.

With the chemical understanding of early 1984, predictions of future ozone depletions from increasing  $\text{ClO}_x$  content generally indicate an eventual average loss of about 3-5% of total stratospheric ozone over the next century. This change is accomplished by much larger decreases (35-50%) around 40 km, combined with an increase in ozone concentrations near 20 km altitude. In these model calculations, the diminution in ozone at 40 km is a direct photochemical consequence of increasing  $\text{ClO}_x$  concentrations, and the operation of the  $\text{ClO}_x$  chain of reactions (2) and (3). At the same time, the increased chlorine content interferes in the lower stratosphere with ozone depletion by the  $\text{NO}/\text{NO}_2$  catalytic chain through the formation of  $\text{ClONO}_2$ , leaving higher ozone concentrations there as a result. Such calculations indicate that  $\text{ClONO}_2$  should be a major chlorine containing species in the 20-30 km region, accounting for as much as 40-50% of total Cl at some altitudes. Confirmation in the atmosphere of the presence of  $\text{ClONO}_2$  and of the existence of these calculated large abundances for it would be an important step in validation of the current predictions of future effects from increasing  $\text{ClO}_x$  concentrations.

Changes in total ozone column concentrations can also arise from changes in other trace species, including  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NO}_x$  and  $\text{CO}_2$ . The growth in the use of subsonic jet aircraft during the past 25 years has

led in most atmospheric calculations to steady increases in the amounts of ozone predicted to be present in the upper troposphere and lower stratosphere. Measurements there generally confirm such an increase, without necessarily establishing its mechanistic origin. A less direct effect on total ozone columns can result from the steady increase in tropospheric methane [Rasmussen and Khalil, 1981; Blake *et al.*, 1982; Khalil and Rasmussen, 1983; Rowland *et al.*, 1984b] which slowly lessen the catalytic efficiency of the stratospheric  $\text{ClO}_x$  chain by increasing the rate of diversion of atomic Cl into less reactive HCl by reaction (7). Methane is also involved in tropospheric reaction sequences which can increase ozone concentrations there. Combinations of such simultaneous changes for each of several trace species can readily lead to predictions of negligible total ozone column changes over the next two or three decades, as well as in the recent past [N.A.S., 1984]. However, all of these calculations are in agreement that none of the projected scenarios for concentration growths in  $\text{N}_2\text{O}$ ,  $\text{NO}_x$ ,  $\text{CO}_2$  and  $\text{CH}_4$  alters the expectation that the increasing content of  $\text{ClO}_x$  in the upper stratosphere will lead in the next few decades to large losses of ozone in a band centered around 40 km altitude.

Multi-decade observations of total ozone concentrations and trends are necessarily limited to the Dobson spectrophotometer ground stations around the world because satellite observations of ozone only began about 1970. The stations are not distributed equally among all geographic areas and tend to be found in the relatively well-developed countries of the north temperate zone. The quality of the data from these stations is quite variable and a program of calibration of the Dobson instruments has shown errors in the 5-10% range upon recalibration, making extraction of trends in the 1%-3% range over one or two decades very difficult to detect. Komhyr [1982] has reported an overall decrease of about 1% in the average amount of total ozone over North America for the period of 1961-1980, the combination of an average increase during the 1960s and a slightly larger decrease in the 1970s. Small increases in average ozone levels have been reported for other regions of the earth over the same time interval [Angell and Korshover, 1983a], and the overall estimation of changes in the world-wide average ozone content has a substantial statistical margin of error. The limits of statistical detectability of total ozone change on a world-wide basis are less sensitive than the predicted changes for almost all hypothetical scenarios



tested in model calculations and no total ozone column change has been established from the data [N.A.S., 1984].

Biological consequences from a decrease in total column ozone can follow through increased penetration to the earth's surface of ultraviolet radiation with wavelengths between 295-320 nm. These wavelengths have the capability of causing deleterious effects for many biological systems, with an increased incidence of skin cancer the primary effect in humans [N.A.S., 1982, 1984]. Such effects are of course contingent on changes in the average total ozone content of the atmosphere, and any such changes to date are within the statistical error of measurement.

The accumulation of chlorofluorocarbons in the troposphere can have physical atmospheric consequences for at least two reasons. As discussed earlier, a decrease in ozone concentration around 40 km can have a direct effect on upper stratospheric temperatures because energy input there is dependent almost entirely on absorption of ultraviolet radiation by ozone. Changes in the ozone concentration at any altitude will affect the energy absorption at that altitude, but these effects are generally more important for ozone in the upper stratosphere than at lower altitudes. The second influential effect of chlorofluorocarbons arises from their direct absorption of outgoing infrared radiation from the earth. The absorption bands in the infrared for molecules containing C-F bonds frequently fall into wavelength regions not strongly absorbed by the more abundant polyatomic molecules, chiefly  $O_3$ ,  $H_2O$  and  $CO_2$  [Ramanathan, 1975; Wang *et al.*, 1976; Lacis *et al.*, 1981; N.A.S., 1983, 1984]. The escape of infrared radiation from the earth is necessary to maintain a terrestrial energy balance with the incoming visible solar radiation, and this energy loss in the infrared can be hindered through absorption in the vibrations of polyatomic molecules such as  $CCl_3F$ ,  $CCl_2F_2$ , etc. When the average infrared escape probability is thus reduced, a higher surface temperature is required for the earth in order to increase the probability of energy escape through those wavelength bands still transparent to infrared. The infrared absorption characteristics of  $CCl_3F$ ,  $CCl_2F_2$  and  $CCl_4$  all add significantly to the greenhouse effect expected from the increasing  $CO_2$  concentrations in the atmosphere. One estimate of the various contributions to the greenhouse effect for the chlorocarbons is, per each 1000 pptv increase:  $CCl_3F$ ,  $0.15^\circ C$ ;  $CCl_2F_2$ ,  $0.13^\circ C$ ;  $CCl_4$ ,  $0.14^\circ C$  [N.A.S., 1983].

### *Increasing concentrations of tropospheric methane*

The availability of tropospheric air samples from 55°N to 53°S latitudes obtained for halocarbon analysis [Makide and Rowland, 1981] has permitted an extension of our measurements of the world-wide distribution of trace atmospheric species to methane [Mayer *et al.*, 1982]. Only about a dozen air samples were available for our initial latitudinal sequence in early 1978, but subsequent collections have provided much larger numbers of samples, as shown in Figures 5 and 6 for two collection periods during 1982 and 1983. From 1978-1981 most of our southern hemisphere sample collections were made at coastal sites in Brazil and Chile. However, comparisons were made of the relative latitudinal behavior of  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$ , based on the assumption that both are chiefly removed

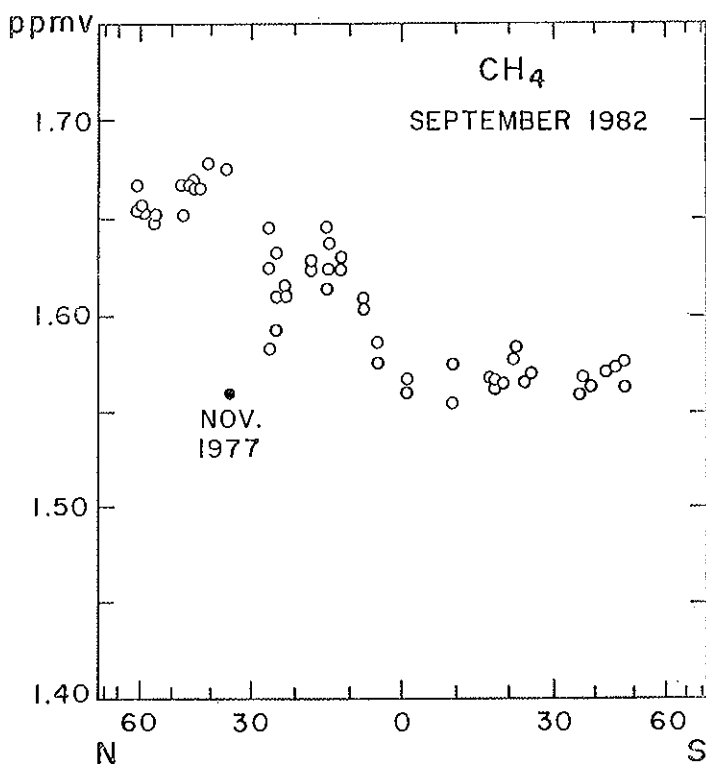


FIG. 5. Tropospheric Concentrations of  $\text{CH}_4$  Measured in Remote Locations during September 1982. Solid circle indicates concentrations in secondary standard collected in California desert, November 1977.

from the atmosphere by HO radicals in reactions (5) and (6). Correlations of these two yields as in Figure 7 led us to conclude that about 10% of the earth's  $\text{CH}_4$  was being emitted in the Amazon region [Mayer *et al.*, 1982], and that air samples collected in coastal sites in northeast Brazil did not contain actual background levels for  $\text{CH}_4$  but were elevated because of emissions from local sources. Our major latitudinal collections below  $20^\circ\text{N}$  have been made since 1982 in Pacific island locations.

The latitudinal distributions for  $\text{CH}_4$  shown in Figures 5 and 6 are quite different from each other, reflecting as with  $\text{CCl}_3\text{F}$  in Figures 1 and 2 appreciable seasonal changes in the transport of trace species from one latitude to another. Measurements at specific sites have shown variations of 3% in the monthly means in northern hemispheric locations [Khalil and Rasmussen, 1983], which complicate estimates of longer

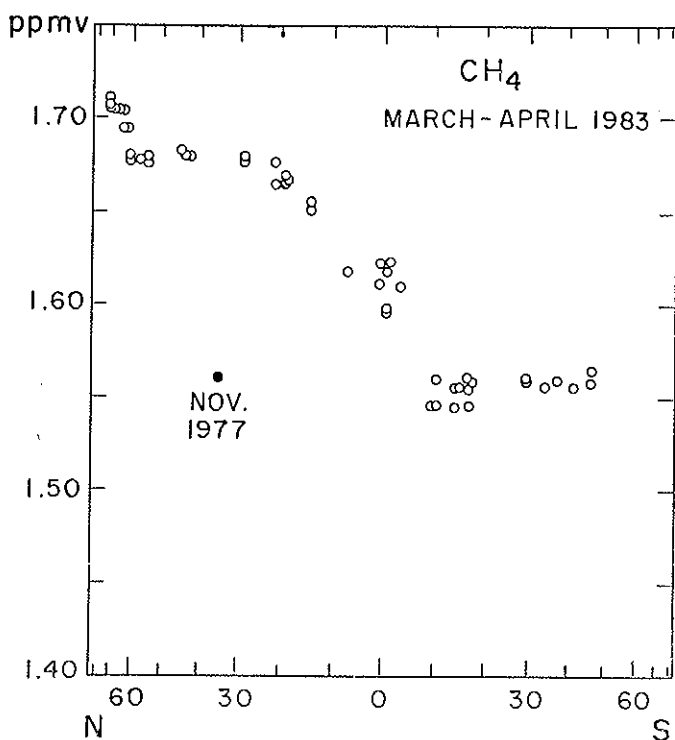


FIG. 6. Tropospheric Concentrations of  $\text{CH}_4$  Measured in Remote Locations during March/April 1983. Solid circle indicates concentration in secondary standard collected in California desert, November 1977.

term trends. We have therefore divided the surface area of the earth into sixteen segments of equal surface area (divisions at the equator, and at 7°, 14°, 22°, 30°, 49°, and 61° in each hemisphere) and calculated the average concentration of methane for each segment in each of eight collection periods beginning in January 1978. Air samples from the Amazon region, as illustrated in Figure 7, have been excluded, as have a few which simultaneously showed elevated levels for several of the halocarbons symbolic of recent urban emissions. Segments in the southern hemisphere left without valid samples have been filled by extrapolation from measurements made between 10°S-53°S. Average world-wide concentrations ob-

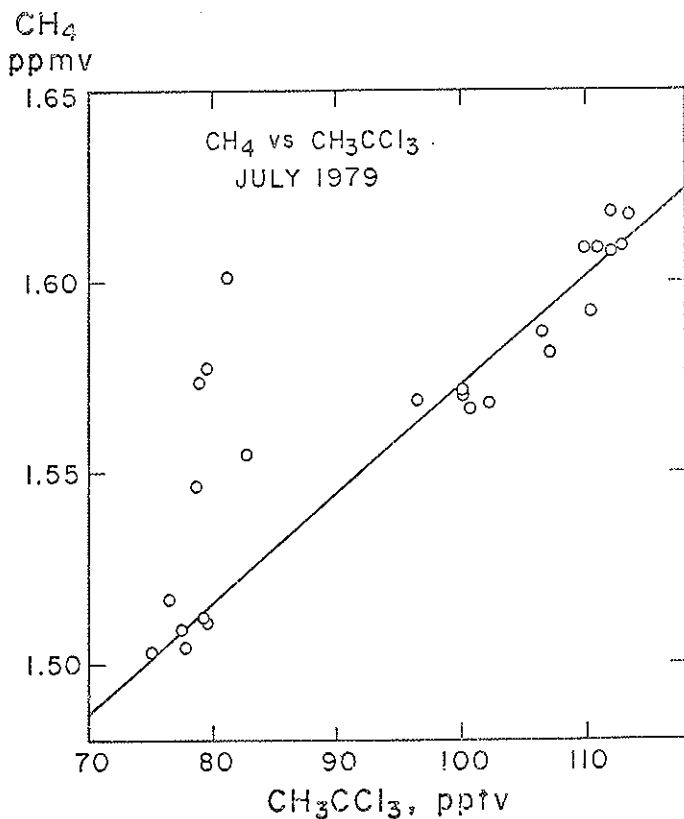


FIG. 7. Correlation of Concentrations of CH<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> Measured in the Same Tropospheric Air Samples Collected in Remote Locations during Summer 1979. The points not fitted by the correlation represent samples collected in the Amazon region of South America.

tained from the sixteen segment averages are graphed in Figure 8 for these eight time periods.

The world-wide tropospheric  $\text{CH}_4$  concentration has increased steadily during the time period since 1978, and this increase is well represented by the solid line in Figure 8 which corresponds to a rate of increase of 0.018 ppmv per year. The two dashed lines demonstrate increases of  $0.018 \pm 0.002$  ppmv per year, providing outer limits for the observed rate of change in concentration. These values correspond in the early 1980s to an increase of  $1.1 \pm 0.2\%$  per year, in general confirmation of the increases derived from shorter time series, although slightly less than the 1.4% per year calculated by Khalil and Rasmussen [1983]. The data are satisfactorily fitted with a straight line, and there is no indication

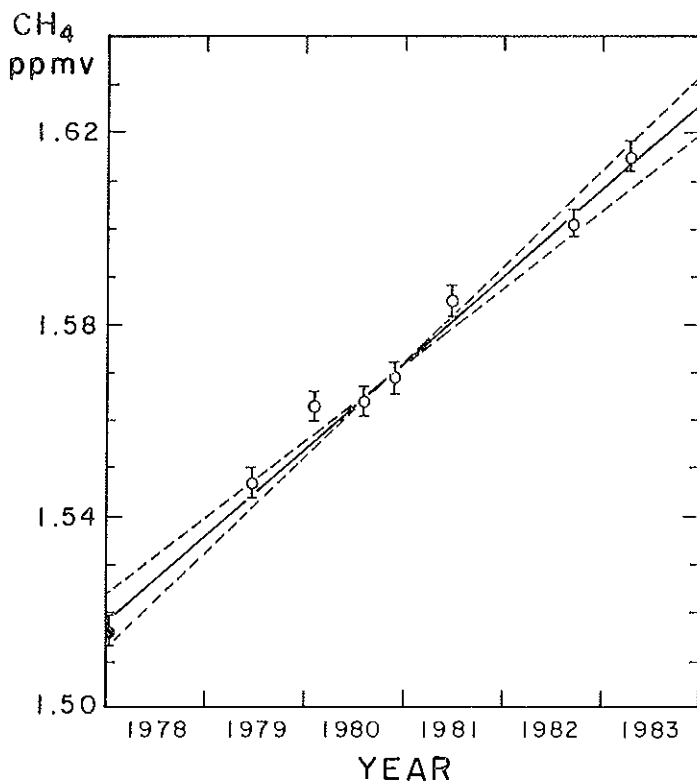


FIG. 8. World-wide Average Tropospheric Concentrations of  $\text{CH}_4$  Measured in Remote Locations, 1978-1983.

of any important change in the yearly rate of increase over the six-year period of measurement.

The atmospheric lifetime for  $\text{CH}_4$  can be estimated from that for  $\text{CH}_3\text{CCl}_3$  through the reaction rate constant ratio  $k_5/k_6 = 1.5$ , leading to an estimate of 9 to 10 years. We have calculated the expected latitude distribution for  $\text{CH}_4$  using (a) the transport parameters evaluated from the latitudinal distribution of  $\text{CCl}_3\text{F}$ ; (b) the latitudinal distribution of HO sinks from the distribution fitted to  $\text{CH}_3\text{CCl}_3$  in Figure 4; (c) an estimate that 72% of all  $\text{CH}_4$  is emitted in the northern hemisphere; and (d) assumed atmospheric lifetimes for  $\text{CH}_4$  of 7, 9, 10 and 13 years. These distributions are shown in Figure 9 in comparison with the  $\text{CH}_4$  concentrations

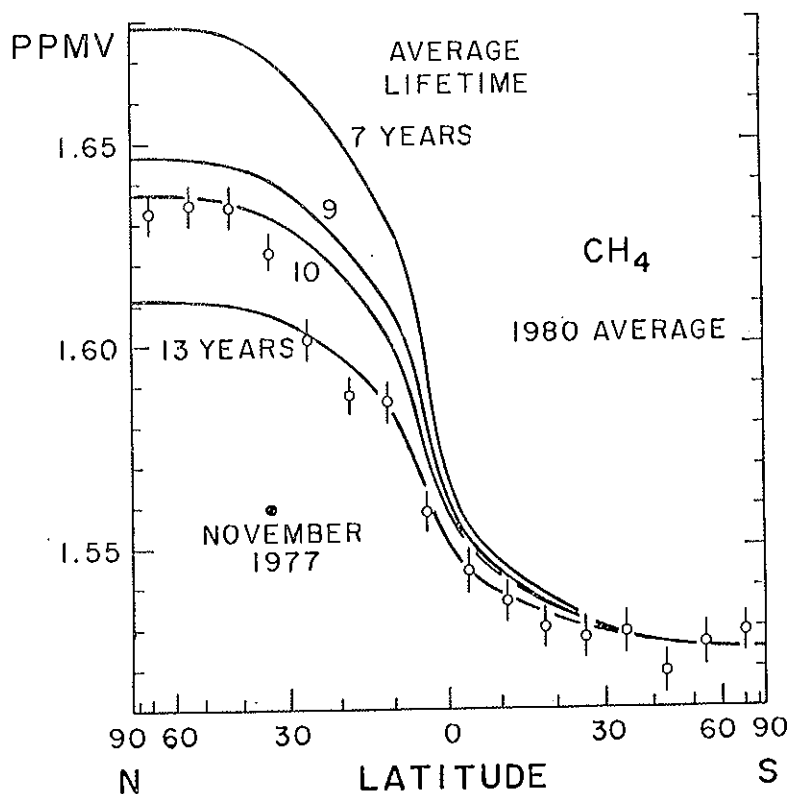


FIG. 9. Year-long 1980 Averages of  $\text{CH}_4$  Tropospheric Concentrations versus Latitude Compared with Various Postulated Atmospheric Lifetimes. Northern hemisphere emissions: 72%. Otherwise as in Figure 4.

have any evidence of olefins produced by other plants? Are they in such concentrations that can be interesting or not? We know that many fruits produce a great amount of ethylene.

ROWLAND

I think I'll defer this to Paul Crutzen. Paul, would you like to answer? He has considered this in more detail than we have.

CRUTZEN

There definitely are very large emissions of higher hydrocarbons from plants, including ethylene. This has been definitely discovered above the tropical forests in Brazil. The most active emissions are actually isoprene and the terpenes, but there are many other hydrocarbons which are chemically very reactive.

LIBERTI

I wish to add the following to what Professor Crutzen was saying. There are large amounts of terpenes which are emitted. However, they are terrifically reactive, especially with ozone, so that in order to measure them particular care has to be taken.

ANDERSON

I would like to resurrect the question that Dr. Chameides raised about the changing rate of oxidation in the troposphere. That to me is the central issue, and if we cannot partition this point between increasing production and decreasing rate of oxidation, what do you think is the approach that should be taken in order to determine what that spot is.

ROWLAND

The question is whether there is a measurement separate from the increasing concentration of methane that bears on this situation. I am not sure that the accuracy is sufficient to give information. Measurements have been made in Paul Crutzen's group in Mainz by Wolfgang Seiler. He has been measuring the concentration of carbon monoxide over an extended period of time, of the

order of a dozen years. The statement which he has made is that he has not observed a change in the carbon monoxide concentration. This is a very difficult statement to make with any accuracy because it is averaged over very substantial variations from one season to another every year. The concentration of carbon monoxide is also controlled by chemical reaction with hydroxyl radical. If the hydroxyl radical concentration has been reduced, then one should see an increase in carbon monoxide concentration that would parallel this increase in methane concentration. It is Seiler's view that his measurements on carbon monoxide do not show evidence for such a change. On the other hand, Rasmussen and Khalil have a paper in press — I received a copy about two months ago — in which they report that they are seeing an increase in carbon monoxide concentrations. Such an increase in carbon monoxide might be an indication of a reduced oxidative capability of the atmosphere.

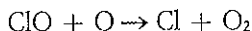
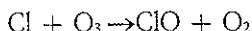


# ROLE AND FATE OF OZONE IN THE ATMOSPHERE

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## I. INTRODUCTION

A new dimension in global toxicology surfaced in the early 1970s with the introduction by Johnston [1] of the concept that rapid gas phase catalysis of ozone recombination to molecular oxygen by nitrogen oxides could alter stratospheric ozone concentrations. Not only did this provide a mechanism for reducing the atmosphere's ability to screen solar ultraviolet radiation, it also provided the means for disturbing natural patterns of heating and cooling in the upper atmosphere. In 1974, Rowland and Molina [2] presented their theory linking the surface release of fluorocarbons to the mid-stratospheric destruction of ozone by the catalytic reaction couplet:



Photolytic decomposition of the fluorocarbon molecule augments the natural concentration of the Cl and ClO radicals, thereby accelerating the "odd oxygen" (ozone plus atomic oxygen) conversion to O<sub>2</sub>.

That theory not only emphasized the importance of chlorine as a component of significant chemical importance to the unperturbed stratosphere, but also introduced the concept that the surface release of an inert and otherwise benign molecule, central to many aspects of our present society, could seriously deplete the concentration of a molecule

in the upper atmosphere which is solely responsible for screening the surface of the Earth from potentially harmful near UV radiation. The work of these scientists profoundly altered our perspective of the global significance of such releases.

Important alterations to the global distribution of stratospheric ozone are currently predicted by the best available models which synthesize the chemistry, radiation and dynamics of the middle atmosphere. While these predictions have fluctuated significantly since the first crude estimates were offered in the mid-1970s [3], progress in many fields has brought a growing realization that the stratosphere may well be the first natural system to submit to the scientific method.

This tractability depends upon a rather unique and fortuitous combination of time constants which results in characteristic chemical response times being considerably shorter than dynamical time constants for many of the key mechanisms. Experimentally this means that "pure" chemical experiments can be executed *in situ*, to test photochemical hypotheses on the microscale within the atmosphere. On the other hand, dynamical experiments addressing the longer time scales can be conducted from Earth orbit via satellite to establish vertical and meridional transport maps.

While evidence that the prognosis is encouraging for defining the scientific bounds of the global problem, the last decade of research has yielded mixed results. Attempts to understand the photochemical structure of the stratosphere at the level of detail required to predict trends in global ozone have challenged, and often found inadequate, large areas of our understanding of gas phase photochemistry and kinetics. The stratospheric data base on trace reactive species which control the course of the chemical transformations in the atmosphere has yielded critical secrets but is in a rather primitive state.

It is not our purpose to comprehensively review the aeronomy of the stratosphere with the requisite discussion of such topics as dynamical meteorology, geochemistry, biochemical cycles, etc. Rather, we seek to summarize our current understanding of the photochemical structure of the stratosphere by focussing on the free radicals which control the rate of transformation between different classes of reactants within the atmosphere. Achieving this objective involves a discussion of recent advances in the kinetics and photochemistry of free radicals, developments in modelling and in the measurement of free radicals in the stratosphere, and finally a means of interpreting these atmospheric measurements in the context of our present understanding of the stratosphere.

In the course of the review, several unique characteristics of the stratosphere will become apparent. We will identify examples of how the mechanistic details of a single reaction can dramatically affect predictions of stratospheric change into the next century. This is a particularly fascinating aspect of these studies — namely that while a reasonably complete (chemical) description of the stratosphere requires approximately 200 reactions, details of the reaction mechanism of a single process can alter predictions of global ozone depletion by more than a factor of three.

This sensitivity of conclusion to a single reaction coupled with the needed to distill a vast number of reactions into tractable subsets, the effect of which can be interpreted and tested by observations, restricts the strategy used to test models with field observations. We seek, therefore, to distill the orchestra of reactions into a few rate limiting steps to highlight which measurements must be made to test the mechanisms central to theories of global ozone depletion.

In the third section, we review recent developments in the field of atmospheric free radical observations so we can explore how effectively these experiments have tested our understanding of atmospheric structure. The fourth section summarizes this progress and then presents the latest predictions of global ozone depletion resulting from fluorocarbon release. Recent and important changes have been reported in this aspect of the problem.

## II. BREAKING DOWN THE REACTION SET

We first simplify the complete set of reactions needed to characterize the photochemical structure of the stratosphere, listed for reference in Appendix A, by classifying the reactants and products into three generic types: (a) "source" molecules which carry a given element to the stratosphere by upward diffusion from the lower atmosphere; (b) radicals which serve to scramble the chemical structure of the trace constituents while controlling the path and rate of transfer to (c) the "reservoir" molecules which are comprised of their terminal products of radical-radical recombination reactions. This last category is responsible for maintaining mass continuity for each element, by downward diffusion which matches the upward flux of the source molecule. Figure 1 summarizes this division superposed on a simple box model, indicating the spatial division between the surface, troposphere and stratosphere.

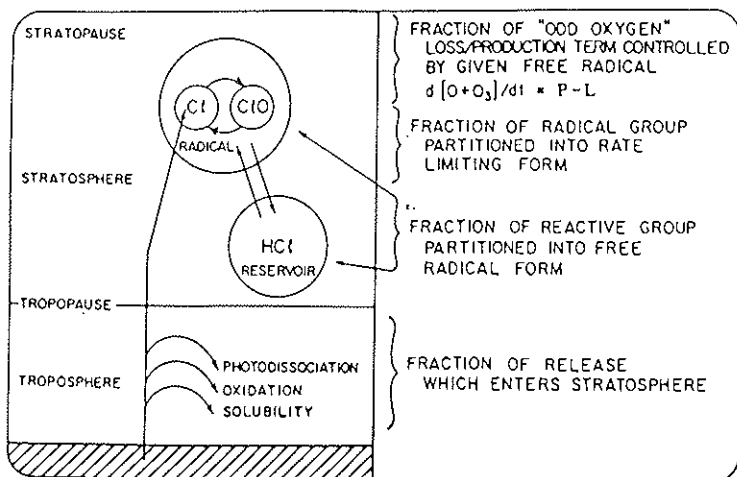


FIG. 1. Box model of the middle and lower atmosphere indicating the major removal processes for *source* molecules carried upward from the surface. The small complement of molecules which actually reach the lower stratosphere then become the precursors for free radical chain carrying reactions which are terminated by radical-radical recombination reactions to form *reservoir* molecules. Downward transport to the tropopause of these reservoir molecules maintains mass continuity.

Separation of reactants and products into the three categories, **SOURCE — RADICAL — RESERVOIR** is done both to abstract the pattern of change in the reaction network and to distinguish the different time constants associated with each category. The spatial division indicated in Figure 1 conveniently emphasizes the filtering between the stratosphere and the Earth's surface afforded by removal processes in the troposphere.

A vast proportion of the molecules released at the surface are rapidly removed by rain-out, oxidation, or photodissociation. In order to "qualify" as a source molecule, the release rate and tropospheric lifetime against removal by the three processes noted in Figure 1 must be such that a significant flux of molecules cross the tropopause. A significant amount of theoretical analysis and observational evidence (see WMO-82, NAS-84) has isolated those few molecules which are of quantitative significance to the photochemistry of the stratosphere. Those studies are summarized in Table 1 which classifies the major source molecules according to which free radical group each sustains. The mole fraction each comprises in the troposphere is also given. Rapid horizontal and vertical mixing in

TABLE 1 — *Major source molecules.*

| Free Radical Group                        | Source Molecule(s)               | Approximate<br>Mole Fraction Trop |
|---|----------------------------------|-----------------------------------|
| Oxides of Nitrogen<br>"NO <sub>x</sub> "  | N <sub>2</sub> O                 | 300 ppb                           |
| Oxides of Hydrogen<br>"HO <sub>x</sub> "  | CH <sub>4</sub>                  | 1700 ppb                          |
|   | C <sub>2</sub> H <sub>6</sub>    | 1000 - 1500 ppb                   |
|   | H <sub>2</sub>                   | 550 ppb                           |
|   | H <sub>2</sub> O*                | 5000 ppb                          |
| Oxides of Chlorine<br>"ClO <sub>x</sub> " | CH <sub>3</sub> Cl               | 650 ppb                           |
|   | CF <sub>2</sub> Cl <sub>2</sub>  | 300 ppb                           |
|   | CFCI <sub>3</sub>                | 190 ppb                           |
|   | CCl <sub>4</sub>                 | 130 ppb                           |
|   | CH <sub>3</sub> CCl <sub>3</sub> | 170 ppb                           |
| Oxides of Bromine<br>"BrO <sub>x</sub> "  | CH <sub>3</sub> Br               | 15 ppb                            |
| Sulfur, HS, HS <sub>2</sub>               | OCS                              | 510 ppb                           |

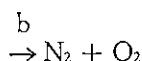
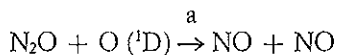
the troposphere maintains, to first order, an invariant (or volume mixing ratio) mole fraction throughout that region of the atmosphere.

A brief glance at Appendix A reveals that each of the reactions involves a free radical either as a reactant or a product. Before dividing the complete reaction set into groups, we trace through the network of transformations:



for the oxides of nitrogen, which is a paradigm for each of the reaction families. This will clarify the reasons behind our subsequent classification strategy.

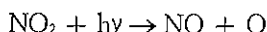
The primary fate of N<sub>2</sub>O in the stratosphere is reaction with O(<sup>1</sup>D) (photolysis occurs but is quantitatively insignificant). The branching ratio into products



and the absolute rate constant has received considerable attention in the laboratory [5].

Nitric oxide is added to the stratosphere by the oxidation of  $\text{N}_2\text{O}$  in a rather wide altitude interval, as indicated by the observed decrease in  $\text{N}_2\text{O}$  shown in Figure 2.

Release of NO into the stratosphere initiates a rapid sequence of exchange reactions which couple NO and its companion radical  $\text{NO}_2$  on time scales of minutes throughout the stratosphere by the reaction sequence



This sequence can be represented schematically by the diagram displayed in Figure 3.

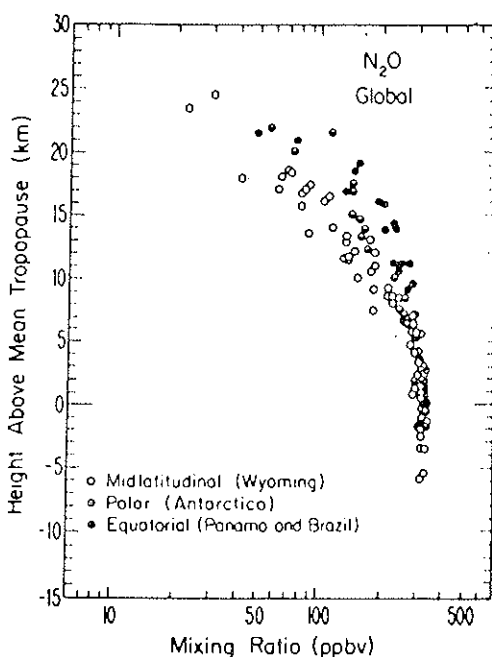


FIG. 2. Altitude dependence of  $\text{N}_2\text{O}$  in the stratosphere showing the oxidation of  $\text{N}_2\text{O}$  by  $\text{O}(^1\text{D})$  which yields NO.



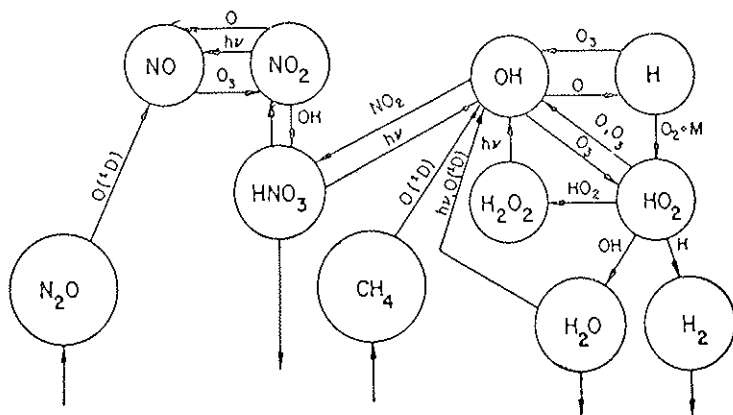
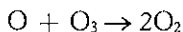
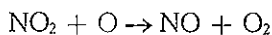
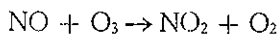


FIG. 5. Coupling of the  $\text{NO}_x$  radicals to the reservoir molecules  $\text{HONO}_2$  and  $\text{HONO}$ .

This completes the first order description of transfer reactions within the  $\text{NO}_x$  system. From this particular example we abstract the following characteristics which hold for all of the radical groups noted in Table 1.

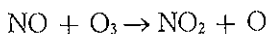
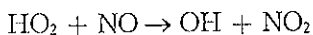
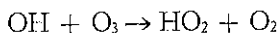
1. Irreversible destruction of the source molecules to initially form the free radicals, is a slow process compared with any other exchange reactions. Conversion from the source is matched at steady state by the downward mixing of the soluble reservoir term for "wash out" below the troposphere.

2. The cyclic nature of the exchange reactions within each radical system underlies the catalytic property of these transfer reactions. For example, the exchange between  $\text{NO}$  and  $\text{NO}_2$  catalyzes the reformation of the  $\text{O}_2$  bond at the expense of atomic oxygen and ozone

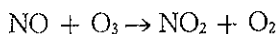
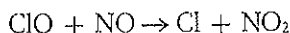
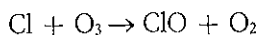


There are a significant number of other catalytic cycles which interconnect radicals and which interlink the various reaction families. For example, the conversion of  $\text{NO}$  to  $\text{NO}_2$  is catalyzed by the presence of hydrogen radicals





and incidentally by the presence of free chlorine radicals



3. Consideration of the transfer rates corresponding to each of the major steps within and out of/into the  $\text{NO}_x$  cycle, tabulated below as a function of altitude (where the  $k$ 's are bimolecular rate constants in units of  $\text{cm}^3 \text{sec}^{-1}$ , bracketed quantities are concentrations in molecules  $\text{cm}^{-3}$ , and  $J$  is the photolytic rate in  $\text{sec}^{-1}$  such that each tabulated quantity is in units of molecules/ $\text{cm}^3\text{-sec}$ ), underscores the fact that the conversion time within the radical group is dramatically shorter than the period for formation or removal and thus a steady state is established between  $\text{NO}$  and  $\text{NO}_2$ . Note also that from the point of view of ozone, there are two important reaction sets in the  $\text{NO}_x$  radical exchange which, when taken together, either constitute a null cycle or result in the reformation of 3 molecular oxygen bonds at the expense of two molecules of ozone. This last point begins to reveal why for the purpose of testing hypotheses of chemical links by observation of free radicals in the stratosphere, it is essential to break the full reaction complement into subsets which have a clearly defined objective of transforming compounds into or out of a given class of reactive compounds. For example, as used above, those reactions which transfer oxygen into and out of the "odd oxygen" pool, or those which transfer hydrogen into or out of the "odd hydrogen" class must first be isolated as a mechanism and then the rate determining step must be established.

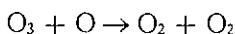
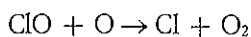
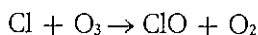
We close this section by summarizing the chemistry of chlorine and ozone in the Earth's stratosphere. There are three essential elements in the Rowland-Molina mechanism linking the release of fluorocarbons to the gas phase catalytic destruction of ozone in the stratosphere:

1. Release of the halogen substituted methanes, principally  $\text{CCl}_3\text{F}$

and  $\text{CCl}_2\text{F}_2$  (FC-11 and FC-12) into the atmosphere is followed by rapid mixing of the compounds throughout the troposphere. To a first approximation, there are no physical or chemical removal processes at the surface or in the gas phase throughout the troposphere. This fact was established by comparing integrated release rates with global measurements by Lovelock, whose shipboard observations as a function of latitude formed a cornerstone in the early formulation of the hypothesis.

2. The uniform mixing of the compounds throughout the troposphere increased the mixing ratio of chlorine at the tropopause and thereby the flux of chlorine compounds into the stratosphere. Vertical mixing continues above the tropopause although at a slower rate dictated by the permanent "temperature inversion" characteristic of the stratosphere, until the molecules reach an altitude where the penetration of solar radiation in the wavelength interval between the major absorption continuum/band system of  $\text{O}_2$  and  $\text{O}_3$  occurs. Photons in this interval are weakly absorbed and have sufficient energy to photodissociate both  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ ;  $\text{CCl}_3\text{F} + h\nu \rightarrow \text{CCl}_2\text{F} + \text{Cl}$  and  $\text{CCl}_2\text{F}_2 \rightarrow \text{CClF}_2 + \text{Cl}$  releasing atomic chlorine.

3. The principal fate of the chlorine atom released is reaction with ozone to form the chlorine monoxide free radical which in turn reacts with atomic oxygen to regenerate the chlorine atom thereby forming a homo-



geneous gas phase catalytic cycle amplifying the rate of odd oxygen destruction. Since (1) both reactions comprising the cycle are fast bimolecular processes and the couplet is completed on the time scale of tens of seconds, and (2) each chlorine atom resides in the stratosphere for a period of years, spending a significant fraction of that time in free radical form, it follows that an amount of chlorine orders of magnitude less than that of ozone can potentially alter the rate of ozone destruction in the stratosphere.

Figure 6 traces the major exchange reactions in the  $\text{SOURCE} \rightarrow \text{RADICAL} \rightleftharpoons \text{RESERVOIR}$  system. The dominant natural source of chlorine in the stratosphere is  $\text{CH}_3\text{Cl}$ ; the main synthetic contribution is from  $\text{CCl}_4$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ . Atomic chlorine and chlorine monoxide are

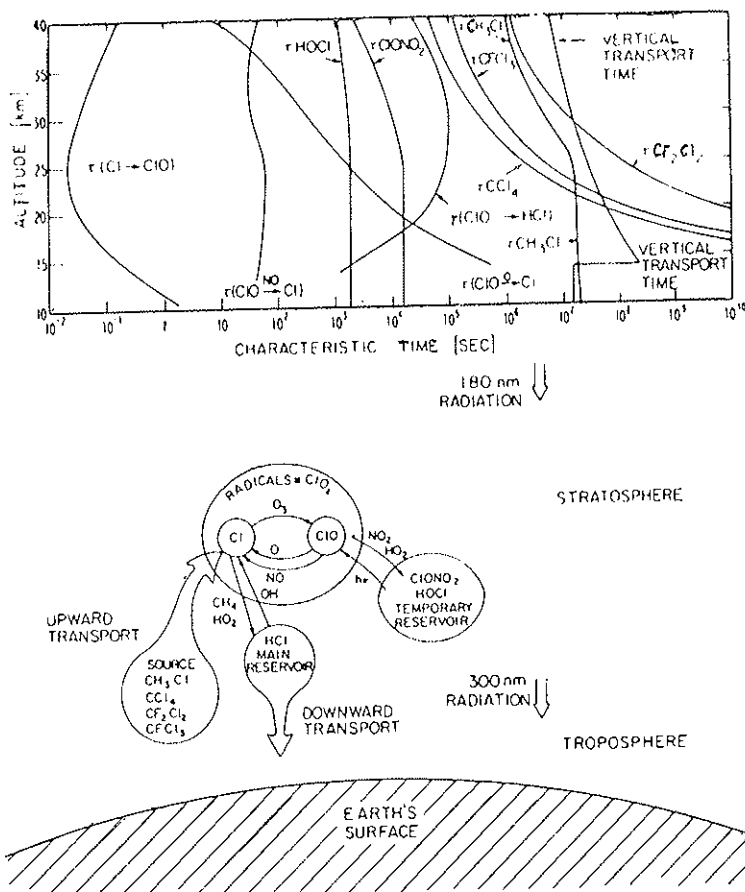
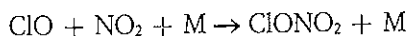


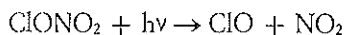
FIG. 6. Schematic of the chlorine reaction system in the stratosphere with an overview of the exchange times among the various subgroups of reactants.

the only important radicals. Exchange times between radicals and photolysis times converting the source molecules to free radicals are also summarized in Figure 6.

The dominant reservoir for chlorine in the stratosphere is HCl which diffuses downward to maintain Cl atom (bound and free) continuity. Two major temporary reservoirs (those molecules with a lifetime on the order of one diurnal period) are critical to the chlorine system. Chlorine nitrate, formed by the three body reaction

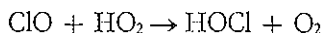


and removed by photolysis

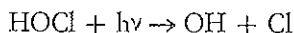


constitutes (1) a major nighttime storage tank for chlorine radicals, and (2) a critically important coupling term between the chlorine and nitrogen systems. That single reaction is predominantly responsible for the diurnal behavior of ClO, summarized at four different altitudes in Figure 7, taken from the most recent work by Ko and Sze [6].

The other major reservoir for chlorine compounds is HOCl, formed in the bimolecular reaction



and removed by direct photolysis



As Figure 7 implies, current theories suggest that while the altitude interval at and below 36 km is dominated by a diurnal exchange between ClONO<sub>2</sub> and ClO, above 40 km the exchange is dominated by a nighttime transition between HOCl and ClO.

The critical question, then, revolves on how the validity of these major hypotheses linking fluorocarbon release at the Earth's surface to (global) changes in stratospheric ozone can be established. There are five elements in the case linking CFC release to changes in stratospheric ozone:

Part. 1: *The CFC release rate and the rate of build up in the troposphere; are there significant losses other than upward transport to the stratosphere?*

The source strength for CFC induced stratospheric ozone removal is, of course, the tropopause mixing ratio for each of the CFC compounds. This must be known to extremely high precision at selected positions across the globe in order to predict steady state concentrations corresponding to a given release rate. Intensive analysis of the time dependence of these mixing ratios over at least a decade is critical in order to establish a lower limit on the atmospheric lifetime.

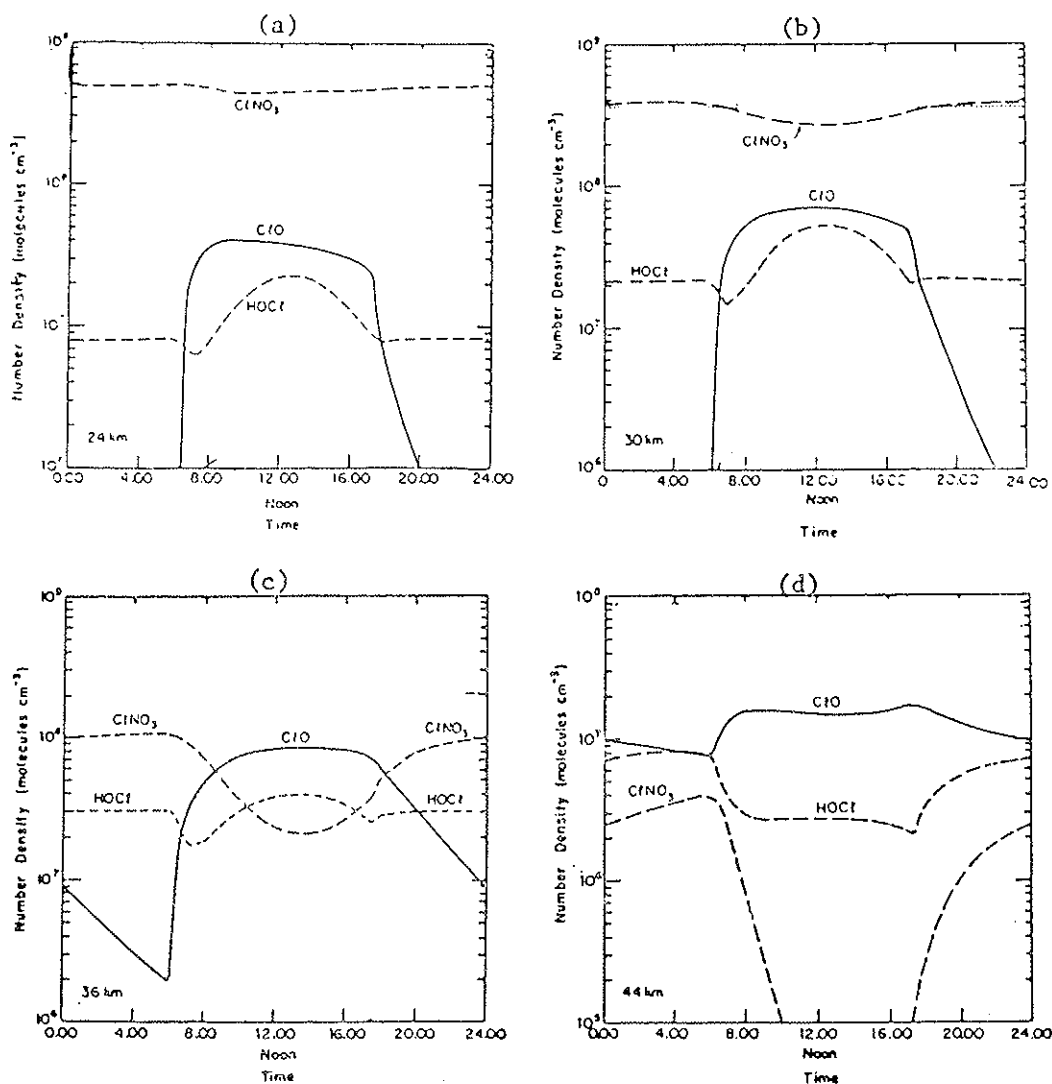


FIG. 7. Diurnal trace of the ClO, ClONO<sub>2</sub> and HOCl concentrations for 4 altitudes in the stratosphere; 24, 30, 36 and 44 km. Note the rapid but easily measured decay of ClO following sunset with considerably steeper decay rates at the lower altitudes reflecting the thermolecular behavior of the primary loss reaction  $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$ . In the altitude interval above 40 km, the dominant diurnal behavior is the day-night exchange between ClO and HOCl. Results are from reference 6 by Ko and Sze.

Part. 2: *The fraction of halogen atoms transported across the tropopause which enter the "bank" of stratospheric halogen compounds in the middle and upper stratosphere.*

The residence time for retention of compounds within the stratosphere increases very rapidly from a low and highly variable quantity in the region just above the tropopause, to a period approaching a decade in the lower-middle stratosphere. Thus the altitude at which CFC photolysis occurs can have important consequences concerning the transfer of halogen compounds into the chemical inventory of the stratosphere, which is in turn a measure of the effectiveness of converting industrially produced halogen into active participants in the stratospheric chemistry.

Part 3: *Partitioning of the halogen compounds among the reservoir, temporary reservoir, and free radical forms. Partitioning of total chlorine into the rate limiting free radical in the dominant catalytic cycle.*

Given that the bottleneck establishing the rate of chlorine-induced ozone destruction is, to first order, the concentration of the rate limiting chlorine free radical in the dominant catalytic cycle destroying odd oxygen, it is essential to establish the propensity of the stratosphere for partitioning total chlorine into the rate limiting radical form. This ratio of ClO to total chlorine as a function of altitude is a quantity of first order importance.

Part. 4: *Quantitative significance of the dominant rate limiting catalytic steps to the total loss rate of odd oxygen as a function of altitude in the stratosphere.*

Odd oxygen destruction rates are, of course, controlled by different free radical groups at different altitudes. The altitude dependent partitioning of the loss side of the odd oxygen budget among the hydrogen, halogen, nitrogen and pure oxygen components provides the first order test of whether current estimates of global ozone production and destruction balance. In addition, such an analysis, when based on observed radical concentrations, defines the altitude interval within which a predicted ozone change would first be observable. Of equal importance, however, is that one must have a solid quantitative understanding of rate limiting processes in the *present day* atmosphere before one can confidently predict future trends. Since those trends point, in the case of CFCs, toward large changes in what is presently a rather small term in the odd oxygen balance in a

limited altitude interval, establishing a detailed understanding of the dominant loss terms (i.e., the  $\text{NO}_2$  rate limited steps) is essential.

*Part 5: Chemical link between radicals and temporary reservoirs in the halogen system and the major catalytic processes controlling the rate of odd oxygen removal throughout the stratosphere.*

Although the direct contribution of the chlorine rate limiting step to the odd oxygen loss rate is obviously a critical quantity, of equal importance is the coupling between the chlorine radicals and the other catalytic cycles, most notably the nitrogen system. Given the overwhelming contribution to the total ozone column from the altitude interval between 20 and 35 km where the  $\text{NO}_x$  system dominates, the large changes in chlorine mixing ratios predicted for the next century, second order coupling may prove to be the dominant consideration. This is why the temporary reservoirs hold the key to important elements in our understanding of the system and why a thorough understanding of  $\text{HO}_x$ - $\text{NO}_x$  radical system in the middle and lower stratosphere is essential.

We turn next to the question of making those critical observations which will transform hypotheses, delineated in this section, to scientific fact. This step requires an approach of developing techniques used to make observations *of* and *within* the Earth's stratosphere.

### III. RECENT ADVANCES IN ATMOSPHERIC MEASUREMENTS

Although it has been more than a decade since the scientific community was alerted to the critical need for the development of a new generation of instrumentation to address the question of global ozone depletion, it is only recently that truly novel and powerful combinations of techniques have begun to appear in the literature. The most notable of these include: (1) ground and balloon-borne mm-wave emission techniques originally developed for radioastronomy applications [7]; (2) far infrared interferometric techniques which achieve spectral resolution adequate to detect part per trillion concentrations in the stratosphere [8]; (2) satellite based high-resolution ( $\sim 10^{-3} \text{ cm}^{-1}$ ) scanning interferometers with broad survey capabilities in the middle infrared and pressure modulated radiometry capable of mapping the global distribution of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  from Earth's orbit with vertical resolution corresponding to less than an atmo-

spheric scale height [9]; (4) metal atmo lasers and eximer lasers capable of detecting radicals at the part per trillion level *in situ* or by lidar from balloon platforms [10]; and (5) balloon-borne tether systems which provide repetitive vertical soundings of the stratosphere over 15 km height increments from the tropopause to the stratopause [11].

We present here only a sampling of the most recent data obtained by those techniques to demonstrate the emerging ability of sophisticated field experiments to challenge the more fundamental hypotheses linking chemical releases at the surface with global ozone depletion.

### 1. Ground based mm-wave emission spectroscopy

One of the most dramatic examples of concrete progress in the field of stratospheric chemistry has come from the work of de Zafra, Solomon, Parrish and coworkers, who adopted radio astronomy techniques to the detection of stratospheric free radicals. Three key reactive constituents have been examined: ClO emissions at both 204 and 278 GHz from a number of sites in the northern hemisphere, with a rapidly growing seasonal coverage and sufficient time resolution to examine the exceedingly important diurnal behavior of the stratospheric column; HO<sub>2</sub> at 266 GHz from the Mauna Kea, Hawaii Observatory; and H<sub>2</sub>O<sub>2</sub> at 270 GHz, again from the Mauna Kea site.

These observations have, first of all, provided the community with a truly independent way of observing the concentration of two critically important rate limiting radicals, ClO and HO<sub>2</sub>. The importance of having completely independent methods for establishing the concentrations of radicals in the stratosphere cannot be overstated. As Section II demonstrates, the scientific case linking chemical release at the surface to ozone depletion in the stratosphere is directly testable only if the rate of catalytic conversion can be checked by observing the rate limiting step in the catalysis cycle. A vastly strongly scientific case can be established given independently acquired data sets using entirely different methods.

Table 2 summarizes the present state of knowledge obtained via the balloon-borne *in situ* optical techniques of Anderson *et al.* [12], and the ground-based mm-wave emission techniques of Solomon *et al.* [7].

In order to critique the differences between these techniques at the  $\pm 30\%$  level, it is necessary to consider both latitudinal, seasonal, and diurnal variation, all of which tend to improve the absolute correlation between the measurements of ClO. Thus, while significant differences



TABLE 2 — *Average ClO column densities.*

| Site          | Period  | Observed<br>Line Frequency<br>(GHz) | Column Density<br>( $\times 10^{14} \text{ cm}^{-2}$ )<br>(30 to 51 km) |
|---------------|---|-------------------------------------|---|
| Massachusetts | January - February 1980   | 204                                 | $0.7 \pm 0.2$<br>$+ 0.15$   |
| Massachusetts | February 1981   | 278                                 | 1.1<br>$- 0.2$  |
| Arizona       | May 1981 (day)<br>(night)   | 278                                 | $0.7 \pm 0.2$<br>$0.15 \pm 0.04$  |
| Hawaii        | Oct (12m - 4pm) 1982  | 278                                 | $0.70 \pm 0.15$   |
|               | Dec (12m - 4pm) 1982  | 278                                 | $0.80 \pm 0.15$   |
|               | June (12m - 4pm) 1983   | 278                                 | $0.96 \pm 0.2$  |
|               | Dec (12m - 4pm) 1983  | 278                                 | $0.70 \pm 0.2$  |
| Texas         | Anderson <i>et al.</i> (noon)<br>7-flight average, excluding<br>07/28/76 and 07/14/77 | —                                   | 1.13  |

remain to be understood, the existence of ClO in the stratosphere at concentrations comparable to present predictions has been finally established. Such a critical step could not have been achieved with a single experimental approach.

Ground-based mm-wave emission techniques have recently provided definitive identification of HO<sub>2</sub> in the upper stratosphere, measurements which can be directly compared with previous *in situ* experiments [13]. Figure 8 presents those recent spectra. These observations can be used both to cross check *in situ* techniques, for which two have been reported, and to extend measurements of this key free radical above the maximum altitude attainable by balloons, specifically above 45 km. We thus find a critical combination of independent techniques with highly complementary temporal and spatial coverage evolving such that the vertical distribution of a key free radical will soon be established in the scientific literature.

Technology in mm-wave detection in the 200 to 400 GHz range has also advanced in the past three years to the point where temporal resolution from ground based observations has improved to such an extent that the diurnal behavior of several key radicals can be achieved. The most notable example is that by de Zafra ([14] who has reported vertical column ClO

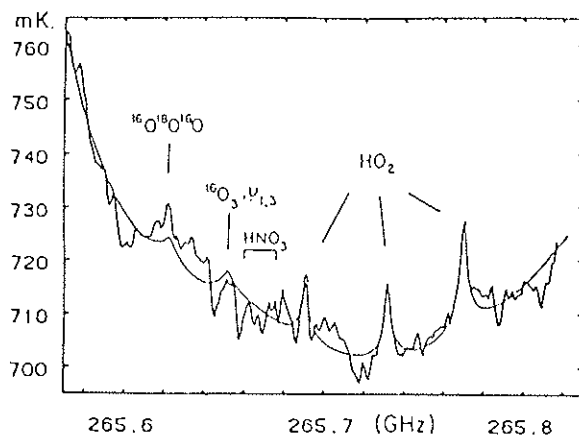


FIG. 8. Ground based mm-wave emission experiments of  $\text{HO}_2$  obtained by de Zafre *et al.*

observations tracked throughout a series of 24-hour surveys. These results have been compared with the most recent calculations by Ko and Sze to test both the model's ability to predict the absolute concentration of  $\text{ClO}$  and its ability to predict the diurnal behavior of  $\text{ClO}$ . Providing the first step is achieved, the latter test is obviously far more stringent for it examines independently the rate of  $\text{ClO}$  production independently from the rate of destruction. The results of that comparison are summarized in Figure 9.

Two research groups have developed Fourier transform spectrometers for high resolution balloon-borne emission observations of stratospheric trace species. Traub and Chance [15] of the Harvard-Smithsonian Center for Astrophysics have reported results on  $\text{H}_2\text{O}_2$ ,  $\text{HCl}$ , and  $\text{OH}$  obtained in the  $80$  to  $240\text{ cm}^{-1}$  spectral region at an (apodized) resolution of  $0.064\text{ cm}^{-1}$ . These results have contributed directly to reported literature values on  $\text{HCl}$ , and have placed an extremely restrictive upper limit on the stratospheric  $\text{H}_2\text{O}_2$  concentrations. Traub and Chance [16] have also reported preliminary results on  $\text{OH}$  in the critical altitude region between  $18$  and  $48\text{ km}$ . These results are particularly critical to advancement in the field because (a) the absolute calibration is direct and unambiguous and (b) observations can be obtained from a balloon platform at any time of the day or night, providing key diurnal data and, in addition, the flexibility to intercompare with other techniques.

A second research group, headed by Dr. Bruno Carli of the Istituto

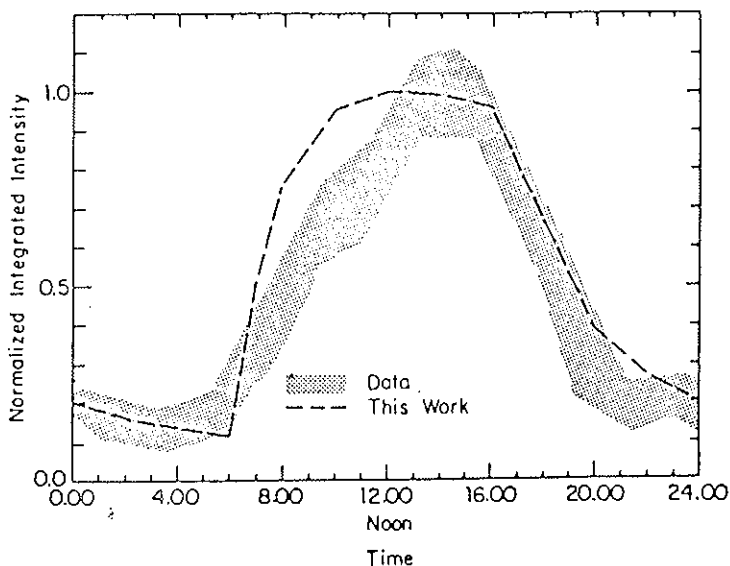


FIG. 9. Comparison between the normalized observed integrated intensity of the ClO emission from Solomon *et al.* and the synthetic intensity derived from calculated concentrations of ClO from Ko and Sze.

di Ricerca sulle Onde Elettromagnetiche IROE/CNR, Via Panciatichi, 56 - 50127 Firenze, Italy, have achieved a spectral resolution of  $0.003 \text{ cm}^{-1}$  in the  $20$  to  $40 \text{ cm}^{-1}$  spectral region using a balloon-borne Fourier transform interferometer. Preliminary results on both OH and ClO have been reported by this group [17]. The superb spectral resolution is a critical element in both the identification of lines and in the rejection of interfering spectral features to enhance the technique's detection threshold. In the next two years, results from the two groups will advance considerably the atmospheric chemistry community's grip on several key radicals.

## 2. Satellite-based high-resolution interferometers and radiometers

The first laboratory quality observations made from balloon platforms were middle infrared absorption experiments of trace atmospheric species using the sun as a source. This work has now been extended to shuttle and satellite-based observations using Fourier interferometers. The ATMOS instrument, developed under the leadership of C.B. Farmer and the NASA Jet Propulsion Laboratory, represents the flagship of this ef-

fort [8]. The proven spectral response of this instrument will provide global maps of HCl, HF, HONO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>, and a number of other important reservoir molecules.

Development of satellite-based pressure-modulated radiometer (PMR) techniques by the Oxford University [9] research team has now dramatically demonstrated the power of global maps of CH<sub>4</sub> and H<sub>2</sub>O for the interpretation and testing of two dimensional models. The first results of this work were reported by Jones and Pyle [9] in a comparison between satellite and *in situ* results using the Oxford two-dimensional model to interpret the results. A critically important extension of this work to include the relationships between methane and water vapor has been reported by Jones. The key concept in the work is that the sum  $[CH_4] + [H_2O]$  is a conserved quantity in the stratosphere so that global maps of methane can be used to deduce the water vapor composition of the atmosphere. This has critical implications for deducing free radical concentrations from satellite measurements.

The Oxford results have recently been used by Solomon and Garcia to examine the distribution of long-lived tracers and chlorine species in the middle atmosphere. This important paper has crystallized many of the issues relating to the hydroxyl and chlorine species, particularly the relationship between the variability in methane concentration and the variability in ClO. Figure 10 summarizes the correlation between the two-dimensional model of Solomon and Garcia [18] and the Oxford CH<sub>4</sub> maps. These results are then used to define the expected variability in local ClO concentrations reported by *in situ* observations.

### 3. *Metal atom lasers and excimer lasers for in situ and LIDAR detection of radicals.*

The critical need to achieve high signal-to-noise ratios for spatially resolved measurement of several free radicals has spawned a number of research efforts aimed at improving our ability to observe such radicals as OH, HO<sub>2</sub>, NO, NO<sub>2</sub>, etc., with orders of magnitude better sensitivity than was previously available. A major impetus behind this research has been the realization that atmospheric variability on the spatial scale of a hundred meters in the vertical drives fluctuations in several of the key reactive species, which provide ample concentration variation to carry out covariance studies to establish cause and effect within subsets of free radical reaction sets.

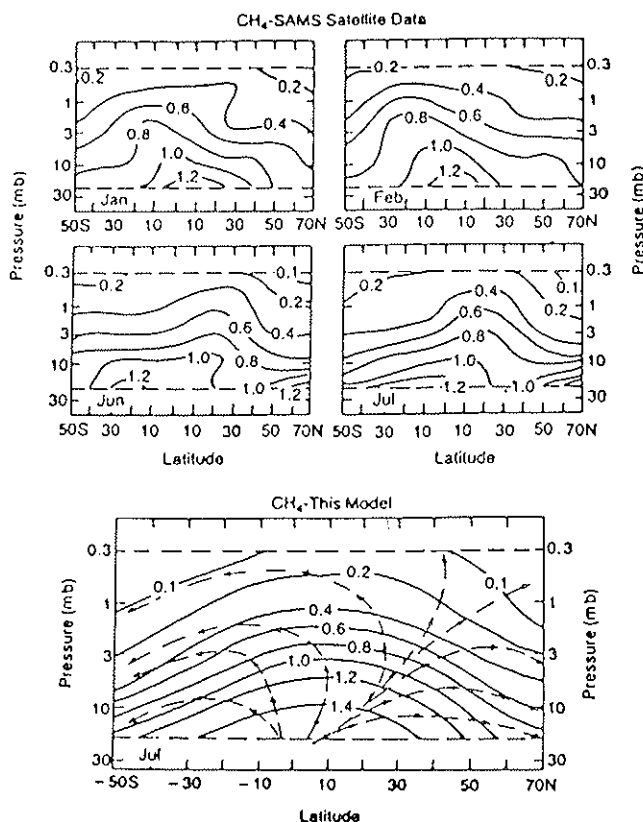
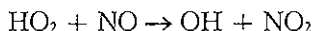


FIG. 10. Some monthly averaged observed distributions of atmospheric methane from the SAMS satellite, Jones and Pyle, near solstice conditions, compared to the model distribution for July by Solomon and Garcia. Light dashed arrows indicate the residual Eulerian stream function, showing the advection pattern.

Two groups within NASA, one at Goddard Space Flight Center, under the direction of Bill Heaps, and the other at the Jet Propulsion Lab under Laudenslager and McDermid, have respectively developed balloon-borne LIDAR methods for OH and developed eximer laser systems for extending the LIDAR method to lower detection thresholds. This research has important implications for both stratospheric and tropospheric research. Such laser ranging techniques also have important implications for intercomparison studies, particularly with mm-wave and far infrared emission experiments.

Another approach to *in situ* free radical detection has been developed

recently at the Harvard Center for Earth and Planetary Physics. That approach, summarized in Figure 11 employs a very high repetition rate copper vapor laser (20 kHz) to pump a dye laser which can be frequency doubled into the ultraviolet and tuned to one or more of the electronic absorption bands of OH, CH, NH, SH and NO<sub>2</sub>. The objective of this approach is to provide high power levels with low peak power levels to achieve low detection thresholds by avoiding (a) saturation effects caused by laser induced depopulation of the quantum level pumped, and (b) photochemically induced OH formed by photochemical reactions initiated within the sample by the interrogating laser pulse. By confining the measurement volume to a detection chamber, two additional objectives are achieved. First, all contributions from Rayleigh scattering of solar radiation are eliminated by optical baffling techniques, and second, the contained nature of the flow allows for the option of combining chemical conversion with resonance fluorescence. For example, detection of the HO<sub>2</sub> radical, which does not possess allowed electronic transitions between bond states, can be accomplished with the same hardware used to detect OH by using the rapid bimolecular reaction



to convert one radical to another with ease in the time scale of the experiment.

Hardware for both the LIDAR and the *in situ* method is either under development or has been field tested on balloon platforms. Within the next 18 months, these results will surface in the scientific literature.

#### 4. *Balloon-borne tether systems for repeated vertical scans obtained from a single balloon launch*

While previously obtained "snap shots" of the free radical concentration provided first order information on concentration regimes as a function of altitude, several drawbacks exist. Problems center primarily on adequate control over flow conditions, platform stability on a given flight, and, for the chemical conversion experiments (such as for ClO and HO<sub>2</sub> where nitric oxide was used to convert the radicals to Cl and OH, respectively), reactant gas mixing times.

Designated the "Reel Down" technique and depicted in Figure 12, a

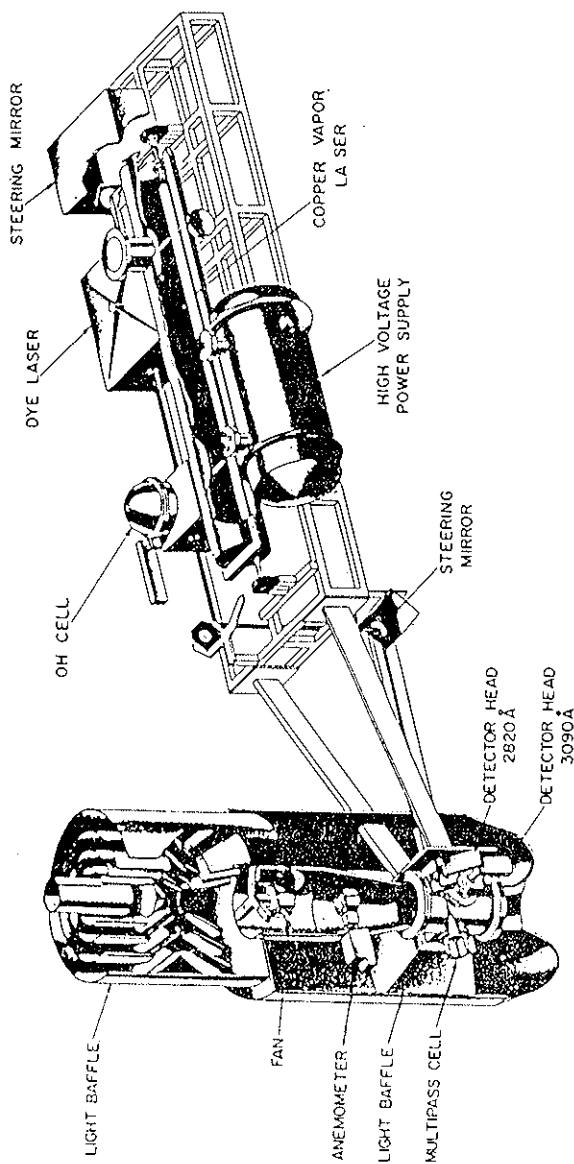


FIG. 11. Schematic view of the copper vapor laser pumped dye laser system developed at Harvard for the detection of OH and HO<sub>2</sub> radicals *in situ* from balloon-borne descent probes.

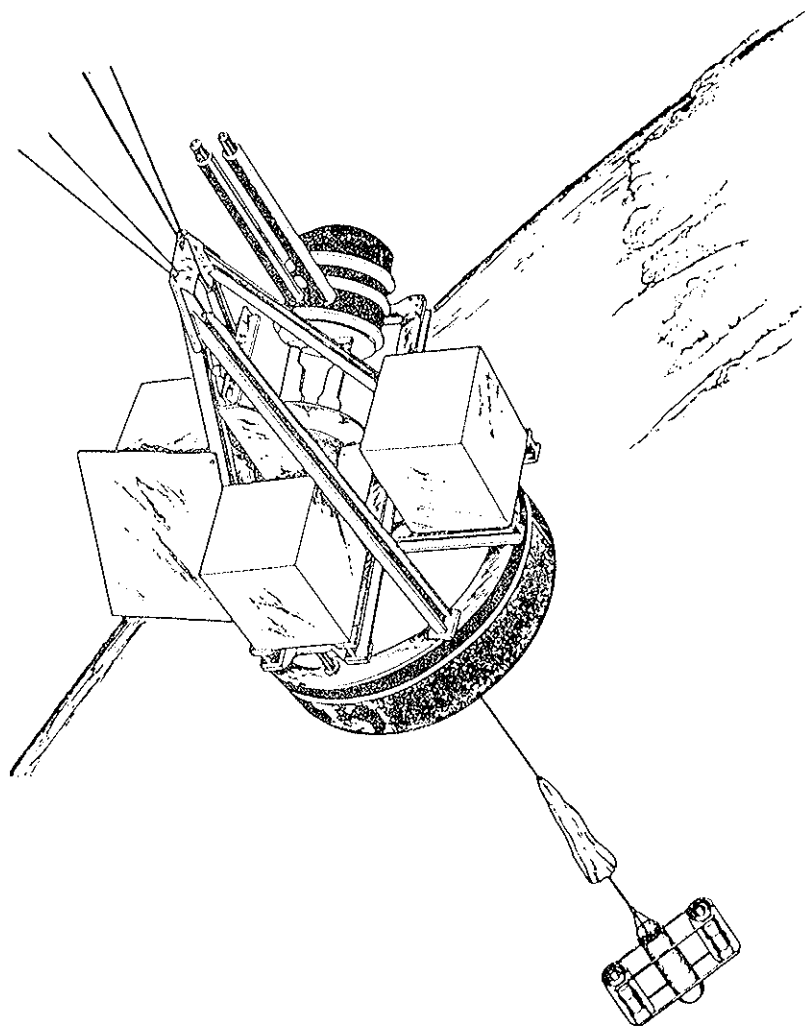


FIG. 12. Rendering of the Reel Down platform with associated suspended payload. This system is capable of vertical scans of greater than 10 km from a balloon floating at or below 40 km.

system was developed at the Harvard Center for Earth and Planetary Physics which consists of (a) a winching system borne by a helium research balloon to an altitude of  $\sim 40$  km (where the atmospheric pressure is approximately 2 mm Hg) and (2) an instrument cluster which is lowered on a filament of Kevlar a distance of 10 km or more, and then



retracted back to the winch station. Vertical soundings can be repeated several times for a given balloon launch.

Success of the Reel Down approach hinges on the stability of the system under stratospheric conditions (characterized by low pressures, but potentially large horizontal wind fields). Oscillatory motion developed in any axis of the suspended experiment cluster can compromise experimental control and thus the quality of the observations. A prototype system was constructed to test the feasibility of such a system in the stratosphere. Technical details are described in detail elsewhere [19].

The architecture of the individual instruments used to detect atoms and small free radicals by atomic and molecular resonance fluorescence or by laser-induced fluorescence is shown in Figure 13, but is discussed in detail elsewhere. Briefly, a nacelle, hollow through the core from nose to tail with an impeller in the anterior section, provides for the laminar flow of stratospheric air around and through the instrument. Detection of trace species is carried out at one (or more) optical axes within the nacelle. A major subset of the important stratospheric radicals can be detected using the configuration shown in Figure 13.

The first flight of the Reel Down system took place on 15 September 1982 from the National Scientific Balloon Facility in Palestine, Texas. When the balloon was properly positioned for the descent phase of the experiments, a pin locking the suspended instrument cluster to the winching system was pulled and the controlled descent phase was initiated by releasing a magnetically controlled brake. Descent velocity was selectable by command from the ground. A line velocity of  $7 \pm 1$  m/sec was used for the experiment reported here. A full treatment of mechanical and electronic systems, as well as the data analysis regarding the dynamics of the system, appears elsewhere [19].

Briefly, dynamical behavior of both the suspended payload and the winching platform were documented in real time by a combination of accelerometers, gyros, load cells, solar sensors and a downward looking video monitor on the winch platform. As the descent phase unfolded, several critical points became apparent:

1. Longitudinal oscillations of the system were observed at the expected periods ( $\sim 15$  seconds at 12 km extension) but the amplitudes were extremely small, typically  $< 1\%$  of  $g$ . Transients introduced by commanded power level changes damped rapidly. No evidence was observed for the presence of acoustical energy in the line.

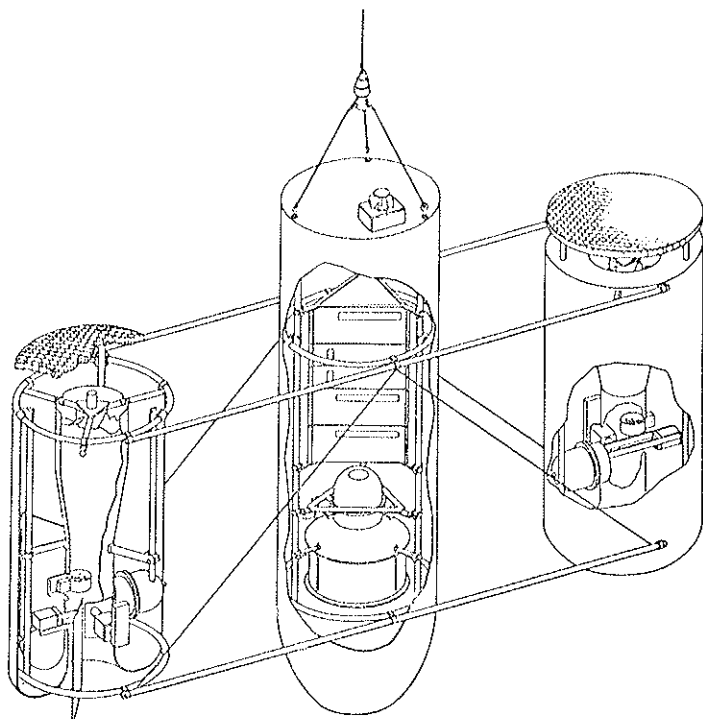


FIG. 13. Cross sectional perspective schematic of the suspended payload showing a cut-away of the detection nacelles with impeller driven flow through chambers, detection head and lamp modules used in the resonance fluorescence detection of radicals.

2. Around the azimuthal axis, the payload described one complete revolution for the remainder of the descent. Three revolutions were recorded in the opposite direction during the last half of the descent.

3. There was a virtual absence of pendulum motion and no measurable body centered perturbations developed. Data suggest a hang-off angle of  $4^\circ$  resulting from wind shear of  $\sim 7-9$  m/sec between the balloon float altitude and the position of the suspended payload at full extension.

This new approach will be used to examine:

1. The covariance between related free radicals and ozone to establish cause and effect;

2. The diurnal behavior of the major free radicals to establish the rate of production and removal of the dominant radicals; and

3. The conversion rates for one radical to another within the same family to establish whether current coupling schemes successfully describe the quantitative conversion rates between radicals.

In summary, the past four years have witnessed a virtual revolution in the technology of stratospheric free radical and trace specie detection techniques. Sensitivities unparalleled even in the laboratory are now becoming available. Of equal importance, there is now a manifold of totally independent techniques extending from the far vacuum ultraviolet to the radio region of the electromagnetic spectrum. This research will lock down the vertical concentration of the major free radicals within the next five years — placing our understanding of the stratospheric ozone layer on a profoundly more satisfactory foundation.

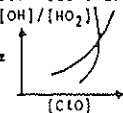
#### IV. PREDICTIONS OF FUTURE TRENDS IN STRATOSPHERIC OZONE: A REVIEW OF RECENT MODEL RESULTS

The history of nitrogen and halogen compound induced depletion of stratospheric ozone is replete with unpredictable changes in predicted ozone reduction figures. Every two years the National Academy of Sciences of the United States publishes a report summarizing the latest research on stratospheric ozone depletion and attempts to bound the range of predicted ozone depletion levels for steady state conditions based on present levels of fluorocarbon production. Those estimates, summarized in Table 3 below, have ranged from three percent to nearly twenty percent. These predictions are punctuated by large and episodic changes caused by inclusion of a single reaction or a change in one or a very few kinetic rate parameters.

Such oscillatory behavior does not give those concerned with translating a scientific position into legislative action a consistent vantage point. While we are all concerned, to one degree or another, with the vitality of the Earth's ozone layer, a far clearer picture of the alternatives must emerge before economically difficult decisions are warranted on an international basis.

How can the validity of these predictions be placed in perspective? What were the causes of past vacillations and are we in a significantly different position today? First, we consider what constraints existed in the period from 1974 to 1984 which could have limited the range of predicted depletion levels. Inspection of Table 3 reveals that the major

TAB. 3

| Year           | Predicted ozone depletion from CFMAs at steady state                      | Reason for Change  | Comment  |
|----------------|---|--|--|
| 1973           | 0   |  |  |
| 1974           | 10%   | Chlorine catalyzed recombination of ozone included in odd oxygen balance   | Mechanism change   |
| 1975           | 7%  | Refinement of Cl-C1O-HCl rate constants  | "Tuning" of existent calculations  |
| 1975-1976      | 15%   | Choice of rate constant for $\text{OH} + \text{HO}_2 \rightarrow$  | Significant impact on $[\text{OH}] + [\text{HO}_2]$ throughout stratosphere  |
| 1976-1977      | 6%  | Inclusion of $\text{ClONO}_2$ in calculations  | Mechanism change   |
| 1977-1978      | 16%   | Revision in $\text{HO}_2 + \text{NO}$ rate constant  | Dramatic shift in $[\text{OH}]/[\text{HO}_2]$<br> |
| 1978-1979      | 16%   | No major changes   |  |
| 1979-1980-1981 | 6%  | Rate constant revision<br>$\text{OH} + \text{MONO}_2 \rightarrow$<br>$\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow$<br>$\text{HO}_2\text{NO}_2 + \text{hv} \rightarrow$<br>$\text{OH} + \text{H}_2\text{O}_2 \rightarrow$<br>$\text{OH} + \text{HO}_2 \rightarrow$ | Dramatic change in $[\text{OH}] + [\text{HO}_2]$ in middle and lower stratosphere  |
| 1982-1983      | 4%  | Rate constant revision<br>$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$<br>$\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$<br>$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$   | Tuning of model  |
| 1984           | 4% until $[\text{ClO}]$ $[\text{NO}_2]$ sharp drop at higher $\text{ClO}$ | Titration of $\text{NO}_2$ from system by $\text{ClO}$ titration   | No change in mechanism, no change in rate constant   |

shifts in predicted ozone levels into the next century are directly reflected in shifts in model calculated OH profiles of the present day atmosphere. Figure 14 sketches this coupling between the calculated OH concentration throughout the stratosphere and predicted ozone depletion levels at steady state.

This provides us with the first major test of the validity of predicted ozone depletion figures — how well do the observed and predicted middle and lower stratospheric OH concentrations in the present atmosphere correlate? The conclusion is clear. There are no dependable middle and lower stratospheric OH observations. Thus, the exceedingly

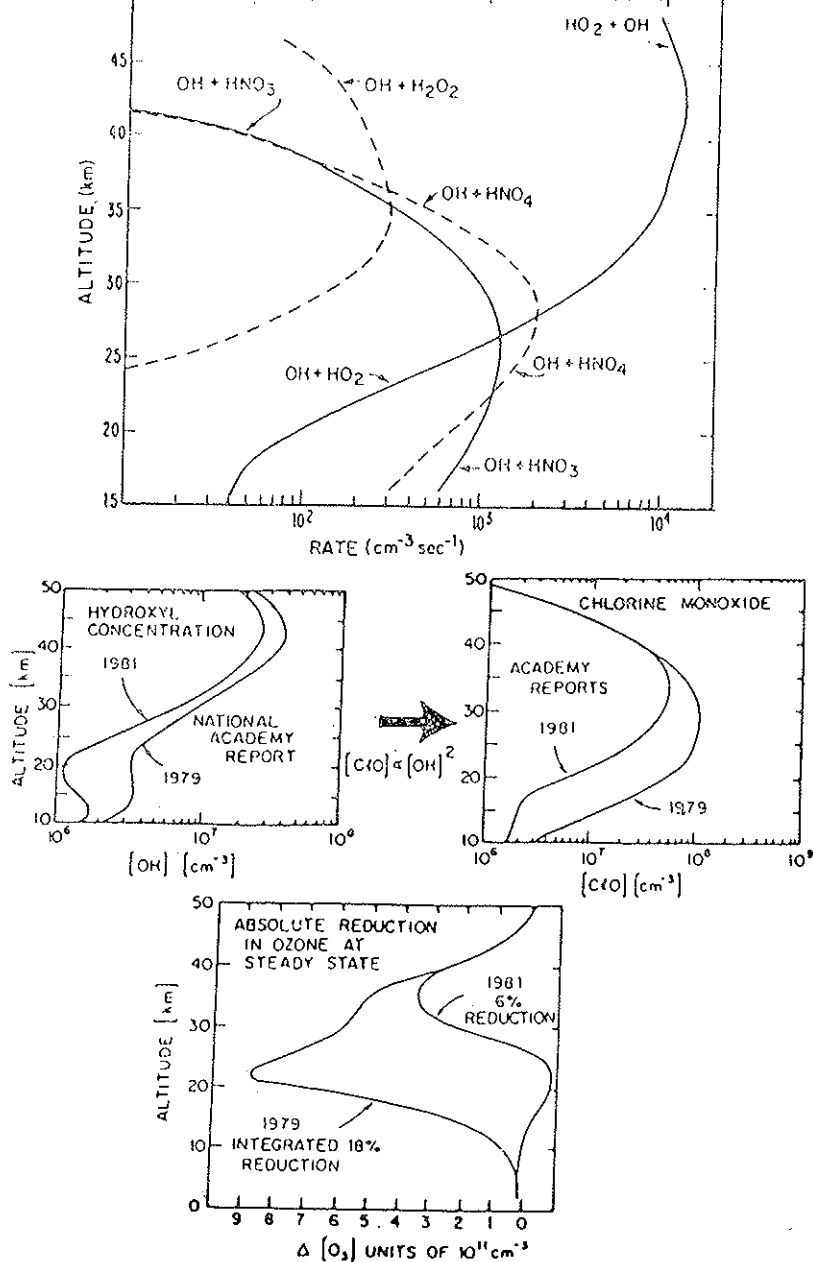
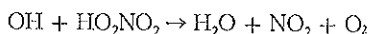
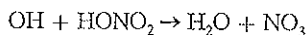
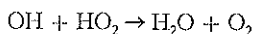


FIG. 14. Coupling between the  $\text{HO}_x$ ,  $\text{ClO}_x$  and ozone reaction systems shown as a sequence linking the assumed removal process for OH radicals in panel (a), dominated by the reaction set



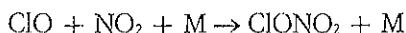
to the resulting concentration of OH in panel (b). OH profiles are shown with and without the nitric and pernitric acid removal mechanism for OH. The impact on the stratospheric distribution of ClO of changing the calculated OH concentration is shown in panel (c), and

important constraint remains untested. Within the next two years, however, the new observational techniques described in Section III will dramatically change this situation. Balloon-borne far-infrared emissions measurements from both the Traub *et al.* [16] and Carli *et al.* [17] research efforts will be available, as will balloon-borne LIDAR data from Heaps *et al.* *In situ* measurements of OH, HO<sub>2</sub> and H<sub>2</sub>O within the same volume element will be available from the Harvard group. These data, when taken together, will permanently eliminate OH as a free variable in stratospheric modelling, thus eliminating a major dimension of uncertainty.

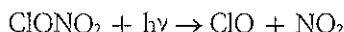
The second major test of model validity is the predicted distribution of ClO in the stratosphere. On this particular point, the data base is considerably stronger. *In situ* optical techniques, ground-based and balloon-borne laser heterodyne observations have reached the literature. There is substantial agreement between the first two data sets and a major controversy surrounding the latter two. Major technical advancements already achieved will bring to the scientific literature a consensus on this key point in the next two years. *In situ* methods have and will employ the Reel Down approach to vastly strengthen the quality of those observations; new detector technology has improved dramatically the signal-to-noise ratio of both the ground-based and balloon-borne mm-wave emission experiments; and laboratory calibration procedures will be incorporated into the laser heterodyne radiometer field preparation. Taken together, these experiments will solidify the data base on the mid latitude vertical distribution of the key rate limiting chlorine radical between the tropopause and the stratopause. The strictness of this constraint can be grasped first by recalling from Section II the fact that ultimately the bottleneck establishing the rate of chlorine catalyzed destruction of ozone is the reaction  $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$  so the establishment of the concentration of O and ClO quantitatively defines the ozone destruction rate by chlorine. The same point can be made in a somewhat different way by examining the last two panels of Figure 14, which shows the relationship between the percentage change in ozone as a function of altitude and the ClO concentration as a function of altitude. Firmly establishing the vertical distribution of ClO eliminates any proposed mechanism for ozone destruction which involves any change in the ClO distribution.

A third critical test for current ozone depletion calculations is the diurnal behavior of ClO as a function of altitude. Figure 15, taken from a recent treatment by Ko and Sze [6], summarizes the distinctive signature

of ClO concentration as a function of time and of altitude following sunset. This altitude-dependent decay of ClO following sunset defines with great precision the primary mechanism coupling the chlorine and nitrogen systems in the stratosphere because the removal of ClO at night occurs, it is believed, as a result of the thermolecular reaction



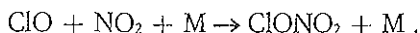
If this mechanism functions as it is currently believed to, both the observed rate of disappearance of ClO as a function of altitude (i.e., pressure) and the observed reappearance of ClO via the direct photolysis of ClONO<sub>2</sub>



must correlate with the calculations. Initial ground-based observations of the total column [ClO] confirms the general diurnal behavior. With both high time resolution and high spatial resolution afforded by the *in situ* techniques coupled with the Reel Down technique, the current picture can be tested with great precision.

While many other fundamentally important measurements can be described, we move on to review the most recent appraisals of ozone depletion levels because recent advances in the area have significantly changed our outlook on this subject.

With little doubt, the most significant change in our understanding of fluorocarbon induced ozone destruction, both qualitatively and quantitatively, since the Rowland-Molina proposition of radical catalyzed recombination of ozone by Cl and ClO in 1974, is described in a recent paper in *Nature* by Prather *et al.* [20]. What that paper defines is the dramatically non-linear dependence of ozone depletion on added chlorine at high levels of total Cl<sub>x</sub> = Cl + ClO + HCl + ClONO<sub>2</sub> + HOCl. The critical point is that at levels of Cl<sub>x</sub> approaching 15 ppbv, ClO "titrates" NO<sub>2</sub> out of the system via the previously described thermolecular reaction



Under conditions in which [ClO] ≥ [NO<sub>2</sub>], the photochemical structure of the middle and lower stratosphere undergoes a profound change. First the titration of NO<sub>2</sub> from the system takes all forms of NO<sub>x</sub> with it, specifically, NO and HONO<sub>2</sub> (see pages 345-349 of this report). This

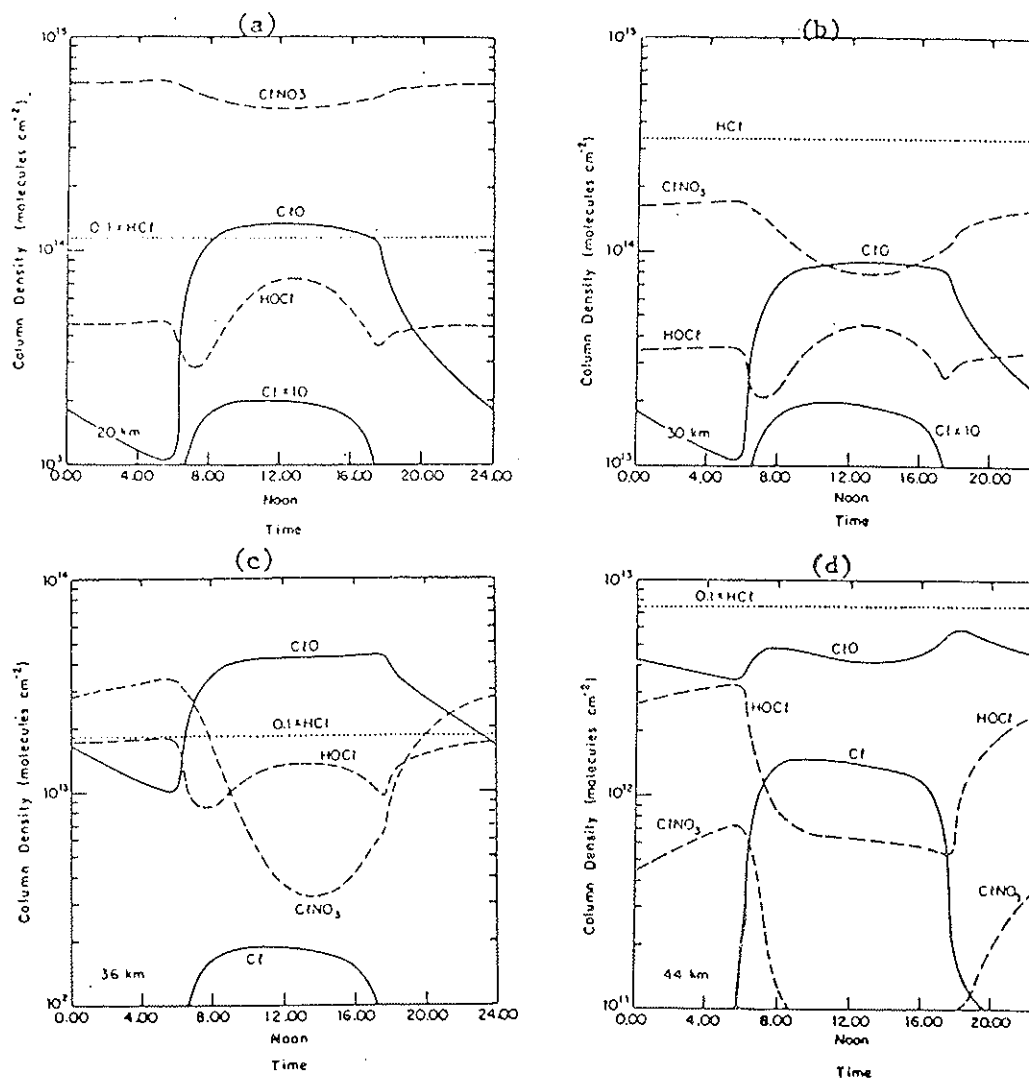
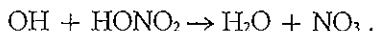


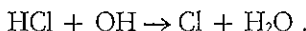
FIG. 15. The diurnal variation of the column densities of  $\text{HCl}$ ,  $\text{ClO}$ ,  $\text{Cl}$ ,  $\text{ClONO}_2$  and  $\text{HOCl}$  from Ko and Sze. Calculated values are for column abundances above 20 km, 30 km, 36 km and 44 km in panels (a), (b), (c) and (d), respectively. Calculations correspond to  $19^\circ\text{N}$  latitude for December conditions.



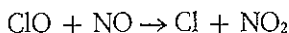
eliminates the major loss mechanism for OH below 30 km, specifically the reaction



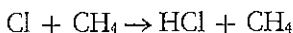
Significantly increased levels of OH act to shift the balance of inorganic chlorine, from the non reactive form, HCl, to the reactive radicals, Cl and ClO, via the reaction



Suppressed levels of NO act to block the conversion of ClO to Cl by the reaction



which both increases the ClO concentration directly and slows the removal of Cl radicals via the reaction



which is the dominant mechanism converting radicals back to the relatively non reactive form, HCl. Finally, enhanced levels of OH accelerate the oxidation of methane in the stratosphere and thereby suppress further the conversion of Cl and ClO to HCl by the above reaction.

Taken together, the effects are profound. Figure 16 from the Prather *et al.* [20] paper summarizes the dependence of column integrated ozone on total Cl<sub>x</sub> for three different mixing ratios of NO<sub>x</sub>: 13, 16.2, and 19.5 ppb by volume. The asterisk denotes the point at which the ozone column has dropped by 10%.

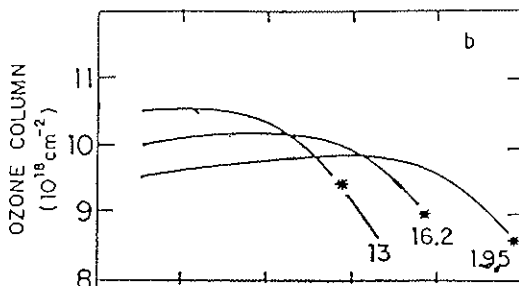


FIG. 16. The column abundance of ozone as a function of stratospheric chlorine for three assumed mixing ratios (by volume) of  $\text{NO}_x = \text{NO} + \text{NO}_2 + \text{HONO}_2$  taken from Prather *et al.*

Note that very little change in total  $O_3$  column occurs over a broad range of  $Cl_x$  mixing ratios, but that once  $[ClO] \approx [NO_2]$ , a very rapid decrease is predicted. The delay between now and the time at which we approach this titration condition is summarized in Figure 17. At a rate of increase of 3% per year, the 16 ppbv level is reached in the middle of the next century. Quite clearly, the issue is not academic since the world is moving in a direction such that a 3% per year increase may well be conservative. We quote directly from the conclusion of Prather *et al.*:

In summary, our models suggest that growth in release of chlorinated and brominated halocarbons can pose future problems for stratospheric  $O_3$ . There are reasons to believe that the chemistry of the lower stratosphere might undergo a significant change if the concentration of chlorine were to rise above that of  $NO_x$ . The concentration of OH could increase markedly and ozone could drop, with reductions potentially larger than 15% in the column density of  $O_3$ . Ozone is expected to remain relatively constant prior to the onset of the  $NO_x$  to chlorine transition below 30 km. It is important to monitor not only the total column density of  $O_3$ , but to search also for evidence of change in the chemical composition of the lower stratosphere.

The large effects predicted here occur primarily below 30 km and involve major changes in the chemistry of radicals such as OH and ClO. Observational data for these species are totally inadequate at lower altitudes and are urgently required to test the validity of current models in a region containing the bulk of atmospheric  $O_3$ .

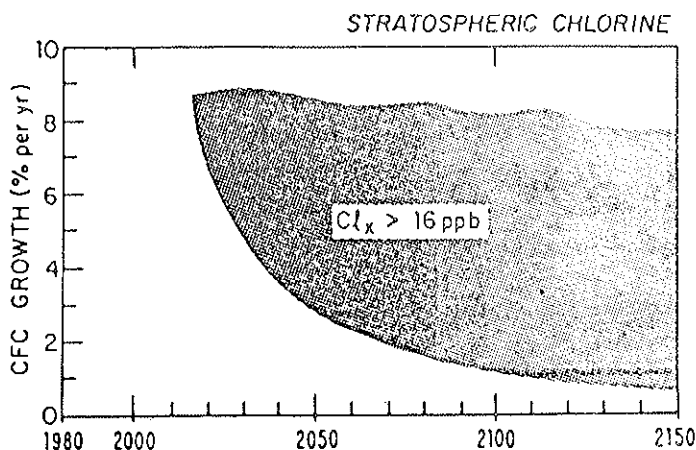


FIG. 17. Relationship between the rate of increase in fluorocarbon production and the year at which the stratosphere will exceed 16 ppbv of  $Cl_x$ .

The present results are based on a one-dimensional model. They should be extended to consider variations of stratospheric chemistry with latitude and season. Extension of the model to more than one dimension may be particularly important in studying the impact of high concentrations of chlorine since results should depend sensitively on details of the calculated latitudinal distributions of chlorine and  $\text{NO}_x$ .

Investigations of the radical chemistry of the stratosphere have focused in past on the region above 30 km. It is clear that the emphasis must shift now to lower altitudes.

Perhaps the most profound turn of events introduced by the Prather *et al.* paper is the fact that these conclusions are simple, robust and testable. They depend only on the amount of OH and ClO present in the middle and lower stratosphere and on the coupling between ClO and  $\text{NO}_2$ , all directly testable using the techniques discussed in Section III.

We conclude by noting that while the subject of chemically induced changes to the ozone layer have been surrounded by uncertainty and by controversy, we stand on the edge of a series of major advances which will establish a far more profound scientific underpinning for this subject. It is now believed by students of this subject that the stratosphere may well be the first natural system of global extent which will submit to the scientific method.

## APPENDIX A

1.  $O(^1D) + N_2 \rightarrow O(^3P) + N_2$
2.  $O(^1D) + O_2 \rightarrow O(^3P) + O_2$
3.  $O(^1D) + N_2O \rightarrow NO + NO \rightarrow N_2 + O_2$
4.  $O(^1D) + CH_4 \rightarrow OH + CH_3$
5.  $OH + CH_4 \rightarrow CH_3 + H_2O$
6.  $OH + CO \rightarrow CO_2 + H$
7.  $CO + O + M \rightarrow CO_2 + M$
8.  $O(^1D) + H_2O \rightarrow OH + OH$
9.  $O(^1D) + H_2 \rightarrow OH + H$
10.  $O + OH \rightarrow O_2 + H$
11.  $H + O_3 \rightarrow OH + O_2$
12.  $OH + O_3 \rightarrow HO_2 + O_2$
13.  $HO_2 + O_3 \rightarrow OH + 2O_2$
14.  $O + H_2O_2 \rightarrow O_2 + H_2O \rightarrow OH + HO_2$
15.  $H + H_2O_2 \rightarrow H_2 + HO_2 \rightarrow OH + H_2O$
16.  $H + HO_2 \rightarrow H_2 + O_2 \rightarrow OH + OH$
17.  $H + O_2 + M \rightarrow HO_2 + M$
18.  $OH + OH \rightarrow H_2O + O$
19.  $O + HO_2 \rightarrow OH + O_2$
20.  $OH + H_2 \rightarrow H_2O + H$
21.  $O + H_2 \rightarrow OH + H$
22.  $OH + H_2O_2 \rightarrow HO_2 + H_2O$
23.  $OH + HO_2 \rightarrow H_2O_2 + O_2$
24.  $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
25.  $N + O_2 \rightarrow NO + O$
26.  $OH + HCl \rightarrow H_2O + Cl$
27.  $Cl + H_2 \rightarrow HCl + H$
28.  $H + HCl \rightarrow Cl + H_2$
29.  $O + HCl \rightarrow OH + Cl$
30.  $Cl + O_3 \rightarrow ClO + O_2$
31.  $Cl + Cl + M \rightarrow Cl_2 + M$
32.  $ClO + NO \rightarrow Cl + NO_2$
33.  $ClO + O \rightarrow Cl + O_2$
34.  $ClO + NO_2 + M \rightarrow ClONO_2 + M$
35.  $O + ClONO_2 \rightarrow \text{products}$
36.  $OH + ClONO_2 \rightarrow \text{products}$
37.  $H + Cl_2 \rightarrow HCl + Cl$
38.  $O + Cl_2 \rightarrow ClO + Cl$
39.  $H + ClO \rightarrow OH + Cl$
40.  $Cl + H_2O_2 \rightarrow HCl + HO_2$
41.  $Cl + HO_2 \rightarrow HCl + O_2$
42.  $ClO + HO_2 \rightarrow HOCl + O_2$
43.  $OH + HOCl \rightarrow H_2O + ClO$
44.  $Cl + CH_4 \rightarrow CH_3 + HCl$
45.  $OH + CH_3Cl \rightarrow \text{products}$
46.  $OH + CH_3CCl_3 \rightarrow \text{products}$
47.  $OH + CH_2O \rightarrow HCO + H_2O$
48.  $N + NO \rightarrow N_2 + O$
49.  $O + NO_2 \rightarrow NO + O_2$
50.  $O_3 + NO \rightarrow NO_2 + O_2$
51.  $H + NO_2 \rightarrow OH + NO$
52.  $O_3 + NO_2 \rightarrow O_2 + NO_3$
53.  $O + NO + M \rightarrow NO_2 + M$
54.  $O + NO_2 + M \rightarrow NO_3 + M$
55.  $NO + NO_3 \rightarrow NO_2 + NO_2$
56.  $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$
57.  $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$
58.  $N + NO_2 \rightarrow N_2O + O$
59.  $OH + HNO_3 \rightarrow H_2O + NO_3$
60.  $HO_2 + NO \rightarrow OH + NO_3$
61.  $N + O_3 \rightarrow NO + O_2$
62.  $OH + NO + M \rightarrow HNO_2 + M$
63.  $O + HNO_3 \rightarrow OH + NO_3$
64.  $H + HNO_3 \rightarrow H_2 + NO_3$
65.  $O + O_2 + M \rightarrow O_3 + M$
66.  $O + O_3 \rightarrow O_2 + O_2$
67.  $O + O + M \rightarrow O_2 + M$
68.  $NO + NO + O_2 \rightarrow NO_2 + NO_2$
69.  $NO_2 + NO_3 + M \rightarrow N_2O_3 + M$
70.  $N_2O_6 + M \rightarrow NO_2 + NO_3$
71.  $N + OH \rightarrow NO + H$
72.  $N + O \rightarrow NO + hv$
73.  $H + H + M \rightarrow H_2 + M$
74.  $NO + O \rightarrow NO_2 + M$
75.  $OH + HNO_3 \rightarrow H_2O + NO_2$
76.  $HO_2 + NO_2 \rightarrow HNO_2 + O_2$

77.  $\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2\text{NO}_2$
78.  $\text{HO}_2\text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2 + \text{NO}_2$
79.  $\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{NO}_2$
80.  $\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$
81.  $\text{CH}_3\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$
82.  $\text{CH}_3\text{OO} + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$
83.  $\text{CH}_3\text{OO} + \text{CH}_3\text{OO} \rightarrow 2\text{CH}_3\text{O} + \text{O}_2$
84.  $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$
85. soluble gas  $\rightarrow$  precipitation scavenging ( $\text{CH}_3\text{OOH}$ )
86.  $\text{NO} + h\nu \rightarrow \text{N} + \text{O}$
87.  $\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3$
88.  $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$
89.  $\text{HNO}_2 + h\nu \rightarrow \text{OH} + \text{NO}$
90.  $\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$
91.  $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^1\text{D})$
92.  $\text{NO}_3 + h\nu \xrightarrow{1} \text{NO} + \text{O}_2 \xrightarrow{2} 2\text{NO}_2 + \text{O}$
93.  $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$
94.  $\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$
95.  $\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH}$
96.  $\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + \text{H}_2$
97.  $\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}$
98.  $\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$
99.  $\text{CH}_3\text{OOH} + h\nu \rightarrow \text{CH}_3\text{O} + \text{OH}$
100.  $\text{HO}_2 + h\nu \rightarrow \text{OH} + \text{H}$
101.  $\text{H}_2\text{CO} + h\nu \rightarrow \text{HCO} + \text{H} \rightarrow \text{H}_2 + \text{CO}$
102.  $\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$
103.  $\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$
104.  $\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}$
105.  $\text{ClNO}_3 + h\nu \rightarrow \text{ClO} + \text{NO}_2$
106.  $\text{CCl}_2\text{F}_2 + h\nu \rightarrow \text{CCl}_2\text{F} + \text{Cl}$
107.  $\text{CCl}_3\text{F} + h\nu \rightarrow \text{CCl}_2\text{F} + \text{Cl}$
108.  $\text{CCl}_4 + h\nu \rightarrow \text{CCl}_3 + \text{Cl}$
109.  $\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3 + \text{Cl}$
110.  $\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{CH}_3\text{CCl}_2 + \text{Cl}$
111.  $\text{HOCl} + h\nu \rightarrow \text{OH} + \text{Cl}$
112.  $\text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{OH} + \text{NO}_3$
113.  $\text{BrONO}_2 + h\nu \rightarrow \text{Br} + \text{NO}_3$
114.  $\text{BrO} + h\nu \rightarrow \text{Br} + \text{O}$
115.  $\text{HOBr} + h\nu \rightarrow \text{OH} + \text{Br}$
116.  $\text{Br}_2 + h\nu \rightarrow \text{Br} + \text{Br}$
117.  $\text{CH}_3\text{Br} + h\nu \rightarrow \text{CH}_3 + \text{Br}$
118.  $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$
119.  $\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$
120.  $\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{HBr} + \text{HO}_2$
121.  $\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$
122.  $\text{O} + \text{HBr} \rightarrow \text{OH} + \text{Br}$
123.  $\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$
124.  $\text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2$
125.  $\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2$
126.  $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$

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## DISCUSSION

KNABE

I have two questions: the story or the depletion of the ozone has been of great concern in the last years, and I missed in your paper the present judgment on this. You showed differences in ozone reduction from 16 or 18 to 6% or 8%. Does it have any meaning? That would be the first question. The other question: I have had many discussions with industrialists, politicians etc. and they use the example of ozone and of fluorocarbons as proof that warnings of scientists to do something or to stop the use of certain chemicals are meaningless, and not really justified. In your opinion, the warning of the National Academy of Science has it been justified?

ANDERSON

I would comment that arriving at one number and holding to that number in an area of this complexity is not a reasonable expectation and it is not the way the subject unfolds. The uncertainties associated with this fluorocarbon-ozone question remained in the region from 4 to 20% for a number of years and as you could gather from the discussion, the scientific issues are to this day unfolding. Now to address the first aspect of your problem briefly, if you detect a rate-limiting free radical in the catalytic cycle that is destroying ozone by virtue of the increasing concentration of the parent molecule that drives that rate of the free radical, then you in fact are at a point where the complexities of the dynamics of the atmosphere are eliminated from the problem. But if you take the next step back and ask: well, why has the projected number oscillated from 5% to 18% back to 10%, you find the reason for that in the concentration of the free radicals which are producing ClO rate-limiting free radical from the chlorine bank that exists in the middle stratosphere. If the observations of the ClO were believed in 1979 and the ozone depletion from that rate-limiting distribution was calculated it would in fact have been 6%, just as it is now in the model calculations when superposed on the rate-limiting free radical. So the changes in the projected percentage decrease in ozone, — in large measure the data on which any reasonable man would base those projections — have in fact not changed. Now, after saying that, I am the last person to say that the subject is finished, because there are significant issues

to be resolved here and we cannot expect a topic of this complexity to center in on a conclusion and then not have it deviate. For example, I am extremely interested in getting to the bottom of this discrepancy between the laser heterodyne absorption measurements of ClO and the in situ emission experiments because if there is no ClO in the atmosphere there is no fluorocarbon.

#### HARE

The speed at which things go in this business means that those of us who are on the fringes of it are always out of date, because by the time you have mastered the chemistry of 1979, you have replaced it with the chemistry of 1983. So let me ask this question. There has been a great deal of emphasis here on ClO and on the role of chlorine in the ozone depletion but years ago from Paul Crutzen I learned the lesson that it was the nitrous oxide of the stratosphere and not Sherry Rowland's halocarbons that really held the control of the thing. Joking aside, the upfluxing molecules that do the damage — or do the necessary control, — what are they? They are water vapor, they are methane, clearly they are synthetic halocarbons, but what is left of the statement that I had learned a few years ago that perhaps the major control is that due to  $N_2O$  on its way up?

#### ANDERSON

The question is very well placed and I did not address the issue of nitrogen because of the time limitations and also we do not have a good method of detecting the rate-limiting radical in the nitrogen, but as soon as we do of course at least a third of the talk will be on this fellow here. The importance of the nitrogen system globally is established by remote measurements of  $NO_2$ . 75% of the global destruction of ozone is a result of the nitrogen catalytic cycle that Dr. Rowland showed yesterday. And the reason it is so crucial to the nitrogen system, to the chlorine system is that when we begin to talk about ozone depletion levels resulting from the release of chlorine, we have to be very, very careful about the coupling of chlorine into the step that forms  $NO_2$  as the non-linearities in the system at low ozone depletion levels from one family reaction can couple into another family and have a reverse effect. That is fairly important and you can see the hint of that in the distribution I showed of chlorine oxide-ozone destruction as a function of altitude, where the curve showed actually more ozone at certain levels resulting from the intrusion of chlorine compounds, and that comes from the coupling between the chlorine



and the nitrogen system. So, as we begin to approach smaller and smaller numbers in the chlorine system, we have to understand the chemistry of stratosphere ozone in the main to a much higher level in order to extract a good projection of ozone depletion into the next century.

#### CRUTZEN

I wanted to clarify here maybe a little more about what Jim said. The different catalytic species have their different domains in the atmosphere where they are active and the oxides of nitrogen are the most active between 25 and 45 kilometers, where they mainly control the levels of ozone. Below 25 kilometers the oxides of hydrogen start to come back into a major role, and at about 45 kilometers the oxides of hydrogen, like OH and HO<sub>2</sub> do the job. And in between chlorine is doing a little bit here and there, and it is of course increasingly doing its work. The main source of the oxides of nitrogen in the stratosphere is oxidation of N<sub>2</sub>O leading to NO. Very important to consider in this whole issue is not only the total ozone changes which are taking place. I think what has not changed very much in the past regarding predictions of ozone depletion is what is happening around 35, 40 kilometers. Chlorine oxides are breaking down ozone — I think we have not changed our opinion there. What has changed is our feeling or understanding of what is happening below 35-30 kilometers, where most of the ozone is, and that will be a major problem in the future. It is my understanding from a recent study we did in the last years, that there are still major problems bringing the production of ozone and the destruction of ozone below 35 kilometers into agreement is, in my opinion, a large surplus of ozone production if one uses current for the chemical processes. Now coming back to total ozone, total ozone is not the entire issue. We may well see in the future a redistribution of ozone showing higher levels in the atmosphere, about 35 kilometers or 30 km., to lower levels, and then one gets into the questions regarding climatic changes. When the total ozone issue gets better, normally it is compensated by more worries about the climatic issue.

#### ROWLAND

The comparison that Jim showed between 1979 and 1981, the depletion of ozone at the altitude of around 40 kilometers was almost unchanged, that down around 20 kilometers one has the change from a substantial loss to an appreciable gain of ozone. One then has to ask why one is worried about a

change in the ozone concentration in the atmosphere, and if your only concern is the penetration of ultraviolet radiation to the surface of the earth, where it could have a biological effect, then it does not make any difference whether the ozone is at 35 kilometers or at 20 kilometers. So that then you are interested only in the total column of ozone. If you are concerned about what was just said, that to the extent that you may be altering the stratospheric temperature structure, then the increase of ozone at a lower altitude tends to make much worse the fact that you have decreased it at a higher altitude. These two effects are making the possibility of temperature structure change and possible climatic change more important, and so as we move back and forth between having a lot of depletion at 25 km. and making ozone at 25 km., this shifts it toward climatic change. I think we ought also to look at what has been observed in the atmosphere as well because there are two papers going around now — one I think is just published and one is in press in the *Journal of Geophysical Research* — which are measurements of the ozone at an altitude around 40 km. Both of these papers are concerned about the measurements with the Dobson instrument from ground level. And each of these papers says that there has been a decrease in the concentration of ozone at the layers which correspond to the 40 km level. The significance of the 40 km. level is that is the altitude at which the models have now for nearly ten years predicted that the effect of chlorine would be the greatest; and so the observation that there is a decrease at the altitude for which the chlorine effect is predicted to be greatest comes close to being a confirmation of ozone loss in the stratosphere at the predicted level, confirming the over-all hypotheses not in the microscopic level, that Anderson is talking about here, but in the total loss of process in the atmosphere itself.

One of the complications that is occurring in this is that the measurements of tropospheric ozone, at least in some locations, are showing substantial increases. Since most of the ozone is not in the troposphere, a substantial increase in the troposphere represents a small increase in the total amount of ozone, and it is quite possible that the summation of a tropospheric increase and a stratospheric decrease end up giving you a negligible change overall at least at the location where that measurement is being made. This again takes you back to asking the question of what your concern is and if it is ultraviolet penetration, then again it does not make any difference where the ozone is. It is my feeling that the rearrangement of the temperature structure of the atmosphere is probably the more important effect.

FIOCCO

In a document which is being circulated in draft the question of the ozone was written down in the sense that the total effect would be one that we would not have to worry about, and this question of the adjustment in climatic changes of course is very important. So I think that those that have a chance of seeing this document should be very well aware of the way in which it has been written. It seems to me that if we compensate the effect in the stratosphere with the effect in the lower stratosphere, then we have emptied the question completely.

HARE

In wishing to pose that awkward question, I forgot to say what must I think be in all of our minds, that is to express appreciation for not only the extraordinary development of experimental technique that has made possible these soundings — I mean the transformation that is being wrought is quite extraordinary to anyone who is not in daily touch with it. And secondly, to thank not only the last speaker, but two or three speakers that have preceded him, for the clarity with which it is being done. It really has been a revelation.

LIBERTY

I have many data about the ground ozone concentration as chemists are working in the ground concentration. My question is the following: usually we have a very low ozone concentration, which is around 40 ppb, which goes up in summer to 100, 150. Now we are considering the first figure as due to the diffusion from the ozone layer, and the other one to the photochemical smog, which brings to the action of ozone. Is this a correct attitude or not?

ANDERSON

Well, the ozone concentration in the absence of the local smog contribution, it is my strong feeling that at that level the ozone is not produced in the stratosphere but is of chemical origin, driven primarily by the natural hydrocarbon oxidation cycles, as Chameides talked about yesterday. The large increase on that of course is the photochemical contribution, and there are a lot of mechanisms involved in that production term. So I do not know how far you want to dive into this question at this time. The ozone that you find in the upper troposphere may in isolated cases come directly from the strato-

sphere, and certainly globally integrated ozone in the troposphere has a component from the stratosphere, but when you get down to the ground that you are discussing, that is not a major contributor.

PHILIPS

It seems very clear from what is being said that climatic changes may be more important than total UV reaching the earth's surface. Is anyone prepared to speculate just how much redistribution has to take place to see specified climatic changes? I mean can anyone quantify what we would expect to see from a redistribution?

ANDERSON

That is a very difficult question. I would not comment on that. It is an extremely delicate question.

ROWLAND

When I spoke in Munich in 1981, the German industrial people sent a man down to ask a number of questions. And one of the statements which he made at that time was that the carbon dioxide problem is going to disrupt the atmosphere so badly that it does not make any difference what else we put into it. This I think probably goes along with the attitude expressed by Dr Knabe, or rather by people that had spoken to him: that the only way that you can judge whether something is a problem, in the American vernacular the term is "Wait until we see the bodies in the street, and then we will admit that we have a problem". I think the fact that we are putting something into the atmosphere, which is accumulating over a very steady period of time and will be there for the next hundred years, is by itself already a serious problem, that you put in something which is so long-lasting that looking into its long-term effects is something that we have to be very much concerned about. And the other is the fact that the models are now predicting that there will be only about a 6% loss. I am not sure that I believe the models of the middle atmosphere that well that I am ready to say that there is not going to be a change in total ozone. And I guess the reason that I think about it in this way is that the place which I think is one of the best or maybe the best ozone measurement station in the world is at Arosa in Switzerland. They have the longest record; they have been measuring total ozone for more

than 50 years, and they keep a 50-year average, and it varies quite a bit, but their yearly average has not been up to their 50-year average since about 1971. Now, the fact that the ozone over Arosa has been low for about 10 or 12 years relative to where it has been for 50 years may be just an accident of the location in Arosa, but it may also be that the measurements at many other stations which are not of equivalent competence to the ones at Arosa that are being averaged in with them are giving the misleading interpretation. It is not clear to me that we are not seeing a total ozone change as well.

#### CRUTZEN

I did not want to leave one of the questions totally unanswered, about the climatic impact of ozone changes in the stratosphere. I cannot from the top of my head give you numbers, but they are sizable and they are being considered in different reports by say, the Academy of Sciences in the U.S. or in the Meteorological Organization report which came out two years ago. Other problems related to climate exist regarding tropospheric ozone and the direct impact of fluorocarbons especially on climate. Even in the troposphere the accumulation of fluorocarbons at steady state will lead to a temperature increase by, if I remember correctly, some 3/10ths of a degree Celsius, but maybe Professor Revelle will present these numbers today later.

#### ROWLAND

There is one other comment that I think I would like to add here. It has to do with the climate and the temperature structure of the stratosphere, and this again is the report of Dr. Angel, that the measurements of the temperature in the stratosphere at the altitude of the stratopause have shown a drop over the decade starting at about 1970 or 1971, of about 5°C. It is a measurement made as the average of about 1000 measurements every year. And the temperature *has* dropped at the stratopause over that period of time. For unexplained reasons, and with I am sure the total consequence of that not evaluated, I have not seen a satisfactory explanation of the drop nor an evaluation of what the consequences of it would be.

#### KNABE

I would like to ask another question. We are measuring at some German stations high ozone concentrations all day and night in areas about 100 or

200 kilometers apart from the industrial areas. All measurements many years ago show a peak in the day and a sink at night, this was attributed to the elimination of ozone by reaction with NO. In the remote areas, we do not have this NO during the night-time. My question is: shouldn't we have some OH radicals or some other mechanisms to reduce this high ozone concentration?

ANDERSON

First, the chemical environment under the conditions described is a result of the isoprenes and hydrocarbons released in the forest and is dependent more on the hydrocarbon chemical cycles than on the NO<sub>x</sub> cycles.

CHAMEIDES

The classical picture of course is that ozone in continental regions disappears at night because the boundary layer is capped and the ozone gets removed at the ground. In the absence of NO remissions, it is rather difficult to remove ozone chemically as well, though actually it is rather surprising that the ozone does not vary at night and perhaps you are not getting a good capping on the boundary layer.

FIOTTO

I would like to say something about the importance of the measurements in this ozone issue. If we compare the amount of money spent on space and satellite instrumentation — numbers that I do not know — I guess that we will come out with a rather unbalanced ratio, considering in the end that what we rely upon is always the Dobson measurements to a large extent. This network was designed about 40 years ago, and since then very little measurements of cross-sections have been made, so I would say that (a) it would be very important to complement each Dobson measurement with stratospheric measurement, because otherwise it is not possible to make a correction properly. You have always to guess what the stratospheric ozone does to your measurements — so the two instruments should really go together. One should have a laser Dobson situated in the same place where the Umker measurements are to be made. There is no question that perhaps the Umker technique itself could be somewhat improved by, first, better knowledge of the cross sections as I said, and do perhaps a little more sophisticated spectroscopic analysis, using several lines instead of only two or four.

ANDERSON

There is a great deal of truth in what you say. I would insert one warning, and that is the extreme localization of the chlorine-induced ozone destruction in 40 km region speaks strongly for the global monitoring of ozone in this region because the early warning will show up there in a very dramatic way, and that is the region which is most difficult to diagnose from the ground. However, the contribution of ground-based observations globally to this issue is extremely great and the movement to the satellite-based system should not de-focus from search on the ground-based measurements, both laboratory measurements and the field observations.

HOWARD

This is a technical question: I noticed you had a chemi-luminescent detector in the kit on your flight instruments for detection of NO. At one time you were using resonance fluorescence; I was curious what happened in the evolution of that system.

ANDERSON

The NO resonance fluorescence method as applied to the use of plasma discharge devices is an extremely poor approach, and the reason for that is the fragmentation step within the plasma aligned with the apparent temperature of NO produced in the fragmentation process following electron impact is so large that the lines broaden to the point where it is a very poor source. I strongly believe, because of the work done at NOAA, on NO chemiluminescence, that is the finest approach to the in situ detection of NO in the stratosphere. Now that in the next two to three years the use of Rahman shifted laser will be possible for NO analysis the much greater level of sensitivity will be applied to the troposphere problem, but I believe that for the light-weight airborne stratospheric experiments the chemiluminescence method will be the basis by which progress is made.

### III.

#### THE EFFECTS ON THE ENVIRONMENT OF CHEMICAL REACTIONS IN THE ATMOSPHERE



# TOWARD A BETTER UNDERSTANDING OF ATMOSPHERIC CHEMISTRY

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It is with mixed feelings that I address the topic assigned to me.

First, it is clear that the subject of atmospheric chemistry has emerged over the past two decades as one of the "frontier research" areas in the atmospheric sciences.

Second, it is equally clear that thoughtful consideration of the issues involved leads to the conclusion that a uniquely international effort is required, and this is therefore a particularly appropriate topic to be addressed by the Pontifical Academy of Sciences.

Third, I can claim no special competence in the intricate details of the subject, and must be constrained to view its development from the perspective of the Chairman of the Board on Atmospheric Sciences and Climate of the National Academy of Sciences.

With these considerations in mind, permit me to address (1) the essence of the subject, as it appears to me, (2) the context within which the topic is properly considered, and (3) some specific suggestions regarding future scientific strategies that have emerged from two thoughtful analyses by the National Academy of Sciences [1, 2].

As the world approaches the threshold of the twenty-first century, higher levels of understanding of the physical environment are becoming necessary and attainable. Just as science and technology have permitted world human population to grow and life expectancy to increase through modern industry and agriculture, so they permit more rigorous investigations into how the earth's planetary life support system works. Prudent management will become imperative if the general health and stability of human life on this planet is to be assured. Effective management will

require a good understanding of the complex physical, chemical and biological processes in that system which enable it to combine solar radiant energy with the cycling of chemical nutrients through the biosphere to sustain plant, animal, and human life.

The important role of chemical and physical processes in the troposphere in the planetary life support system has been brought into sharp focus in recent years not only by our research discoveries, but also by a disturbing, recurring sequence of problem identification and response, e.g., impacts of smog on health, of acid on lakes, forests, and agriculture, of increasing carbon dioxide and other trace gases on climate, and of chemicals moving upward through the troposphere to the stratosphere. It has become clear that the troposphere is an integral component of the planetary life support system — receiving, transporting, transforming and depositing substances that either contribute to the efficiency of the system or deleteriously perturb it. Yet there has been relatively little effort expended in obtaining fundamental understanding of the global troposphere, its dynamical behavior and cycles. Perturbations can be expected to increase in frequency and variety during the next several decades, and their significant economic impact will grow. Because the atmosphere is a moving and restless continuum enveloping the planet, the issues are international; since physical, chemical and biological processes are inextricably intertwined, the effort to understand them must be interdisciplinary.

Accordingly, it is timely that a conceptual framework and scientific strategy for the study of the chemistry of the global troposphere be initiated. Rapid advances in theoretical understanding of chemical reactions in the troposphere, field-measurement capabilities, remote sensing, laboratory techniques, data handling, and numerical modeling capacities strongly support the conviction that a coordinated international effort can lead, before the end of the century, to the kind of understanding that would provide the predictive capability necessary to anticipate the impact on our planetary ecosystem of natural or anthropogenic changes in the chemistry of the lower atmosphere.

Three specific issues and four generic programs constitute the context within which a major international effort is warranted.

The first issue is the possibility raised in the early 1970's that human activities might add certain chlorine, nitrogen, and other catalytic substances to the stratosphere. These substances, in turn, would upset the balance between the production and destruction of ozone in a manner that could increase the intensity of ultraviolet light reaching the biosphere with

potentially deleterious results on animals, marine life, plants, and humans (increased incidence of basal cell carcinoma and squamous cell carcinoma). Increasingly sophisticated models of the chemical and physical processes deemed to be important, laboratory experiments to determine the photochemical rate coefficients used in the models, and increasingly reliable techniques of field measurements from balloons and satellites have illuminated the matter but have underscored the complexity of the problem. In brief, the most recent assessment [3] suggests that the theory of humanly induced changes in the stratosphere remains valid. The exchange of trace gases between the stratosphere and the troposphere is emerging as one of the essential steps in the ozone perturbation process. Coupled, three-dimensional, dynamical-radiative-photochemical simulation models will be required for definitive studies and a sustained global observational system will be required to validate the models.

A second issue in acid deposition (popularly known as "acid rain") resulting from the emissions of oxides of sulfur and nitrogen associated with the combustion of fossil fuels. The potentially harmful effects on ecosystems have been documented, especially in areas with low geochemical capacities for neutralizing acid inputs. The matter is complex, involving the generation and interpretation of scientific evidence, assessment of risks, costs and benefits and domestic and international political considerations. Crucial to the decision-making process is the development of realistic, validated models of the meteorological processes of transport, mixing, physical and chemical reactions, and deposition of gases, suspended particles and water droplets as well as the relationship between emissions and deposition. Again, the listing of research needs embraces field studies, laboratory investigations as well as the modeling effort. A review of the current scientific understanding is available for North America [4] and the scientific issues are again being assessed for Western Europe.

Finally, there is the issue of the possible influence on global climate of the buildup of carbon dioxide in the atmosphere from the combustion of fossil fuels. Since this topic is covered of this study week by Professor R. Revelle, mention will be limited to reference to a sustained attempt by a group with a wide range of expertise to achieve a comprehensive and internally consistent assessment [5]. It is worth noting, however, that resolution of this intrinsically international problem requires a sustained program of geophysical and biospheric monitoring and an array of physical, biogeochemical and econometric models sufficiently credible that global decision-making can proceed before irreversible climate changes

take place to the advantage of some regions and the disadvantage of others. So broad is the subject and so global its scope that as the Academy Report noted: "It is conceivable that CO<sub>2</sub> could serve as a stimulus not only for the integration of the sciences but for increasingly effective cooperative treatment of world issues".

Among the generic programs there is, first, the Global Atmospheric Research Program — GARP — [6], first suggested by President Kennedy in an address to the United Nations in 1961, and developed under the guidance of a Joint Organizing Committee established by the nongovernmental International Council of Scientific Unions and the Intergovernmental World Meteorological Organization. Implemented in 1979-80 as the First Garp Global Experimental, this international collaborative effort broke new ground in international scientific cooperation. Premised on the contention that an understanding of the dynamics of global weather circulation patterns had outstripped the observational power that clearly lay within each, GARP succeeded brilliantly in advancing our knowledge of the dynamics of large-scale atmospheric circulation and extending by a significant degree the time interval over which meaningful weather predictions can be made. Five geostationary satellites were launched by several nations, networks of drifting buoys were placed in the oceans, and fleets of aircraft and ships were deployed to fill gaps in the global network of meteorological organizations. Notably lacking, however, is a meaningful insight into the physical processes linking ocean and atmosphere and the chemical and biological processes by which the behavior of the global atmosphere is linked to the underlying marine and terrestrial ecosystems. It is now clear that without addressing these facets of a complex hydrodynamic, thermodynamic and biogeochemical system, our understanding and predictive capability will be severely limited.

More recently, emphasis has been focused on the mesoscale phenomena of the atmosphere [7], since these features are embedded within the global circulation patterns and exercise a strong influence on — and are influenced by — anthropogenic activity, as well as by the natural interaction between the atmosphere and its boundary of land, vegetation, and water. Just as global observational capacity and computer modeling opened up new dimensions in the analysis of large circulation patterns in the 1970's, so have advances in mesoscale modeling and the measurement of the internal structure and motion within individual clouds by doppler radar opened an avenue to observe and predict small-scale weather phenomena — squall lines, thunderstorms, flash floods, freezing rain or dense

fog — with the accuracy and reliability necessary to protect the public, and make effective use of climate and weather information by government, industry, and agriculture. It will be important to include in the research phase of this study an examination in the mesoscale of the chemical flux to land and water surface and the aqueous-phase reaction mechanism and scavenging processes.

A third generic program is the World Climate Research Program [8] which built upon the Global Atmospheric Research Program and is guided by a Joint Scientific Committee of the International Council of Scientific Unions and the World Meteorological Organization. The objectives are to determine (a) to what extent climate can be predicted, and (b) the extent of man's influence on climate. Understanding climate and climate variability involves a detailed study of a great many physical, chemical and biological processes of the atmosphere, oceans, land and sea ice as well as the terrestrial ecosystems that influence the atmosphere over time scales of several weeks to several decades. The program is structured in three streams:

(a) The first stream seeks to establish the physical basis for the prediction of weather anomalies over periods of several weeks.

(b) The second stream is concerned with interannual variability of the global atmospheric climate over periods of one to several years.

(c) The third stream seeks to illuminate the long-term variations and the response of the planetary climate to man-made or natural forcing factors over periods of several decades.

There is an intimate interaction among the cycling of chemical elements such as nitrogen, oxygen, carbon and sulphur through the soil air, water and biomass and the characteristics of the natural or man-made ecosystems which, in turn, influence climate. Increasingly, trace gases are recognized as contributing significantly to the earth's radiative equilibrium temperature and may turn out to be as important in the aggregate as carbon dioxide. As this program proceeds, the need for better information on tropospheric chemistry will become more urgent.

Finally, there is the program of the Scientific Committee on Problems of the Environment (SCOPE) of the International Council of Scientific Unions which for the past decade has been focused on the major biogeochemical cycles and their interaction [9], as well as methods for assessing the effects of chemicals on reproductive functions [10]. Particular attention has been directed to:

(a) the effect upon carbon storage in sediments, soils, and vegetation (primary production) of additional N, P, and S from fossil fuel burning and deforestation;

(b) soil management practices — the potential deterioration of soils through alteration of the N, P, and S via cultivation;

(c) the biosphere as a source of trace gases which influence the chemistry of the atmosphere; the processes within the biosphere that produce these gases;

(d) the eutrophication of coastal marine waters through the entry of N, P, and S by man's activities;

(e) water quality changes from the mountains to the sea as a consequence of N, P, and S entry from man's activities;

(f) the long term effects of population increases and material utilization via N, P, and S dispersion upon the carrying of the earth for humanity.

The study of methodology for assessing the consequences of releasing chemicals into natural and modified ecosystems is the first step in a projected series which seeks, through a collaboration effort, to explore a rapidly enlarging problem. In addition to homocentric considerations, there are important implications emerging of nonhuman reproduction. This is a facet of tropospheric chemistry that is far more than an exercise in toxicology.

In concluding this discussion of the context for a global troposphere chemistry program, mention should be made of the outline of a research program on biogeochemical cycles developed under sponsorship of the National Aeronautics and Space Administration under the rubric of "habitability" and reported by McElroy [11]. Five major goals are persuasively set forth:

(a) to understand the principal components of the hydrological cycle;

(b) to understand the processes which regulate the distribution and abundance of lower atmospheric oxidants, notably  $O_3$ ,  $SO_2$ , and  $NO_2$ 's;

(c) to define the factors which influence the chemistry of deposition both dry and moist;

(d) to identify processes which affect the abundance of aerosols and of gases such as  $CO_2$ ,  $N_2O$ ,  $CH_4$ ,  $NH_3$  and  $H_2O$ ;

(e) to assess the impact of anthropogenic infrared absorbers on the radiative budget of the atmosphere and on climate.

It seems clear from this brief reference to issues and programs that the stage is set for a comprehensive investigation of the chemistry of the global troposphere. As outlined by the report of the National Academy of Sciences [2], the goals would be:

(a) to understand the basic chemical cycles in the troposphere through field investigations, theory aided by numerical modeling, and laboratory studies;

(b) to predict tropospheric responses to perturbations, both natural and human-induced, of these cycles; and

(c) to provide the information required for the maintenance and effective future management of the atmospheric component of our global life support system.

The following specific objectives are proposed to achieve these goals:

(a) *To evaluate biological sources of chemical substances in the troposphere.* Primary emphasis should be placed on investigations of temperate and tropical forests and grasslands, intensely cultivated areas, coastal waters and salt marshes, open ocean regions, tundra regions, and biomass burning.

(b) *To determine the global distribution of tropospheric trace gases and aerosol particles and to assess relevant physical properties.* This program calls for field measurements and analyses coordinated with the development and validation of tropospheric chemical-transport models, the development of tropospheric chemical-transport models, the development of a regional and global data base for key species in chemical cycles, and the continuation and improvement of existing monitoring programs for the accurate measurement of long term trends in environmentally important trace gases and aerosol particles.

(c) *To test photochemical theory through field and laboratory investigations of photochemically driven transformation processes.* Particularly important tests will be investigations over tropical oceans and rain forests with additional studies in midlatitudes.

(d) *To investigate wet and dry removal processes for trace gases and aerosol particles.* Research should be directed not only toward evaluating chemical fluxes to land and water surfaces, but also toward a fundamental understanding of aqueous-phase reaction mechanisms and scavenging processes.

(e) *To develop global tropospheric chemistry systems models (TCSMs)*

*and the critical sub-models required for the successful application of TCSMs.* A wide range of models must be developed of individual processes important for tropospheric chemistry as well as comprehensive global models that include the most important chemical and meteorological processes. Modeling, laboratory, and field studies are necessarily symbiotic; progress in each area is dependent upon contributions from the others.

The institutional framework exists in the International Council of Scientific Unions. Now would seem to be a propitious time to act.



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## DISCUSSION

MARINI-BETTÒLO

In effect biologists are not represented here as are other scientists, but tomorrow we will have with us Silvio Ranzi, Professor of Zoology at the University of Milan, who for many years has been responsible for the Consiglio Nazionale delle Ricerche's program for lake and river pollution of northern Italy.

MALONE

I did not intend that as a criticism but more as a commentary on the good statement.

MARINI-BETTÒLO

In my plans there was an invitation to a botanist, but it is quite difficult to find somebody who is working in this field.

HARE

I really wanted to say, Mr. Chairman, that the trouble with botanists is that many of them do not know anything about plants. Biologists these days are so much concerned with the cell, with the nucleus and with the genome that the questions that are important in the area — and I am serious about this — are now largely tackled by non-botanists, non-biologists, because they are so much concerned with the molecular control of their discipline that they have forgotten to a large extent the things that we are discussing. The problem that you have, Sir, is the problem that we all have when you try to involve biologists in these discussions.

MARINI-BETTÒLO

Thank you, Professor Hare. I think that it is quite a problem. We need taxonomists and ecologists. Even the ecologists have their own programs. In effect we miss very much the presence of Dr. Di Castri, secretary of the

Biosphere program at the UNESCO, who could not come because of the coincidence with the UNESCO general conference.

KNABE

Professor Malone, you gave quite a good explanation of a program for future work. The difficulty is that at present decisions had to be made and I would like to make some statement from the point of view of the ecologist on the chemistry of the troposphere. What we observe and what we are concerned about are several items. First, there has been an increase of the masses of  $\text{SO}_2$  and  $\text{NO}_2$  or  $\text{NO}$ ,  $\text{NO}_x$  you could say, and hydrocarbons in general, all over the world over the last decades, especially after World War II. Secondly, the emissions of those gases have been concentrated on two sources, one source of high stacks at relatively high elevations between 200 and 300 meters, and so the concentrations downwind for each stack is at levels which they have not reached before. The other source is the automobile traffic fumes may be half a meter, or a truck may be 2 or 3 meters; so that you have dense concentrations near the ground. What has changed not only in recent times and makes us concerned is the amount of masses but also the number of chemicals. We do know a bit about the effects of  $\text{SO}_2$  or  $\text{NO}_x$  and ozone, but we do not know really anything about many organic chemicals which are so numerous today. What has also changed is the combination of solid components of the atmosphere, dust and fine particles on the one hand and the gases on the other hand. So by the removal of the ash from the stack we have quite a change in the industrial region. And this might also effect then the air pollution in the regions far off.

The present change in conditions is the increase of pollution in the regions far from industrial areas, and this demands — and that is the only reason I mention it — the measuring of pollution not only in the industrial areas but in a well distributed network over the whole globe. It has also changed the relation of acidic and of photochemical reactive parts, that means the oxidants, the photo-oxidant cycle.  $\text{SO}_2$  is also included in this, I know this, but the special line of building up and also other oxidant hydrocarbons which has started in the Los Angeles basin is now present in many parts of Europe, and this should be of concern. However, at the same time we have the great impact of acidity.

I do not want to go into Professor Liberti's paper — he will do this in more detail — but it is a fact we have a very great input of acids, not only sulphuric acid but also nitric acid. We are asking you as chemists: could you

help us to explain what is going on on the plant surface? You have to make measurements with very fine instrumentation in the stratosphere, and discover radicals and other components, but we are missing the same experiments, the same measurements at the plant surface. What is going on there? Do you believe the same radicals occur there? Can they help us to explain the present damage? Well, just these general remarks, or thoughts, are necessary because you have just given the program for the future and so as an ecologist I want to add my problems.

MALONE

I cannot take exception to anything you said at all. I concur. I might have mentioned in this matter of the relation between plant life and chemistry of the atmosphere, as you are all aware, that when the atmosphere was first present, three and a half billion years ago, there was no oxygen at all, and it was not until one billion years later that there was about 1% oxygen, and it was not until 670 million years ago that it was about 7%; then it rose to its approximate level today, about 400 million years ago at the time of the flowering of plants in the middle paleozoic. I am not trying to divert attention from the immediate problems by going back 100 million years. I am just saying that this geological record suggests the importance of the very thing you are underscoring.

WANDIGA

Professor Malone, I would like you to possibly comment on the topics listed. I saw you listed "The Study of Tropical Forests" as one of the areas that need to be further studied. As you might recall, forests in most tropical regions are an endangered species. There is much more activity occurring in the savanna regions, which I believe are going to have a greater impact on the regional climate or the global climate in the long run. I would mention the encroaching deserts, the solid particles being emitted into the atmosphere and other such activities due to lack of vegetational covers. Furthermore, there is also the estuarine siltation which is affecting the aquatic life and altering quite a number of systems, even the aquatic system. Would it not also be proper to include studies of such nature in this program?

MALONE

Very much so. You will find a very nice analysis of these problems and

the discrepancies in the estimates of tropical forests in the paper by Mr. McElroy. He also goes into some detail about the coastal marine problem, the issues that need to be resolved there, and the outflow of nutrients from the rivers into the ocean.

ROWLAND

Perhaps you should just give a reference to the McElroy article.

MALONE

Its publisher is the Jet Propulsion Laboratory - Publication 85-51, July 15, 1983.

REVELLE

We need biogeochemists, people who are concerned with the whole ecosystem and how it reacts. That is a rather special kind of biology. You won't get much out of botanists or physiologists; you do get something out of the ecologists, and more out of people who would treat ecology in a quantitative way.

MALONE

Your colleague, Ed Goldberg, is a classical example.

REVELLE

So are Michael McElroy, and James McCarthy both at Harvard, and some people in Germany.

# CARBON DIOXIDE AND OTHER GREENHOUSE GASES IN OCEAN, ATMOSPHERE, AND BIOSPHERE, AND FUTURE CLIMATIC IMPACTS

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## *Recent Anthropogenic Changes in Carbon Dioxide and Other Radiatively Active Gases*

The concentration of carbon dioxide in Earth's atmosphere is now about 340 ppm by volume; it is increasing at a rate in excess of 1ppmv/year. By the latter half of the next century, atmospheric CO<sub>2</sub> could be more than 600 ppmv, double the pre-Industrial values. Three-dimensional, general circulation models of the atmosphere indicate that, because of various feedback effects, the rise in atmospheric CO<sub>2</sub> will probably result in an increase in Earth's average surface temperature of 2°-3°C (Manabe and Wetherald, 1975; Hansen *et al.*, 1981). The warming will be much greater at high latitudes — possibly 9°C in arctic regions during the winter-time.

Other so-called greenhouse gases, notably methane, nitrous oxide, and the chlorofluorocarbons are also increasing in the atmosphere at about the same percentage rate as carbon dioxide (Machta, 1983a). This should bring about a further rise in temperature, of the same order of magnitude as the carbon dioxide-induced increase (Lacis *et al.*, 1981). Because the upper layers of the ocean must warm if the atmosphere does, the expected rise in temperature will lag two or three decades behind the increasing levels of atmospheric CO<sub>2</sub> and the other greenhouse gases (Bryan *et al.*, 1982). Melting of methane hydrate in continental slope sediments as a consequence of the ocean warming is a potential major source of methane

which has not yet been taken into account by most workers in the field (Revelle, 1983a).

On a worldwide basis, the temperature rise will be accompanied by an increase in both evaporation and precipitation. But the dry climatic zones are likely to shift to higher latitudes. For example, the dry climatic zone which is now centered at 20°-30°N may move northward to 30°-40°N (Manabe and Wetherald, 1980).

Only about 40 percent of the carbon dioxide being released by fossil fuel combustion and forest clearing remains in the atmosphere (Brewer, 1983; Bacastow and Keeling, 1981). Between 30 and 40 percent enters the ocean, and the remainder is probably taken up by the land biosphere, mostly in forest trees and soil humus (Revelle and Munk, 1977). Carbon dioxide acts as a fertilizer for plant growth, and it also reduces the water required by plants; hence, plant growth should be greater in relatively dry seasons and regions when the CO<sub>2</sub> content of the air increases (Gifford, 1979).

There is little direct evidence of a biospheric uptake during the last few decades. However, indirect evidence exists. The amplitude of the seasonal swings in atmospheric CO<sub>2</sub> concentration appears to have increased during the past 25 years (Machta, 1983b; Keeling, 1983). These seasonal fluctuations are the result of differences in rates of photosynthesis and respiration during different seasons of the year, and it is inferred that increases in their amplitude in part reflect increases in the size of the biosphere in temperate and higher latitudes (Kohlmaier *et al.*, 1983).

On the whole, the effects of increased atmospheric carbon dioxide and expected climatic change may be beneficial for rain-fed agriculture (Waggoner, 1983; Rosenberg, 1982). Certainly, the growing season for crops will lengthen at high latitudes, and the overall increase in precipitation, as well as the CO<sub>2</sub> fertilizer effect, should be beneficial. However, some areas will be deleteriously affected by the shifts in climatic zones. The story may be far different for irrigated agriculture. In regions where rainfall does not increase, the rise in temperature will cause greater evaporation of soil moisture and snow cover and consequently less river run-off. For example, the flow of the Colorado River in the Western United States may be reduced by 30 percent, and this could have disastrous effects on irrigation farming in the Southwest (Revelle and Waggoner, 1983).

The warming of the ocean waters and probable increased ablation of the Greenland ice cap (Ambach, 1980) and of mountain glaciers will bring about a significant rise in sea level, estimated at between 60 and

100 centimeters, during the next 100 years (Revelle, 1983b). A further rise in sea level of about 5 meters could occur during subsequent centuries if the West Antarctic ice cap disintegrates (Bentley, 1983). Disintegration of the West Antarctic ice cap apparently occurred during the last interglacial period, but it is not certain how rapidly this took place (Figure 1) (Moore, 1982).

### *Past Changes in Atmospheric Carbon Dioxide - Evidence from Ice Cores*

Development of techniques for analyzing air trapped at different depths in the ice sheets of Greenland and Antarctica has made it possible to reconstruct an accurate record of past atmospheric carbon dioxide concentrations, during the present interglacial and part of the last glacial period. This work has been done on ice cores from deep drill holes in the ice sheets, by D. Raynaud and his co-workers at the Laboratoire de Glaciologie et Geophysique de l'Environnement at Grenoble, France, and by Oeschger and colleagues of the Physics Institute of the University of

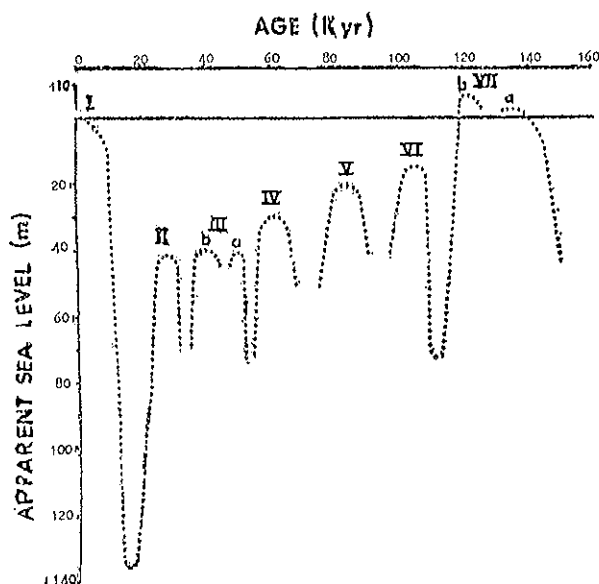


FIG. 1. High stands of sea level during the past 150,000 years. Note 6-meter terrace above present sea level, 120-125,000 years ago. This probably represents a rise in sea level resulting from the disintegration of the West Antarctic ice cap. (From Moore, 1982).



Bern, Switzerland (Neftel *et al.*, 1982). The experimental error of the gas analyses is of the order of  $\pm 1\%$  (3 ppmv of CO<sub>2</sub>); the overall error, including errors in extracting air from the ice, and possibly sample variability, is about  $\pm 3\%$  (10 ppmv of CO<sub>2</sub>). Measurements from the two laboratories agree within analytical errors. Although accurate dating of the samples remains difficult, several notable results have been achieved.

The early measurements suggested that the "preindustrial concentration" of atmospheric CO<sub>2</sub> during the middle of the 19th century was 260-270 ppmv. More recent analyses of larger ice samples indicate that a better estimate of this concentration is 280 ppmv, about 60 ppmv (corresponding to 125 gigatons of carbon) below the 1980 value at Mauna Loa, Hawaii, of 340 ppmv (Oeschger and Stauffer, 1985). Thus, atmospheric CO<sub>2</sub> has increased by 20% in the last 120 years. Depending on the value of the "Airborne Fraction" (the proportion of CO<sub>2</sub> added to the air by human activities which has remained in the air) the total quantity of carbon entering the air from fossil fuel combustion and clearing of forests was probably between 250 and 310 gigatons. Of this amount, fossil fuels contributed around 180 gigatons (Rotty, 1981) and forest clearing most of the remaining 70 to 130 gigatons (Richards *et al.* 1983). Depending on the time required to approach air-ocean temperature equilibrium, and on estimates of the magnitude of a possible CO<sub>2</sub>-induced global temperature rise during the last 120 years, the estimated 20% increase in atmospheric CO<sub>2</sub> provides an indication of the sensitivity of global surface air temperatures to rising CO<sub>2</sub> (Hansen *et al.*, 1981).

A second result from the ice-cores is that the atmospheric carbon dioxide concentration near the coldest time of the Wisconsin glaciation, about 18,000 years ago, was much lower than in post-glacial times, the minimum value being about 175 ppmv. This low atmospheric CO<sub>2</sub> content may have played a major role in bringing about the extremely low temperatures which prevailed 18,000 years ago. These are reflected in very low values of the  $O^{18}/O^{16}$  ratio measured in the same cores. The atmospheric CO<sub>2</sub> content rose during the Bølling-Allerød warm phase about 12,000 years ago, and then fell slightly during the final Dryas cold period 10,000-11,000 years ago (Figure 2).

The most startling result of the ice-core analyses is that atmospheric CO<sub>2</sub> concentrations 30 to 40 thousand years ago apparently varied by nearly a factor of 2 over periods of less than a few hundred years (Figures 3 and 4) (Oeschger and Stauffer, 1985). That these apparent fluctuations are real is indicated by measurements of oxygen isotopes which reflect the

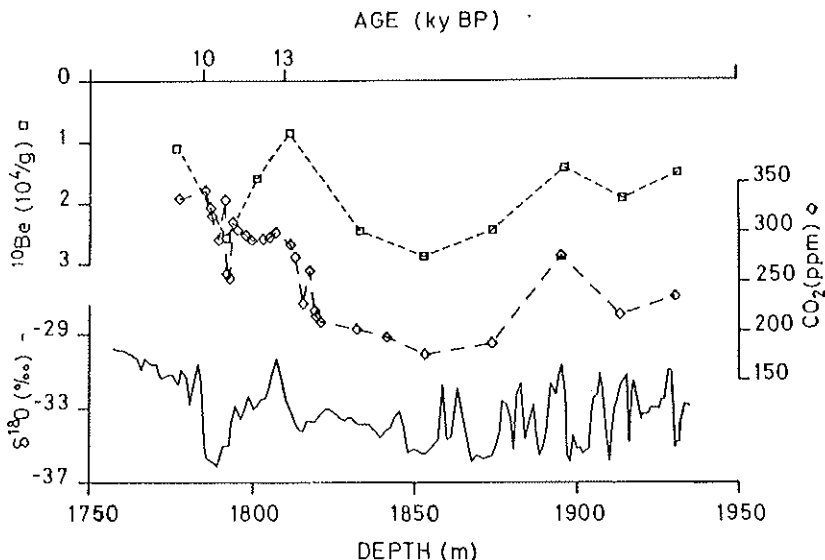


FIG. 2.  $\text{CO}_2$  concentrations (ppmv) and  $\delta^{18}\text{O}$  (‰) in air trapped in an ice-core (Dye 3) from Greenland. The tentative time marks at 10 and 13,000 years BP are suggested by comparison with European lake sediments dated by carbon 14. Also shown is the  $\text{Be}/^{10}$  concentration ( $10^4$  atoms per g of ice) in the core. The approximate parallelism with the  $\delta^{18}\text{O}$  and the carbon dioxide concentration indicates that when the climate became colder the rate of snowfall on Greenland diminished. (From Neftel *et al.*, 1982).

expected atmospheric temperature change corresponding to the  $\text{CO}_2$  variations. Rapid climatic variations during the Wisconsin glacial period are also suggested by the sea-level record inferred from ancient terraces (Figure 1) (Moore, 1982).

It is hard to see how the observed differences in atmospheric  $\text{CO}_2$  between late glacial and post-glacial times, let alone the likely variations over a few hundred years, could occur without the existence of some kind of feedback process between the ocean and the atmosphere. One such process could be changes in the level or character of biological productivity in the upper ocean waters.

During late glacial times, the "fixed" nitrogen and phosphorus contents of ocean waters may have markedly increased through weathering and release of nutrients from the vast areas of continental shelf sediments that were exposed to the atmosphere by falling sea level (Broecker, 1982a, b). Destruction of boreal forests and other high latitude biomes by the

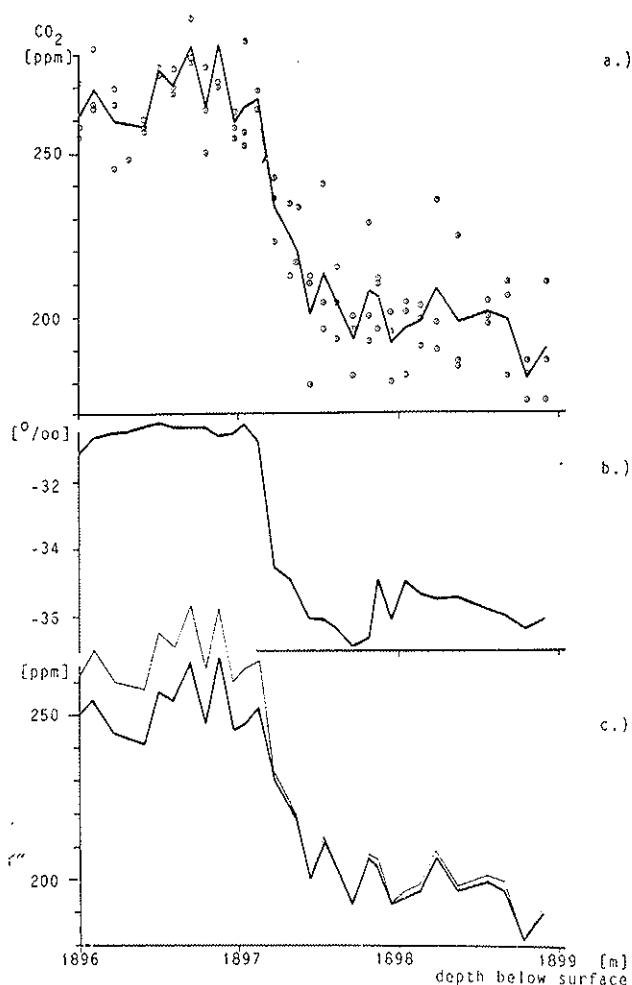


FIG. 3.  $\text{CO}_2$  and  $\delta^{18}\text{O}$  measured on ice samples from the Dye 3 core in Greenland. The 30 m increment in the core corresponds to about 10,000 years, between about 30 and 40,000 years BP. (From Oeschger and Stauffer, 1985).

a) Circles indicate single measurements of the  $\text{CO}_2$  concentration of air extracted from ice samples. The solid line connects the mean values for each depth.

b) The solid line connects the  $\delta^{18}\text{O}$  measurements done on 0.1 m core increments.

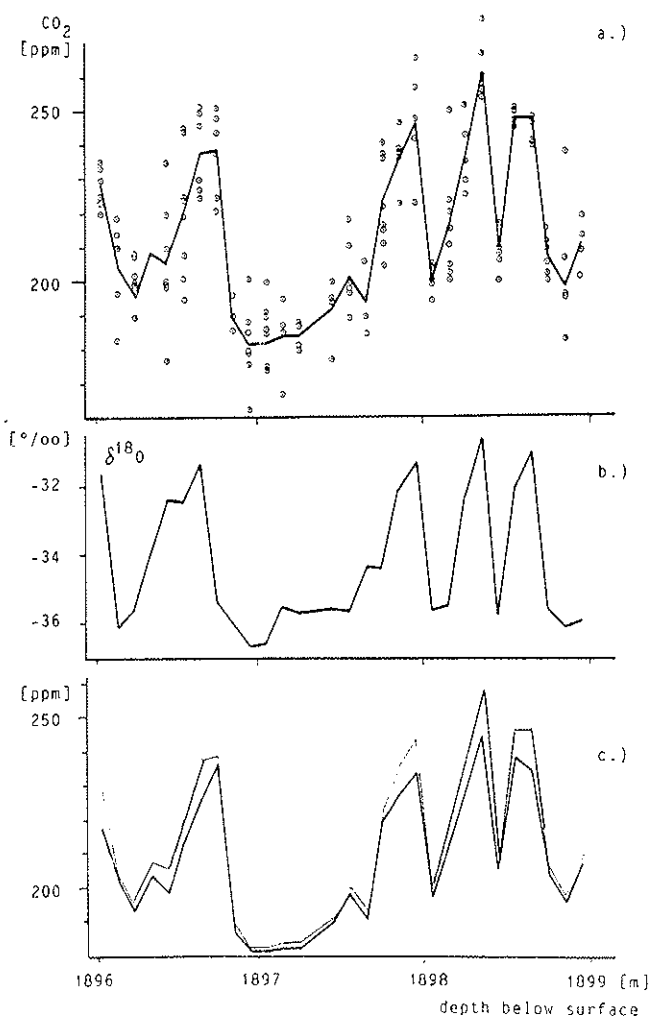


FIG. 4.  $\text{CO}_2$  and  $\delta^{18}\text{O}$  values measured on ice samples from Dye 3 at a somewhat greater depth than in fig. 3. The 3 m increment corresponds to about 1000 years. (From Oeschger and Stauffer, 1985).

- a) Circles indicate single measurements of the  $\text{CO}_2$  concentration of air extracted from ice samples. The solid line connects the mean values calculated for increments of about 0.1 m.  
 b) The solid line connects the  $\delta^{18}\text{O}$  measurements done on 0.1 m core increments.

advancing ice sheets could also have resulted in a discharge of nutrients to the oceans. Plankton production in the oceans should have been markedly stimulated by this increase in oceanic nutrient content. If the resulting organic materials were sequestered for some time in bottom sediments on the continental slopes or in the deep sea, large quantities of  $\text{CO}_2$  could have been extracted from the atmosphere.

Over time, this process would be self-limiting as nitrogen and phosphorus were also sequestered in the organic matter of the sediments and the deep waters and, consequently, smaller quantities of nutrients entered the sunlit upper layers of the sea where phytoplankton production occurs. The removal of nutrients from the ocean waters and the diminution of the supply of nutrients from the land could have been accelerated at the end of the Ice Age, when active biological production was reestablished in previously ice-covered areas and the continental shelves were again covered by rising sea level. Because of the lower level of phytoplankton production, there should have been a net flux of  $\text{CO}_2$  from the sea to the air and a corresponding rise in the atmospheric content of carbon dioxide. The abruptness of the rise in atmospheric  $\text{CO}_2$  at the end of the Ice Age 13,000 years ago is hard to explain with this hypothesis, however. It may be necessary to appeal to changes in ocean circulation accompanying the climatic change, which resulted in a markedly lower rate of upwelling of deeper nutrient-rich waters into the sunlit zone of phytoplankton production.

The short-term changes in atmospheric  $\text{CO}_2$  occurring over a few hundred years, observed in the Greenland ice cores, may be a local phenomenon related in some way to the processes of ice deposition and air entrapment in the ice. However, if they represent worldwide changes in atmospheric  $\text{CO}_2$ , these changes must almost certainly be related to changes in oceanic circulation which resulted in large scale changes in biological production that, in turn, affected the net flux of  $\text{CO}_2$  between the sea and the air.

Figure 5 shows, on a global basis, estimated differences in the partial pressure of  $\text{CO}_2$  between the surface ocean waters and the overlying atmosphere (Keeling, 1968). During most years, in the equatorial Pacific and the eastern equatorial Atlantic, oceanic  $\text{CO}_2$  is 30-90 micro-atmospheres higher than the atmospheric value, and hence in these regions the ocean is a net source of  $\text{CO}_2$  to the atmosphere. Higher oceanic than atmospheric values are also found in the ocean areas of upwelling off the west coasts of North and South America and Africa, in the region of the Somali Cur-

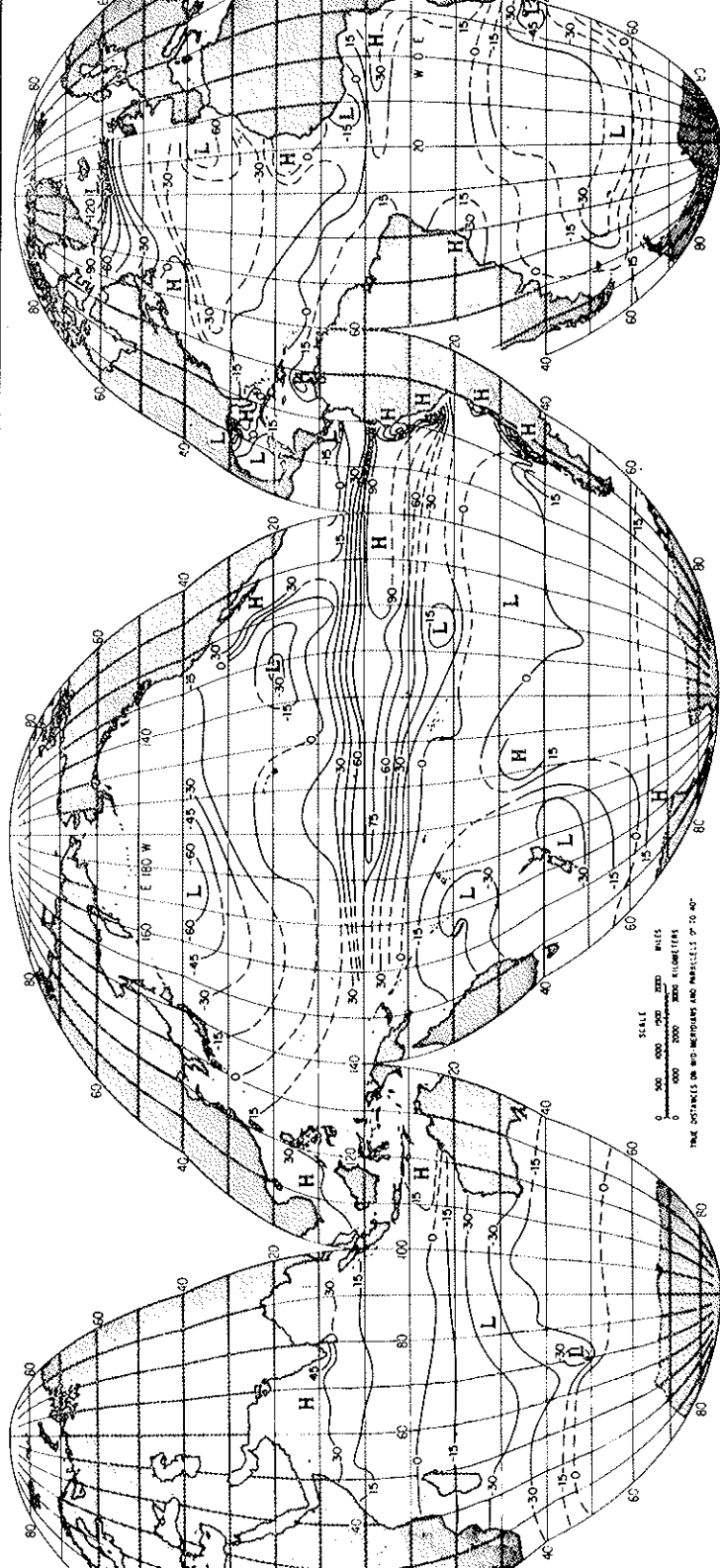


FIG. 5. Estimated approximate differences between the  $\text{CO}_2$  partial pressure in the overlying atmosphere, about 1965. Positive values indicate that oceanic  $\text{PCO}_2$  is higher than in the atmosphere. Negative values indicate the reverse. (From Keeling, 1968).

rent off East Africa, in the Arabian Sea, the western limb of the Gulf Stream, and off Central Brazil. In mid latitudes of both the Pacific and the Atlantic and in high latitudes of the North Atlantic,  $\text{CO}_2$  in the surface ocean is lower than in the atmosphere; and these ocean areas act as a net sink for  $\text{CO}_2$ . The reverse is true in high latitudes around Antarctica and in the South Pacific as far north as 40 degrees south.

The regional differences between oceanic and atmospheric  $\text{CO}_2$  result in annual fluxes between the sea and the air of approximately 5 gigatons of carbon, corresponding to 2.5 parts per million by volume of atmospheric  $\text{CO}_2$ . This is just about equal to the present annual input of 5 gigatons of carbon to the atmosphere from combustion of fossil fuels. Roughly half this quantity of  $\text{CO}_2$  from fossil fuel combustion, i.e. between 2 and 3 gigatons, enters the ocean, probably largely in mid-latitudes. This is in addition to the mid-latitude flux into the ocean of about 2.5 gigatons that would exist in the absence of fossil fuel  $\text{CO}_2$ .

The map shown in Figure 5 is based on relatively sparse data. It is at best a rough, schematic presentation of summer conditions in both hemispheres, and does not take into account either seasonal or interannual variations. These could result in marked differences in the areal extent and intensity of the regions in which there is a net flux of  $\text{CO}_2$  from the sea to the air, and vice-versa.

As an example of possible seasonal variations, observations from an ocean-color scanning satellite indicate that in the northwest Atlantic there is a short, intense late-spring phytoplankton bloom in which a high chlorophyll content exists for a few weeks and then disappears. The phosphate content in the top 100 meters is known to decrease by about 2 grams  $\text{m}^{-2}$  between spring and summer in areas of high productivity. If this occurs over 3 percent of the ocean area, about one gigaton of carbon could settle gravitationally into the deep water after such blooms. This process is in effect a "biological pump", by which carbon is transferred from one water mass to a completely different one.

The phosphorus and "fixed" nitrogen contents could be replaced annually by upwelling from a different water mass than that into which the carbon has settled. Over a few hundred years, the process could extract several hundred gigatons of carbon from the atmosphere. Conversely, if the spring blooms ceased or were sharply reduced in intensity and extent, one would expect carbon dioxide to accumulate in the atmosphere.

### *The Effect of the El Niño - Southern Oscillation on Atmospheric Carbon Dioxide*

The flux from the sea to the air along the equatorial belt varies markedly from year to year, depending on the presence or absence of the phenomenon known as the Southern Oscillation - El Niño. During "normal" years total CO<sub>2</sub> is high at 160° west along a narrow band centered on the equator (Figure 6). Phosphate and nitrate are also high along the equator and the surface temperature is relatively low. Further east, along longitude 120° west, the belt of high CO<sub>2</sub>, phosphate and nitrate extends from near the equator to about 20° south latitude. These are the regions of upwelling in which relatively cold water is brought near the surface from depths of several hundred meters. The dissolved CO<sub>2</sub>, phosphate, and nitrate, remain high throughout the year. This indicates that for reasons that are not entirely clear phytoplankton production is not able to keep up with the influx of nutrients and CO<sub>2</sub> from the deeper water, and the upwelling CO<sub>2</sub> is continually released into the atmosphere (Figure 7).

Consequently, under "normal" trade wind conditions there is a secondary maximum of atmospheric CO<sub>2</sub> in the neighborhood of the equator in the eastern Tropical Pacific (Figure 8). That this is due to an influx of oceanic CO<sub>2</sub> to the atmosphere and not to tropical deforestation is clearly shown by the isotopic ratio of carbon 13 to carbon 12, which increases continuously from high northern latitudes where fossil fuel CO<sub>2</sub> which, like the CO<sub>2</sub> of the land biota, is low in carbon 13, enters the atmosphere, to about 20° south latitude.

At intervals of 2 to 10 years the trade winds in the eastern Tropical Pacific die down or even reverse direction, and warm low CO<sub>2</sub> water from the western Pacific flows over the eastern equatorial waters. Upwelling ceases, the phosphate, nitrate, and inorganic carbon contents markedly diminish, while the temperature rises by as much as 4 or 5 degrees (Figure 9) (Bacastow, 1976; Newell and Weare, 1977).

In principle, the equatorial maximum in CO<sub>2</sub> should diminish during an El Niño, and the secular increase of atmospheric CO<sub>2</sub> from fossil fuel combustion should be counterbalanced by the diminution of the equatorial oceanic flux. That this did not occur during the strong El Niño of 1972-73 is shown in Figure 10. During 1982-83 the secular increase in CO<sub>2</sub> likewise appears not to have been affected by the diminution of the equatorial oceanic flux (Keeling and Revelle, 1985). A possible explanation is given



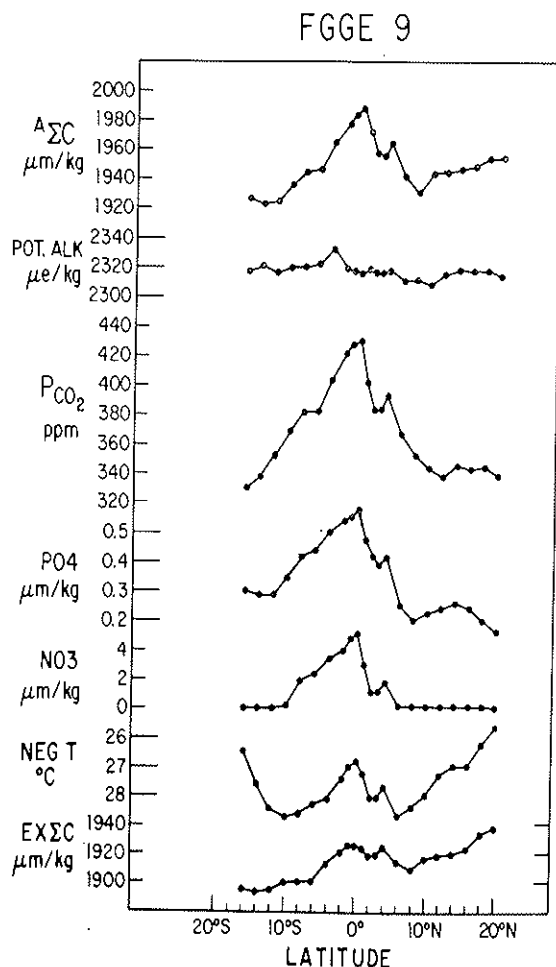


FIG. 6. CO<sub>2</sub> components, nutrients and temperature in a north-south section along 150° west in 1979. Note the high P<sub>CO<sub>2</sub></sub>, phosphate and nitrate concentrations along the Equator, and the relatively low temperature. Measurements by C. D. Keeling and others during the "First Garp Global Experiment" (FGGE).

by the C13/C12 ratios during the 1982-83 El Niño at both Mauna Loa and the South Pole. These ratios appear to have become more negative during 1982-83, indicating an increased flux of CO<sub>2</sub> from the land biosphere (Figure 11). We know that during this period severe droughts occurred in Australia, Indonesia, Southern India, Northeast Brazil, and West Africa. Presumably heterotrophic respiration remained constant or

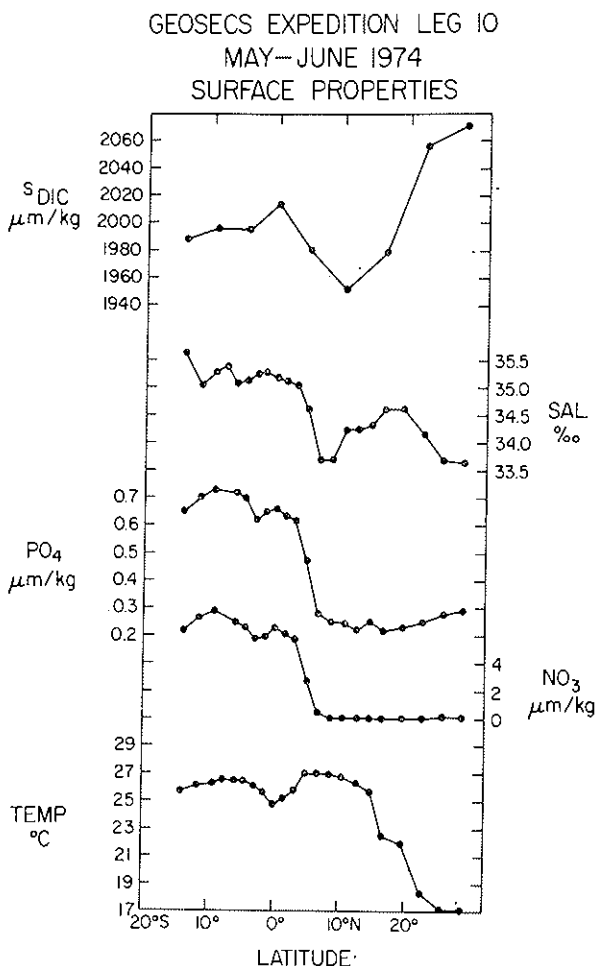


FIG. 7. Dissolved inorganic carbon, salinity, phosphate, nitrate and temperature along an approximate north-south line at 90° west longitude, in 1974. Note that high  $\text{CO}_2$  and nutrients extend southward at least 15° from the equator in this section, which is closer to the South American coast than that shown in Fig. 6. (From GEOSECS Atlas, vol. 4).

increased while net primary production markedly diminished, hence several gigatons of  $\text{CO}_2$  may have been released from the biota and the soil, compensating for the cessation of the  $\text{CO}_2$  flux from the equatorial ocean.

If "El Niño" conditions persisted for several years, however, this effect of drought-caused heterotrophic respiration of the land biota would disappear. The balance between the mid-latitude areas of net  $\text{CO}_2$  flux

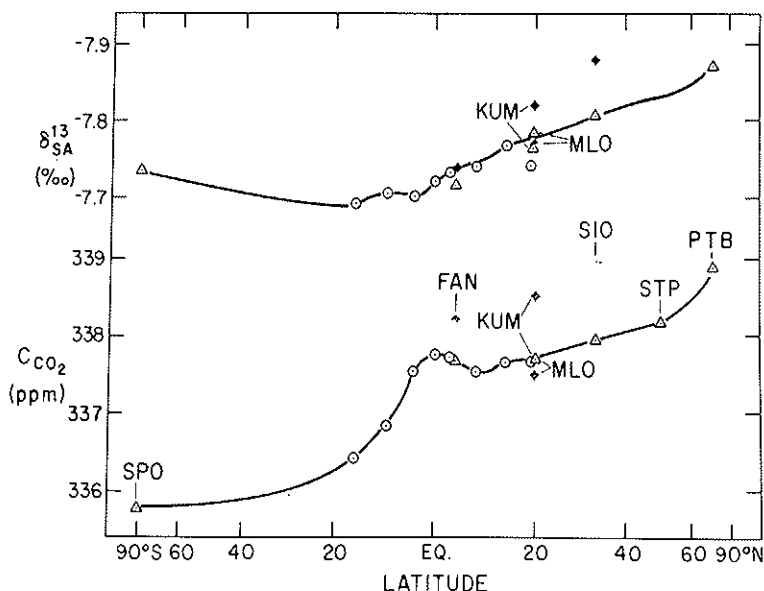


FIG. 8. The concentration of atmospheric  $\text{CO}_2$  and an index of the carbon 13/carbon 12 ratio along an approximate north-south section from Point Barrow (PTB) weather station Papa (STP), the Scripps Institution of Oceanography (SIO), Mauna Loa (MLO) and Cape Kumakahi (KUM) on Hawaii, Fanning Island (FAN), near the equator, and the South Pole (SPO), about 1978. Circles indicate samples collected on shipboard. (From Keeling, 1983).

to the ocean and the equatorial regions of net flux to the atmosphere would shift and a net loss of atmospheric  $\text{CO}_2$  would result. Conceivably such persistent "El Niño" conditions could have existed at intervals over periods of a century or more during glacial times.

### *Needed Observations*

What measurements should be made to study these processes? Perhaps most important would be accurate ocean-wide time-series measurements of the inorganic  $\text{CO}_2$  content of upper ocean waters and of the seasonal and interannual change in the difference between  $\text{CO}_2$  partial pressure in the ocean and the atmosphere, particularly at high latitudes and in equatorial regions (Keeling, 1983).

A start on understanding large scale space and time changes in biological productivity might be made by satellite observation of chlorophyll content in the upper ocean waters. Provided difficulties of interpretation

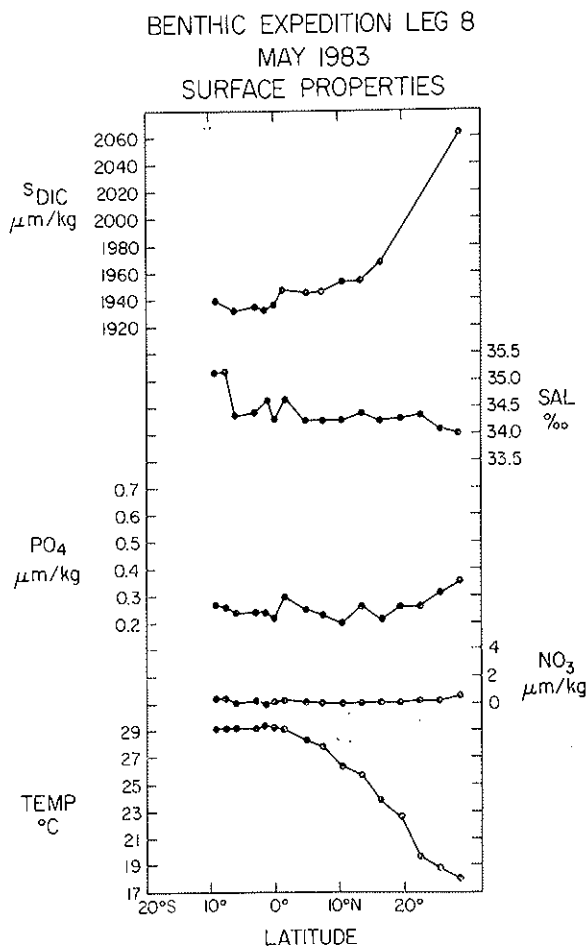


Fig. 9. Dissolved inorganic carbon, salinity, phosphate, nitrate, and temperature in surface ocean waters, during the 1982-83 El Nino, at the same longitude as in Fig. 7. Note that the high values for CO<sub>2</sub> and nutrients south from the equator have disappeared while the water temperature has become warmer as warm waters from the Western Pacific flooded over the region. Measurements by C. D. Keeling, R. F. Weiss and others.

can be overcome, these should be planned as a continuing program for many years, supplemented by studies of time variability in the efficiency of the "biological pump" referred to above; and of the biological processes that affect the opacity of sea water and hence the depth of penetration of sunlight into the upper ocean waters. The latter may profoundly affect mixed-layer thermocline processes.

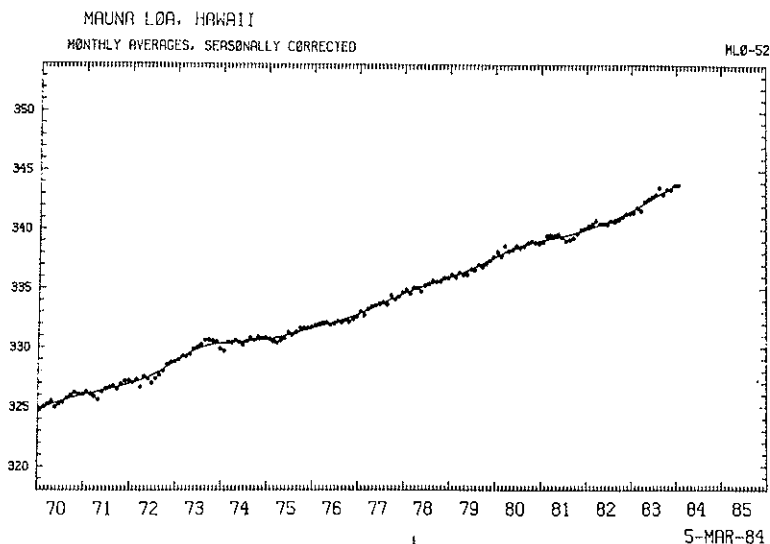


FIG. 10. Monthly averages of atmospheric  $\text{CO}_2$  at Mauna Loa, corrected for the seasonal swing. Note that in the 1972-73 El Niño  $\text{CO}_2$  apparently increased more rapidly than the normal secular increase, while in 1982-83 the normal secular increase was maintained. (From Keeling and Revelle, 1985).

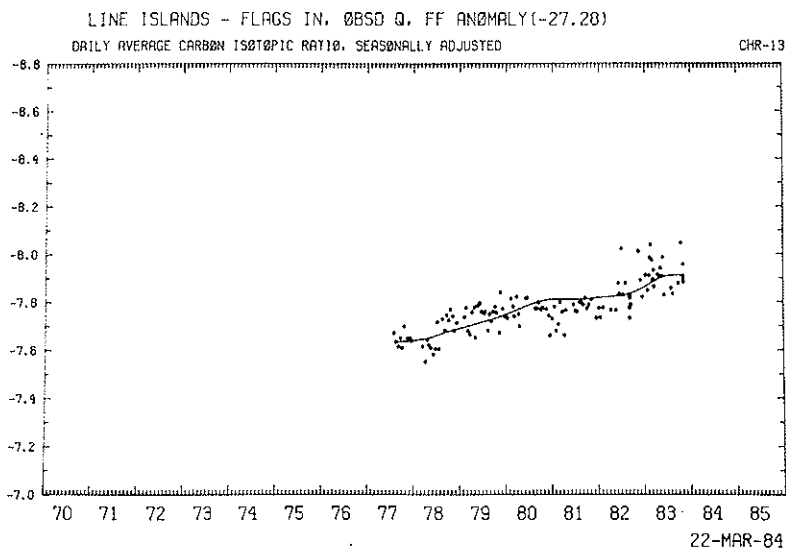


FIG. 11. Seasonally adjusted daily averages of  $\delta \text{C}^{13}$  near the equator between 1977 and Dec. 1983. Note that during the 1982-83 El Niño  $\delta \text{C}^{13}$  became more negative, indicating a flux of  $\text{CO}_2$  to the air from the land biota. (From Keeling and Revelle, 1985).

TABLE I - Some "trace" gases in the atmosphere and the estimated increase in global surface temperature for the indicated change in mixing ratio.

| Constituent   | Mixing Ratio Change (ppb) |              | Surface Temperature Change (°C) | Source <sup>a</sup> |
|---|---------------------------|--------------|---------------------------------|---------------------|
|   | From                      | To           |                                 |                     |
| Nitrous oxide (N <sub>2</sub> O)                      | 300                       | 600          | 0.3-0.4                         | 1,3                 |
| Methane (CH <sub>4</sub> )                            | 1500                      | 3000         | 0.3                             | 3,4                 |
| CFC-11 (CFCl <sub>3</sub> )                           | 0                         | 1            | 0.15                            | 1,5                 |
| CFC-12 (CF <sub>2</sub> Cl <sub>2</sub> )             | 0                         | 1            | 0.13                            | 1,5                 |
| CFC-22 (CF <sub>2</sub> HCl)                          | 0                         | 1            | 0.04                            | 7                   |
| Carbon tetrachloride (CCl <sub>4</sub> )              | 0                         | 1            | 0.14                            | 1,5                 |
| Carbon tetrafluoride (CF <sub>4</sub> )               | 0                         | 1            | 0.07                            | 2                   |
| Methyl chloride (CH <sub>3</sub> Cl)                  | 0                         | 1            | 0.013                           | 1,5                 |
| Methylene chloride (CH <sub>2</sub> Cl <sub>2</sub> ) | 0                         | 1            | 0.05                            | 1,5                 |
| Chloroform (CHCl <sub>3</sub> )                       | 0                         | 1            | 0.1                             | 1,5                 |
| Methyl chloroform (CH <sub>3</sub> CCl <sub>3</sub> ) | 0                         | 1            | 0.02                            | 7                   |
| Ethylene (C <sub>2</sub> H <sub>4</sub> )             | 0.2                       | 0.4          | 0.01                            | 1                   |
| Sulfur dioxide (SO <sub>2</sub> )                     | 2                         | 4            | 0.02                            | 1                   |
| Ammonia (NH <sub>3</sub> )                            | 6                         | 12           | 0.09                            | 1                   |
| Tropospheric ozone (O <sub>3</sub> )                  | F (Lat, ht)               | 2F (Lat, ht) | 0.9                             | 4,6                 |
| Stratospheric water vapor (H <sub>2</sub> O)          | 3000                      | 6000         | 0.6                             | 1                   |

Sources: 1, Wang *et al.* (1976); 2, Wang *et al.* (1980); 3, Donner and Ramanathan (1980); 4, Hameed *et al.* (1980); 5, Ramanathan (1975); 6, Fishman *et al.* (1979); 7, Hummel and Reck (1981).

### Other "Greenhouse" Gases in the Lower Atmosphere

As shown in Table I, a large number of "trace" gases in the atmosphere absorb and emit infrared radiation in a manner similar to carbon dioxide (Lacis *et al.*, 1981). At the present time the concentrations of some of these gases, notably methane (CH<sub>4</sub>), the chloro-fluoro carbons (CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, and CF<sub>2</sub>HCl) and possibly tropospheric ozone (O<sub>3</sub>), are rising at relatively rapid rates. A doubling of present concentrations of these gases, taken together, would have an effect on global air temperatures, of the same order as a doubling of CO<sub>2</sub>. It should be noted that Table I does not take into account feedback effects of increased water vapor and lower snow-ice albedo, which are usually included in discussions of the CO<sub>2</sub> effect.

It is estimated that about 500 million tons of methane are being added to the air each year (Craig and Chou, 1982), largely by anaerobic production in rice paddies and wetlands as well as from the metabolism of ruminant domestic animals and, possibly, African termites (Rasmussen and Khalil, 1981; Zimmerman *et al.*, 1982). This gas is slowly oxidized by reactions with Hydroxyl free radical. Its atmospheric content is around 5 gigatons, indicating that the residence time in the atmosphere is about 10 years. As Figure 12 shows, since 1965 the atmospheric concentration of methane has increased by about 30%. If this rate continues, the methane concentration will have doubled early in the 21st century.

The causes of the increase in atmospheric methane are not clear. It is possible that the concentration of hydroxyl radical in the atmosphere is diminishing and consequently that the rate of oxidation of methane is decreasing, i.e., the residence time of methane in the atmosphere is becoming longer. Alternatively, with the growth in human population and the intensification of paddy rice production, the increase in methane may be due to larger populations of ruminants and to an increase in anaerobic

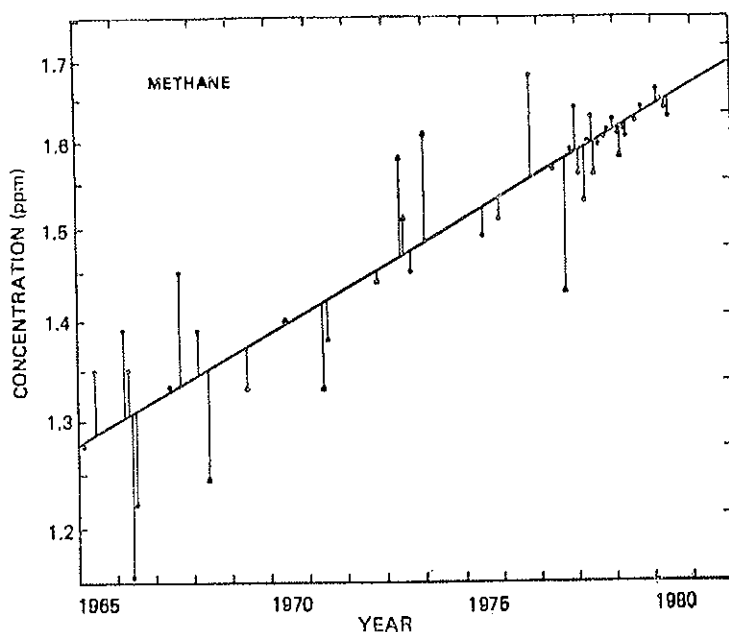


FIG. 12. Measurements of atmospheric methane (ppmv) between 1965 and 1980. The straight line is an approximate average of the data. (From Wang *et al.*, 1980).

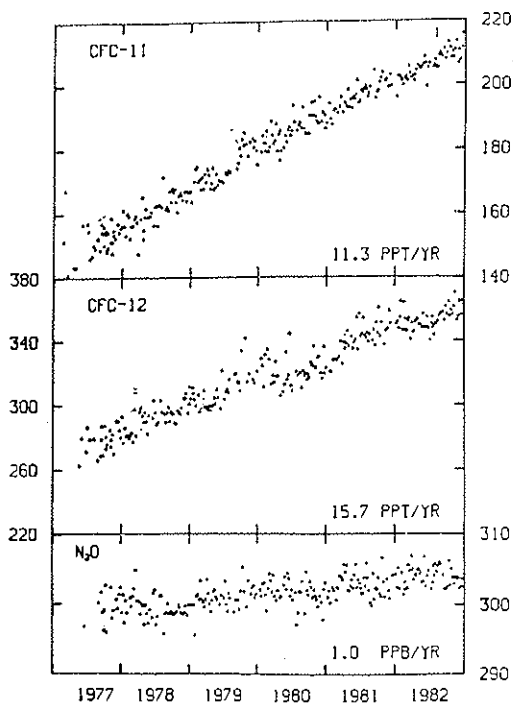


FIG. 13. Measurements of atmospheric  $\text{CFC1}_3$  (CFC-11), and  $\text{CF}_2\text{Cl}_2$  (CFS-12), in parts per trillion by volume between 1977 and 1982. Also shown are measurements of atmospheric nitrous oxide ( $\text{N}_2\text{O}$ ) in parts per billion. (From U.S. Government, 1982).

production in rice paddies. Large quantities of methane (of the order of 10,000 gigatons) are believed to exist as methane hydrates (clathrates) in the sediments of continental slopes. Parts of these deposits will be released if the upper ocean and the underlying sediments become warmer under the influence of increased atmospheric  $\text{CO}_2$ . This could result in another doubling of atmospheric methane during the next 100 years and an enhanced greenhouse effect (Revelle, 1983a).

The chloro-fluoro carbons are increasing at relatively rapid rates, about 7% a year (Figure 13), and their concentrations in the lower atmosphere may reach one part per billion within the next century, bringing about a climatic warming of several tenths of a degree (Hummel and Reck, 1981; Ramanathan, 1975; Wang *et al.*, 1976). On the other hand, nitrous oxide ( $\text{N}_2\text{O}$ ) appears to be increasing very slowly; several hundred years



would be required for a doubling at present rates of increase (U.S. Government, 1982).

Observations of tropospheric ozone ( $O_3$ ) (Figure 14) (Angell, 1983), during the past 15 years give equivocal results. Ozone appears to be increasing significantly in the Northern hemisphere, but it is remaining relatively constant in Australia.

### *Early Detection of Climate Change*

A lively debate exists with respect to the  $CO_2$ /Climate signal (Weller *et al.*, 1983). A minority of climatologists maintain that the  $CO_2$  signal can already be detected in climatic data (Hansen *et al.*, 1981), while others feel that it would require  $CO_2$  levels in the atmosphere predicted for the next century for a clear signal to emerge from background variability due to other causes (Revelle, 1982). The discrimination of long-term climatic

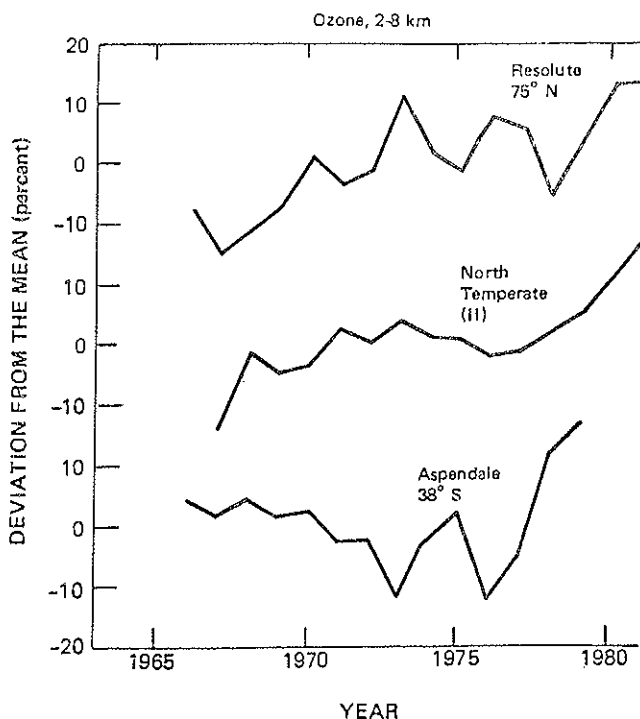


FIG. 14. Changes in tropospheric ozone at two stations in the Northern Hemisphere and one in Australia, 1965-1980. (From Angell, 1983).

trends from noisy historical data is extremely difficult. For example, surface measurements of temperature over land are difficult to interpret without corresponding measurements over the sea. Routine sea temperature measurements taken in different decades may not be comparable because of changing methods and size of the reporting vessels. Intercomparisons are very difficult between "bucket" temperatures, injection temperatures, bathy thermograph data, and microwave measurements of the "temperature" of the sea surface. The detection of long-term climatic trends requires the design of a measurement system which will overcome these difficulties of existing data sets. For this purpose measurements of water properties below the seasonal thermocline offer a possible approach to the detection problem.

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# CARBON DIOXIDE AND ENVIRONMENT

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## *Abstract*

There are six major impacts of rising CO<sub>2</sub>: on climate, on natural ecosystems, on agriculture (and the supporting technology), on continental and oceanic ice conditions, and on the stability of the desert margin. A rise of sea-level is also probable, but major effects are likely to be deferred for a few centuries. Several uncertainties remain in the budget of the carbon cycle. Of these, the suggestion that the temperate and boreal forests act as a major sink for atmospheric carbon is queried, based on recent studies in Canada. The impact on agriculture is examined. Benefits as well as losses may result from CO<sub>2</sub> increase. These need to be foreseen, so that useful adaptation can be worked towards. Other economic impacts may include altered power consumption, northern navigation and perhaps forest yield. Analysis of overall ecosystem impact continues to be difficult. The CO<sub>2</sub> effect should remain high on the scientific agenda, so that governments may have the chance of preparing for the consequences.

## *Introduction*

The rapid increase in the atmospheric reservoir of carbon dioxide (CO<sub>2</sub>) is one of the dramatic realities of our times. Equivalent today to over 720 gigatonnes (Gt) of carbon, the reservoir is increasing at almost 3 Gt per annum (\*), or about 0.4 per cent per annum. Since carbon dioxide is a raw material for photosynthesis and a radiatively significant gas, this increase has major implications for climatologists and biologists. It also

(\*) 3 gigatonnes (10<sup>12</sup> kilograms) per annum.

implies important economic effects, which are as yet imperfectly specified. I shall speak mainly from the perspective of impacts due to climate change, but shall try to identify interactions in other domains; an interdisciplinary approach is needed in dealing with this issue. Elsewhere Revelle will address the primary characteristics of the carbon dioxide effect. I shall hence lay most emphasis on higher order problems. My outlook is influenced by the fact that I come from a northern country, as my treatment will show.

In broad outline, the following appear likely to be the six main consequences of the increase:

(i) the direct impact of CO<sub>2</sub> increase (and of associated infrared absorbers such as nitrous oxide, N<sub>2</sub>O, methane, CH<sub>4</sub> and various synthetic pollutants) on climate is expected to be large, exceeding anything observed in the whole course of civilization;

(ii) indirect potential effects on natural ecosystems may include possible fertilization of plant growth, altered soil moisture and structural effects, and, in general, disequilibria in many aspects of ecosystem dynamics;

(iii) major challenges will be posed to farmers, pastoralists, foresters and agricultural scientists as the result of altered climate and soil conditions, especially along the dry and cold margins of agriculture;

(iv) other economic changes will include altered water régimes, domestic and industrial energy budgets, and probably fish catches;

(v) big changes are most likely in high latitudes, most notably drastic alterations in river, lake and sea ice conditions, and hence ease of navigation. Permafrost, snowcover and the tundra ecosystems will also be affected;

(vi) along desert margins the increased heat-stress and increase in potential evapotranspiration imply a worsening of desertification, already critical in many populated areas.

There is already in progress a rise of sea-level (see Revelle's chapter) due to glacial melting and the warming and hence expansion of the ocean water column. The rise over the past century is believed to be about 15 cm, with some uncertainty. A further rise of 70-100 cm is probable in the next century from the same processes. Much larger rises are possible over the next few centuries if the effect persists. In this paper emphasis is placed on the next century, and the sea-level rise is hence not stressed, though its effects may well be serious in estuarine, deltaic and floodplain environments.

Whether any or all of these things happen depends crucially on the

reality of the predicted temperature change. For doubled  $\text{CO}_2$ , possible in the latter half of the 21st century, and with some allowance for the rôle of other infrared absorbers, an increase in equilibrium mean annual surface temperatures of from  $2^\circ$  to  $3^\circ$  C is likely in lower latitudes, with sharply higher values ( $4^\circ$  to  $8^\circ$  C) possible in higher northern latitudes. These changes may be retarded by the heat capacity of the intermediate layers of the ocean, possibly by two to three decades (the so-called *transient effect*). There are sceptics who go further, and maintain that the ocean must warm first, because the so-called  $\text{CO}_2$  effect depends mainly on the associated increase in water vapour shielding. These dissenting opinions are well covered in recent reviews, and will be disregarded here (Clark, 1982; N.A.S., 1982). But one must keep in mind that air-ocean interactions may well be the key to this problem, and that present generation models incorporate them only crudely.

It is my intention to stress two aspects of the problem that are of special interest in middle and high latitudes. These are (i) the possible rôle of the biota in these zones as a sink for  $\text{CO}_2$ ; and (ii) the economic impacts special to such latitudes, because of their importance to the world economy.

### *Some Major Uncertainties*

Carbon moves between the following reservoirs at rates that are variously understood:

(i) a large but almost balanced flow occurs between living terrestrial biota and the atmosphere, where both photosynthetic absorption and respiratory release of carbon exceed  $50 \text{ Gt a}^{-1}$ , and may exceed  $70 \text{ Gt a}^{-1}$ . A recent conservative estimate of phytomass on land is  $560 \pm 100 \text{ Gt C}$  (Olson, 1982), which implies an exchange between land vegetation and atmosphere about every ten years;

(ii) very large but unbalanced exchanges take place between atmosphere and ocean surface layers, coupled with some flux of carbon into the intermediate waters. These exchanges have been extensively modelled by a SCOPE project (Bolin, 1981) and others. A net downward flux is agreed, but its precise size and geographic distribution remain unspecified;

(iii) losses of carbon to the atmosphere arise from the oxidation of litter and soil humus (whose total storage of carbon is now usually estimated as close to  $1,500 \text{ Gt}$ ) due to forest clearance and more intensive land use;



(iv) net transfers of carbon occur in streamflow to the continental shelf; and

(v) a well-monitored flux of 5 to 6 Gt  $\text{a}^{-1}$  C from fossil fuel burning is added annually to the atmosphere.

Major efforts have been made to sharpen this sketch of the global carbon cycle. In part such work consists of quantitative system modelling (e.g., Bolin, 1981), where the chief gains derive from the need to grasp and quantify the nature of the various exchange processes. For the rest, the effort is directed primarily towards actual measurement of the fluxes, or of reservoir content (e.g., Woodwell *et al.*, 1978; Ajtay *et al.*, 1979; Olson, 1982).

In this short space I can discuss only one of the uncertainties in the balance. This concerns the phytomass-soil-atmosphere exchange. Most recent estimates imply that clearance of tropical forests for agriculture or pasture, together with deterioration of tropical dryland ecosystems, have produced a large transfer of carbon. Olson (1982) gives a net transfer of  $1.6 \pm 1$  Gt C per annum to the atmosphere from this source. Myers (1980) prefers a substantially larger figure. Olson and others have suggested, however, that temperate and boreal forests may actually accumulate carbon. A recent modelling exercise by Higuchi (1982) suggests that the magnitude of this sink may be about 2 Gt per annum. If this is true, then it may justify the belief of some ocean scientists that a net transfer *to* the biota *from* the atmosphere is essential to a balanced cycle.

For several years various Canadian groups, my own among them, have been trying to quantify the capacity of the sub-arctic — the Boreal forest biome — to remove carbon from the atmosphere. There is little sign of any increase in standing biomass. If anything the forest industries are cutting more trees than regrowth can replace. But the soils and wetlands of the Boreal biome can and do absorb carbon, and then retain it under poorly aerated conditions that inhibit oxidation.

Table I summarizes the estimated level of storage, and of annual accumulation rates, in Canada (Boville *et al.*, 1982). The data refer to dead organic carbon. They do not include living biomass, nor the litter of forest soils. Since the Wisconsin glaciers (i.e. the final Pleistocene ice sheets) covered all Canada (except for small areas in the Yukon), it can be assumed that all the carbon shown in Table I has accumulated in post-glacial (i.e., Holocene) times. The following points can be made:

(i) total net post-glacial withdrawals from the atmosphere in wet-

TABLE I - *Summary results of Non-living Organic Carbon Reservoirs and Rates of Change* (excluding crops and major forest areas).

|                     | Area $\times$<br>(100 km) <sup>2</sup> | Error<br>estimate | Organic Carbon<br>Gt | Error<br>estimate |
|---------------------|--|-------------------|----------------------|-------------------|
| Major Bogs          | 85                                     | > $\pm 15$        | 85                   | > $\pm 20$        |
| Shallow Peatlands   | 20                                     |                   | 10                   |                   |
| Other Organic Soils | 145                                    | $\pm 45$          | 35                   | factor 2          |
| Accumulation Rate   | 14 M tonnes per year                   |                   |                      | range 8 - 20      |
| Lakes               | 80                                     | $\pm 10$          | 50                   | factor 2          |
| Accumulation Rate   | 6 M tonnes per year                    |                   |                      | range 3 - 10      |

After Boville, Kwizak and Davies (1982)

lands, organic soils and lakes amount to 180 Gt of carbon (within a factor of 2), equivalent to a quarter of present atmospheric content;

(ii) withdrawals were slow in early Holocene times, especially in wetlands and organic soils. Most rapid accumulation appears to have been about 5,000 B.P. in all reservoirs, but rates remained high throughout the late Holocene;

(iii) present day annual withdrawals amount to  $14 \times 10^6$  t per annum on land, and  $6 \times 10^6$  t per annum on lakes, or a total of  $20 \times 10^6$  t per annum, again with large potential error.

Canada has about 36 per cent of the world peat area, and at least 50 per cent of the lake surfaces within the Boreal and Arctic biomes. If the figures of Table I are weighted with these areas, on the assumption that conditions have been similar in Eurasia it can be estimated that world post-glacial carbon accumulation in high latitude bogs, peats, soils and lakes may have been close to 500 Gt, equivalent to 70 per cent of present atmospheric storage. Present annual rates of withdrawal may be close to  $80 \times 10^6$  t a<sup>-1</sup> ( $\sim 0.1$  Gt per annum).

This last figure is far short of what Higuchi's model estimate calls for ( $\sim 2$  Gt per annum). Nevertheless, if sustained it would be fully capable of yielding the 500 Gt of storage during post-glacial time. Moreover, withdrawals from other reservoirs must have been considerable. To

the 500 Gt of dead organic carbon must be added a figure for the living biomass and litter now occupying the formerly glaciated areas. We do not yet have a Canadian estimate for this addition, but other studies (e.g., Pollard, 1982, citing Armentano and Hatt, 1979, in Canada, 1982) suggest that on a world basis it exceeds 50 Gt. Atmospheric increases since late Wisconsin times have been about 250 Gt. The post-glacial millennia have thus seen transfers of order 800 Gt into the atmosphere and into Boreal terrestrial storage.

The uncertainties in these estimates are very great. Large disparities exist between the figures adopted by the groups studying the overall carbon cycle (e.g., Olson, 1982; Rodin and Bazilevich, 1967; Woodwell, 1978). Anyone who works on carbon storage at once comes up against the immense complexity and heterogeneity of the biotic, edaphic and oceanic reservoirs. Only the atmosphere is reasonably well-mixed, and yields fairly firm answers when monitored.

### *Impacts on Agriculture*

Revelle has spoken of the plant fertilizing effect, at least on the C-3 photosynthesizers, of rising ambient CO<sub>2</sub> levels. This favourable impact, inferred largely from laboratory experiments, may be enhanced by the fact (Wittwer, 1980) that some plants use water more efficiently at high CO<sub>2</sub> concentrations. Hence it is easy to conclude that rising CO<sub>2</sub> may raise agricultural productivity.

It is likely, however, that the main impact on agriculture will be via the induced climatic changes. Two obvious effects have been widely discussed:

(i) several major modelling exercises suggest that rising CO<sub>2</sub> concentrations may induce lower soil moisture availability in mid-latitude cereal growing areas (e.g., Manabe and Stouffer, 1980. See also Kellogg and Schwarc, 1981).

(ii) most such exercises predict a rise of summer temperatures of order 2° to 4° C during the growing season, and a lengthening of the latter by several weeks at either end (in middle and high latitude areas).

These predictions have caused much concern in North America. Sharp decreases of corn and wheat yield from the major granaries of the mid-west and Great Plains (Abrahamson, 1983) have been seen as a likely outcome, because these crops are already grown at temperatures above their optima,

and because the maintenance of adequate soil moisture is already a problem. On the drier Great Plains, corn cultivation is dependent on irrigation from the Ogallala aquifer, whose water is being rapidly depleted. A reversion to ranching, low-yield dry (rainfed) farming, or possibly land abandonment has been predicted for these areas, even without the CO<sub>2</sub> effect.

The summer of 1983 provided a rehearsal for the potential doubled CO<sub>2</sub> effect. Temperature was above normal and precipitation below normal on scales not unlike those predicted by models of the doubled CO<sub>2</sub> effect, or of conditions typical of mid-twenty-first century if other absorbers are included. In 1983 corn yields were halved (by reference to the previous crop year). About half this reduction was probably due to the hostile climate. Winter wheat was adversely affected in some areas, but escaped the worst effects of the summer drought, because of early harvesting dates. Spring wheat was badly affected in many areas. Thus a natural rehearsal of future events appeared to confirm the pessimistic estimates of the Abrahamson forum.

In Canada (and by inference Scandinavia and the Soviet Union) these concerns appear in a different light. Our agriculture is circumscribed by the short, cool growing season. Rises of temperature imply for us the possibility of a more diverse, productive and profitable system of cropping. We are, of course, worried about the possibility of reduced soil-water availability — and in many areas a switch to an irrigated system is not possible. Nevertheless we foresee gains.

I recently calculated that in my home province of Ontario growing degree days may increase by 10 to 25 per cent by 2050 AD, with a net increase in the growing season of five to seven weeks (Hare, 1982). This would allow the penetration of typical corn belt agriculture into southern areas of Ontario. On the Canadian Prairies, now dominated by spring wheat-barley-oilseeds cultivation, winter wheat might become the dominant crop. These gains would, however, be lost if rainfall failed to make up for the increased water demands that are implied.

Projected temperature and precipitation changes for the tropical countries are more worrisome. Though some model calculations predict strengthened summer monsoonal circulations over Africa, Asia and Australasia, and hence enhanced rainfall in the areas covered, there is as yet no reliable prediction of specific regional changes. What is certain is that a rise of temperature of 2° to 3° C year-round is the last thing that tropical agriculture and pastoralism need; the absence of strong seasonal changes

means that the entire annual temperature curve is lifted by this amount. The deterioration of the tropical drylands, already a grim reality, may well accelerate (Hare, 1983).

How will such changes affect world issues, and how can they be coped with? The world's food system is already stressed, more by disparity of income and increase in human numbers than by adverse climate. The major implication of the above sketch is that some countries may gain from the impending changes, but many will lose. Fundamental strategic issues will arise. Africa, already facing intolerable losses of productivity from protracted drought, is unlikely to be rescued from the decline in food supply experienced in the past two decades. South America — especially north-eastern Brazil — faces some of the same problems.

Over the largely self-sufficient countries in the humid tropics and sub-tropics, the CO<sub>2</sub> issue hangs as a cloud of uncertainty. There are many regions where a small rise in rainfall — predicted by some models — might greatly improve the prospects for agriculture. There are others — notably the great alluvial deltas of the east — where the small rises in sea-level predicted from the CO<sub>2</sub> effect (70-100 cm in the next century) might imperil precious land. And for food-importing countries everywhere lies the possibility that the productivity of the major exporting granary — inland North America — may be significantly reduced. No-one can doubt the seriousness of the strategic issues.

Yet it is a mistake to assume, as many have done, that an adverse outcome is inevitable. Western agriculture, at least, is highly adaptable, and is supported by first rate science and technology. The big crop losses of 1983 in the U.S. came because the heat and drought were unpredicted. If such climate became the norm, a variety of responses would be possible:

- (i) New crops, or new genetic varieties of existing crops, might be introduced. This process already has a long record of success.
- (ii) Altered field-techniques and farm calendars (dates of seeding, harvesting, *et cetera*) might make possible better use of available soil water.
- (iii) Extension of irrigation might be possible in some areas.

It is highly improbable that the western farmer, confronted with a slow shift towards warmer, dryer conditions, would sit back and allow the changes to bankrupt him. Instead he would respond in one or more of these ways. On the agricultural map of the world the integrated response would appear both as a change in characteristics of the major agricultural

regions (such as the U.S.S.R. and North American spring wheat belts), and also as a migration of the region following the climate. In Canada, for example, the climates of the Prairies and south-western Ontario *after* the CO<sub>2</sub> warming would be similar to those *now* experienced in parts of the U.S. mid-west and Great Plains, where profitable agriculture is already practiced. In other words there is already experience of future climates — in other places. And years like 1983 give us a useful foretaste of what may happen.

Nevertheless there are limits to adaptation. Over the Canadian Prairies, and in Soviet Asia, for example, a northward migration of spring wheat cultivation may be difficult or impossible, because of adverse soil conditions. In fact there will everywhere be a protracted delay in bringing climate, soil and vegetation into a new equilibrium. The resulting misfit may have adverse economic consequences in many places.

Nor can one simply dismiss the problems of the desert margin. Africa is at this moment in the grip of widespread drought that has compounded the problems of over-population and bad land use so widespread in the continent (WMO, 1983). It is conceivable that a CO<sub>2</sub> enriched atmosphere will ultimately bring more adequate rainfall to the savannah and semi-arid lands that sustain so much of the continent's burgeoning population. But the trend of rainfall in the past fifteen years has been downward over most of the continent. There is little sign that nature is about to come to the aid of the faltering national economies of the world's most distressed continent.

The domain of agriculture is undoubtedly where the CO<sub>2</sub> effects will be most dramatic. If they are not negative, it will be necessary to foresee them, and to plan world wide responses. This calls for major efforts by scientists, economists and engineers on the technical side, and for political foresight. I am much surer of the former than of the latter.

### *Other Economic Impacts*

I cannot deal in detail with the many other impacts of CO<sub>2</sub> increase on the economy. They are very numerous. In Canada, for example, we have thought extensively about these possibilities:

(i) Rising air temperatures will lessen space-heating costs, and increase air conditioning costs. Calculations suggest that by 2050 winter space-heating costs in Ontario might, with strong economic growth, be decreased by 15 to 30 per cent, and that this would exceed air conditioning increases

(Hare, 1982). The reverse will hold in the United States, where peak loads already come in summer to meet this latter need.

(ii) Also by 2050 it is conceivable that ice will cease to impede winter navigation on the Great Lakes and St. Lawrence River, one of the world's great waterways. Little ice formed in the winter of 1982-83, when temperatures were about 3 °C above normal.

(iii) By the same date there should be a marked improvement in summer ice conditions in Hudson's Bay and Strait, and in the complex channels of the Arctic Archipelago. A similar improvement can be foreseen along the Siberian coast (benefiting the U.S.S.R.'s Northern Sea Route) and in the Beaufort Sea, where submarine oil exploration is now under way.

(iv) Northern forests should show some improvement in yield per unit area, as CO<sub>2</sub> fertilization and rise of soil temperatures encourage tree growth. On the other hand forest fire losses, already high in warm, dry summers, would become even more significant — as might insect infestation.

These and other considerations make it difficult for Canadians to take a wholly pessimistic view of the potential CO<sub>2</sub> impact. As a major trading nation, however, Canada depends crucially on the health of the world economy. Hence the overall CO<sub>2</sub> impact on her welfare — and that on the northern countries — may well be determined by what happens elsewhere. More than any other issue the CO<sub>2</sub> effect is truly global in character. Every country should at this moment be preparing a check-list of possible consequences for itself and its trading partners. And world organizations should prepare for constructive action, when the reality of the effect is firmly established, which should happen quite soon, almost certainly within the next two decades.

### *Ecosystem Impact*

Though one can consider the effect of CO<sub>2</sub> increase on individual plants, animals and human beings, it is next to impossible to say anything meaningful about the effect on entire ecosystems. This is because it is hard to express in functional terms the present relations between ecosystem composition, function and dynamics and either CO<sub>2</sub> levels or the existing climate. By pure chance I happened to be present when Tansley first used the term "ecosystem". In the ensuing half-century I have seen it become a household word, and the central notion in the theory of the

human environment. Yet it is an elusive idea, and one that is hard to fit in to the methodology of research. The interdisciplinary teams who laboured during the International Biological Programme to unravel the structure of sample ecosystems did so essentially by analyses, *inter alia*, of the carbon and energy exchanges within the systems, including that between vegetation and atmosphere. Highly successful analyses were made in my own country, for example, of the tundra and grassland biomes. But neither of these analyses answers the question: what would doubled CO<sub>2</sub> concentration do to the functions revealed?

Instead one must still grope towards qualitative, spatial coincidences. The forest and tundra biomes of Canada coincide fairly well with certain climatic distributions. The southern limit of the boreal coniferous forest is close to a specific isoline of net radiant energy input from Alaska to Newfoundland. The arctic treeline is close to a specific isotherm for mean daily July temperature. These climatic isolines will be shifted northwards by 150 to 400 km at equilibrium with doubled CO<sub>2</sub>. Will the vegetation follow them? There is scattered evidence that the dryer, warmer conditions of early mid-Holocene times did indeed see northward shifts of individual species, and that temperatures were then about as much above present levels as one would infer from the vegetational shifts. Closer than this one cannot go. The science of linking climatic variation to ecosystem structure, function and dynamics is still in a primitive state.

Elsewhere (Hare, 1976) I have pointed out, for example, the fallacy of assuming that the displaced Boreal forest of late Wisconsin times (~ 18,000 B.P.) had a bioclimate like that of the modern forest. The temperature régime *may* have been a close analogue, but the radiation climate could not have been similar. And there is evidence that the specific composition of the forest was different.

The pessimism of these remarks needs qualification. Many attempts are in progress to prove them wrong. There are several large modelling exercises under way aimed at answering the question: how will CO<sub>2</sub> change alter ecosystems? I am supportive of such work, but still doubtful that reliable answers are just around the corner. It is one thing to work out the system whereby carbon, energy and materials cycle through existing ecosystems. It is another and more formidable thing to work out all the first and second derivatives — the rates of change, and of accelerated change, that will follow the imposed change of CO<sub>2</sub>.



### *Conclusions*

In common with many colleagues elsewhere, I regard the rise of CO<sub>2</sub> concentration as a central environmental question of our day. It transcends in importance the acid rain issue now so predominant in Europe and North America. It is a truly global issue on two grounds: first, that the atmosphere carries added CO<sub>2</sub> to every part of the globe within a year or two; and second, because CO<sub>2</sub> concentration touches on life itself, and on the central life-support systems.

In this review I have stressed the many uncertainties that persist. Most notably we are far from understanding how the biota interacts with the atmosphere as a functioning community. We are very unsure of the transfers of carbon between air and biota, as we are of the transfers and transformations of carbon within the ocean (as Revelle has stressed). Standing out in contrast is the upward march of atmospheric CO<sub>2</sub>, which is firmly established. Increasingly there is also consensus as to the climatic change that may flow from the increase. Presumably one can also rely on the estimate of fossil fuel consumption, though the future course of this consumption is uncertain.

I have suggested that the economic consequences of the CO<sub>2</sub> increase will be complex and many-sided. There will be economic gains for some countries, most probably those of the north. Others will lose. There is a threat to the productivity of the world's most important source of grain exports, inland North America. There is also a hazard, in my judgement, for the arid zone, and for the deltaic and flood plain cultivators of the eastern countries. It is nevertheless misleading to see the CO<sub>2</sub> issue as an unmitigated threat to human well-being. It also a challenge to ingenuity.

This issue must be kept very high on the agenda of the scientific community. The Pontifical Academy of Sciences is to be congratulated on recognizing this before our arrival in Rome. It is also vital that the world political system prepare for what may be a huge strategic issue within a few decades. This is a potential environmental crisis that science has, for once, foreseen. If that foresight is confirmed by events, there will still be time for the nations and their international institutions to work for solutions.

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## DISCUSSION

REVELLE

I am part of a team with Professor Hare, and we are going to try to put on a joint act. So it might be a good idea to postpone the discussion until after his turn and then we will have a kind of dialogue between us.

One thing we did not say much about is how long this effect is going to last. Estimates are that we are going to have a warm world for at least 1000 years after it warms up.  $\text{CO}_2$  will eventually get into the ocean; that will take a very long time and it depends on overturning this thing which we might call the time constant of the circulation of the deep water. It is probably of the order of 500 to 1000 years, so that the maximum warming will be at the time carbon dioxide reaches its maximum value. There will be a slow decline after that for many centuries.

MARINI-BETTÒLO

I believe that you have pointed out one of the most important points, and that is the equilibrium between  $\text{CO}_2$  and the water of the oceans. That is the main thing out of the photosynthesis by chlorophyll. Oceans should therefore be protected against excessive oil spills and other contaminants because although they can metabolize hydrocarbons, in some areas the formation of layers of hydrocarbons can make more difficult the interchange between the atmospheric  $\text{CO}_2$  and the surface waters.

REVELLE

I guess it is clear that the equilibration with the ocean will delay predicted warming, we do not know by how many decades. It is also true that, as you say, the interchange between the surface layers of the ocean and the atmosphere in some way determines the  $\text{CO}_2$  content of the atmosphere, that is quite right. We have a very good illustration of that in the analyses of the ice cores. The carbon dioxide content of the air has risen fairly rapidly in the last 100 years, and before that it was more or less constant. Then about 120,000 years ago there was a marked decrease in carbon dioxide, with a minimum — that was the time of the maximum deglaciation. It apparently went up again over the

previous time, but it went down and up again, the top figure being about 250 and the bottom figure about 125 parts per million. What is interesting here I think is the very abrupt transitions between the 250 parts per million and the 125 parts per million. Now what is the real cause of these abrupt transitions? Perhaps it must be something to do with the sources and sinks in the ocean. When at high latitudes there were large areas where the  $\text{CO}_2$  in the water was higher than in the air, carbon was released to the air. At other times when there were large areas where the ocean was a sink, carbon was washed out of the air, and you have some kind of a feedback in fact, so that once you get some carbon going into the air it keeps on going in that direction, up to some kind of a maximum — or when some comes out of the air it keeps on going to a minimum. This may very well be due to changes in biological productivity. If the biological productivity is high, you have in effect a pump operating in the ocean, in which a lot of organic carbon settles out of the mixed layer into deep water where it cannot get back as much as one gigaton a year, year after year, so that after 100 years you have a change of about 100 parts per million.

MARINI-BETTÒLO

What is the nature of the feedback effect?

REVELLE

It keeps on going in the same direction. We just really do not understand this at all. And this could happen now, but in the future this could have happened 20,000 or 30,000 years ago, I think, which would be a very large perturbation of the total atmospheric  $\text{CO}_2$  content, having nothing to do with human activities at all. And this is something which I think we need to really understand a lot better than we do now. This will require certainly satellite observations of the color of the ocean, to establish the chlorophyll content of the ocean, and it will involve contrast with the U shift, which will measure the areas of high  $\text{CO}_2$  in the surface layers and of low  $\text{CO}_2$  in surface areas in high level, particularly in the north Pacific, the northeast Pacific, northwest and north Atlantic and all around Antarctica up to 40 degrees of latitude. I am very enthusiastic about Tom Malone's geosphere-biosphere program and it must show from this particular standpoint what happens to the carbon dioxide.

## MARINI-BETTÒLO

What you are saying is very interesting. I was just wondering if this is not possible with the presence of the extra activity in this period of algae or other phytoplankton, which can under particular conditions have increased the photosynthesis in water, in the oceans.

## REVELLE

That is exactly what I think it is: phytoplankton productivity. In the northwest Atlantic, for example, one finds right now a fairly large area of high phytoplankton production in springtime. The ocean becomes green over many square kilometers, due to high chlorophyll content. That disappears in about two weeks, and if you can calculate the changes in phosphorus content of about 2 grams per square meter to zero grams per square meter, that implies a productivity of about 100 grams per square meter of carbon, all of which settles out very quickly.

## SALATI

There is a possible negative feedback to control the increase in  $\text{CO}_2$  in the atmosphere by increasing the partition rate after you reach some concentration of the  $\text{CO}_2$  in the atmosphere.

## REVELLE

You are talking about the  $\text{CO}_2$  fertilizer effect? I think that is a real process, that the  $\text{CO}_2$  will act as a fertilizer and will cause a biotic accumulation of carbon, but this is very controversial and many colleagues do not believe this.

## HARE

I really do not believe it either as far as natural vegetation is concerned, because there will also be under these conditions an increased respiratory loss. Respiration is a temperature-sensitive process, so to do any good you would have to be able to increase the standing biomass by probably something of the order of 7 gigatons a year. Such a figure boggles the mind. To keep the biotic regulator on, you would have to take in photosynthetically an extra 7 gigatons a year.

REVELLE

I do not think that is possible at all. But I think there is some fertilizer effect.

CANUTO

If, going back to the question of the sea, the fact that the ocean is so difficult to quantify, to understand actually, how reliable are those numbers that predict a working of 1.8 to 2° C or the number you quoted this morning and that were able to show that they change the physics or the understanding of clouds, etc.? But this is such a large uncertainty as you say; then what reliability do those numbers have? or do they take into account some kind of model of the ocean? How do they do that?

REVELLE

You are talking about the temperature increase with the carbon dioxide increase? (Yes) I would not like to comment on the validity of those model predictions. That is really a question of atmosphere physics, — which I do not understand that well — these climatic models. But I will say that if you can rely on authority, it looks pretty good, in the sense that all of the modelers agree, and all of the people who understand radiating balance, the behavior of radiators, like carbon dioxide, they all agree that the temperature increase for a doubling of CO<sub>2</sub> will be between one and a half and perhaps 4, or 5 degrees over all. There is a man named Sherwood Idso in Arizona who says that this is not so, but the modelers tell me that Idso's data in fact infer what they are saying — if they are interpreted correctly.

CRUTZEN

The origin of the methane clathrates interests me. How are they formed in the sediments? Do they come from below, or above? If they would come from above, I cannot see how they ever could form there in such high concentrations because they first go through a higher temperature régime. It is something that I do not understand, I am afraid.

REVELLE

Well, I think that there are two possibilities. One very simple and straightforward possibility is that the amount of organic carbon in those sediments

is of the order of 1-1/2 percent, between 1 and 2%. These are anaerobic conditions which prevail. Right at the surface you get reduction of sulphate, so that within the top meter some organic matter is reduced, or rather some organic matter is oxidized and inorganic sulphate is reduced to provide the electronic exchange for that process. But that is a very small effect. Within a half minute or so all the sulphate is reduced. Below that point you have methane production instead, and if you just make the analogy of one of these biogas producers that they use in China and India — where about a third to a half of the organic matter is turned into methane — you get plenty of methane by that process. That will go down, it will keep on going for a long time; the rate of deposition of those continental slope sediments is of the order of 10 to 27 centimeters per thousand years. The deep-sea drilling cores show that you go down maybe 200 meters and you get plyocene sediments on the slope. You have essentially an infinity of time for these anaerobic processes to go on.

Now there is a man named Gordon Erdman of the Philips Petroleum Company — there are companies of course very much interested in these methane deposits — and he has looked into this process with more sophistication than I was able to, but he thinks that there is another process that may be responsible for the methane rather than simply microbial fermentation, and that is pyrolysis, at great depths where the thermogradient is quite high. Remember I said that there was a thermogradient of around 30° per kilometer. Within a few kilometers you get to the boiling point, above the boiling point of water. And he thinks that it is because of these high temperatures that methane is formed. In this case the methane will rise up to a point where clathrate is stable. So he thinks that the production is from below and that methane rises until it finally freezes in the clathrate. He estimates, as I do too, that the total quantity is of the order of 10,000 gigatons. That is about twice the entire fossil fuel reserves.

#### WANDIGA

I would like to pose the question differently. I know that something unusual happened in North America this season. How do we know it is a permanent feature? Because I know at the same time that in Africa we have these seasonal variations. And we have a very unusual high rain pattern in some areas and very dry, rainy or both seasons in some other areas. The two of you have painted a picture which tends to indicate that we are sure we are going to get warming up. Is it a reflection of what

has happened this year? Because there is also a trend of cooling that we studied in the 40's. How do we know this is not going to balance the warming up? Finally, how do we know, with the increased particulate input into the air, whether the cooling off will overcome the warming up and therefore we will have a permanent cooling?

HARE

I would like to make it clear that I use 1983 as an example, not because I think it is a permanent effect — I am quite sure it is not — but because it is a marvelous, cheap experiment that nature has provided for us to get some broad numerical estimates from the economic domain. Surely we ought to say scientifically that the CO<sub>2</sub> effect is not yet in the bank; we have not, in my personal opinion — this is highly controversial — unmistakably seen the CO<sub>2</sub> signal. Equally well I am persuaded that we shall see the signal, if it is real, by the end of the century. In other words, the enormous noise, as you very rightly say, affects this record. Inter-annual variations of rainfall and temperature are extremely high. The differences year to year of mean annual hemispheric temperature are as great as that which corresponds to something like a 50-year period in relationship to the carbon dioxide effect. It will be a long time before we can say for sure we have seen the signal through that noise. Now there are people in the United States and the USSR — I am thinking of Budyko in the USSR and Hanson in the USA — who persuade themselves they can see it, because if you take the last century, it is warmer now than it was in 1885; but it still is colder than it was in 1940. Well, things have really broken out all over in the last two or three years; but it is a great mistake to be misled by short-period variations. I appreciate your point, because in using '83 there I may have conveyed the impression that I thought the CO<sub>2</sub> warming had finally emerged; I must make it clear I thought no such thing.

REVELLE

I think what Wandiga is saying is something different, that there may be countervailing factors like the growth of particulates in the air. I do not think that is so. Particulates are not increasing without limit. Sometimes they are high and sometimes they are not. It is only when you have a lot of volcanism that you get much effect on the climate. You do not get it from man-made, from anthropogenic causes.



HARE

That is the point I was trying to make in those last two slides. Anthropogenic low-level haze, large particle haze, is very photogenic; but I do not think it has a lot of significance for the solar radiation level.

WANDIGA

May I add something? I think the experience you may be having in North America and in other developed countries might be totally different from the experience in the tropical regions because we have or we have seen a very high rate of vegetation destruction, and the amount of particulates being put up into the atmosphere by wind is much higher than you will see anywhere in your country. And we are also worried about this, but we might be seeing something different.

MARINI-BETTÒLO

I think that another point that was stressed yesterday is that there are certain cultivars like rice that give a considerable amount of gases and methane which can modify the atmosphere.

ARNOLD

I am just wondering about your statement that aerosols may have an effect on climate only during periods of strong volcanic activity by increasing the albedo. I am no expert in cloud physics, but I am wondering if increased aerosol burnings in the troposphere could affect cloud processes and thereby have an impact on climate.

REVELLE

But how are these aerosols going to increase except by the process that Wandiga talks about, namely the destruction of tropical forests? We are going to run out of tropical forests pretty soon. There is no reason to believe that this is going to keep on going. The aerosols are not a permanent feature, they have a very short half-life in the air.

## ROWLAND

I have both a technical question and also a sort of an intuitive comment. The technical question has to do with the analysis of the bases which have come out of what you are calling the methane clathrates as to the knowledge of what the actual composition is: whether it is pure methane, whether there are other hydrocarbons, etc. The intuitive comment I think has to do more with the questions; as I see the carbon dioxide effects, it is almost as if the changes are going to be a uniform increase of temperature. And I am sure that is not meant. The kind of feeling that I have is that the particular climatic circulation that we have is very much a characteristic of the particular set of temperature distributions that we have and the fact that living where I do we have 12 inches of rain a year. If I lived in San Francisco, which is 400 miles north, I would have 25 inches of rain a year; if I lived in Seattle I would have 150 inches of rain a year. I have a feeling that perhaps the major effects of the warming would be rather in large shifts in small regions as the whole climatic system adjusted again, such that the impacts that one could see on averages might not be depicting what would really be the major effects.

## HARE

Of course I have simplified to a great extent the original model prediction that I put up to start the thing off with. That does show strong geographical differences in the impact; but I would be prepared to bet that the way the changes would be perceived will not be as a slow upward trend of temperature, but as different sequences of drought years, warm years and cold years. The variability of climate is great. The internal variability is part and parcel of the huge general circulation system itself. That includes the ocean, and such phenomena as the quasi-periodic el Niño. This variability is so much greater than the trends that we are talking about that we are generally unaware of the trend. It requires tremendous statistical sophistication to see any trend, and to be sure that we are seeing it. But what I think a warming means, Sherry, is that gradually there will be more years like 1983 and more stresses like those that we have just undergone. Therefore we shall see a greater tendency to adapt technology to sequences of extreme years, and not to perceived trends, because people do not notice this kind of slow trend.

KNABE

Maybe no professor is thinking of the challenge Dr. Hare mentioned. Couldn't we also say we should increase the production of beer and stop the consumption of beer to store all the  $\text{CO}_2$  in bottles? But may I have really a question? I got two different figures — maybe I am wrong. One figure was the content of the atmosphere would amount to 100 gigatons in the first paper and this would be every year all would pass to the environment. And the other figure in the second paper was 750 gigatons of  $\text{CO}_2$  in the atmosphere. Did I get the wrong figures? I would like to have an answer here. The other question: have the people who are concerned with  $\text{CO}_2$  considered the possibility of depositing organic waste, or municipal waste for instance, in piles that exclude burning, to store some of the carbon under cover and avoid additional  $\text{CO}_2$  emission?

REVELLE

As far as your first question is concerned, I think maybe you got confused between the past and the future. When we talk about a doubling of carbon dioxide in the atmosphere, we are talking in terms of the atmospheric content of carbon of something like 1200 gigatons in the atmosphere. A hundred years ago it was a little bit less than 600 gigatons — we are talking about an increase of 600 gigatons. That is a lot. You just cannot do much if I started carboning trees to countervail a big effect like that. The only thing about trees is: if you are going to, go in that direction to try to overcome the  $\text{CO}_2$  effect, the best thing to do with trees is to burn them as a source of energy, because you can recycle them and use nothing but biotic energy instead of using the bottled fuel energy. That would be a better way to utilize trees to countervail the  $\text{CO}_2$  effect.

FIOCCO

Clouds are the main mechanism that affects the albedo of the earth, and the relationship of the cloud coverage to the  $\text{CO}_2$  increase seems to be a rather difficult problem to treat in models. We have attempted some calculation two or three years ago, the result of which I do not even remember due to the difficulties we went through, but we could practically obtain positive or negative feedback according to various other parameters we had to include in the calculation, a sort of "off the hat" — how much is the humidity going to increase? How much is the radical transfer of water into the troposphere

going to be affected by an increase in temperature? Where is the cloud going to be formed? In most models which have a radical definition, the cloud is assigned to a specific height, but the radiating effects are largely dependent on where in the atmosphere you are going to locate this cloud. We thought that this kind of problem would of course be dealt with with 2D or even 3D models, but that in this case the difficulties become immense and the question of the presence of clouds at high latitudes becomes really a major issue. Do you have any comments on that?

HARE

Of course I entirely agree that the whole business of clouds is worrisome. Various modelers have tried to look at this. We have even done a one-dimensional model of the same kind that you referred to quite recently in my own little backyard. But most of the answers you get are that the acceleration of the hydrologic cycle that is inherent in this does not seem to increase the total cloud amount. Actually it probably does; potentially it also increases the level at which that cloud will sit, in other words, alter its effective radiation temperature. As you know, it is very hard to find good English to express the greenhouse effect. Quite responsible scientists say that what happens is that the carbon dioxide traps heat and prevents it from escaping, which is a valid comment for the warming phase, but is no good for describing equilibrium. What the carbon dioxide effect does is not drastically to alter the radiative temperature of the earth, but to alter the level in the atmosphere where you find that effective radiative temperature. And that must mean ultimately a rise in the level of the cloud tops. But I know of no model that could do that, or will do it, and I think you do not have to parameterize it as we do now.

REVELLE

What these modeling people say is that if you retain a fixed cloud temperature rather than a fixed cloud altitude, that has a big feedback effect on the CO<sub>2</sub> — of warmth — as much of an effect as the reduction of the albedo by melting of snow and ice — they both have about a one degree feedback effect. There is a Russian climatologist by the name of Borisenkov, who is skeptical about the CO<sub>2</sub> warming because he thinks that the area of clouds will increase, not the height but the area. And I do not really know how to answer him. That is something which we really have to face at the present

time, and we just have to wait and see, but if there were an increase in albedo due to larger area of cloud, that would certainly counteract the CO<sub>2</sub> radiative warming. Most of the modelers, however, do not think that is going to happen, for reasons that I do not understand. Do you understand it at all?

HARE

I do not understand everything, but I do know that empirically warm years are not cloudier than cold years, and vice versa.

MARINI-BETTÒLO

Have we considered sufficiently in all these the parameter due to particulates?

REVELLE

I think so. Hansen of the Goddard Institute for Space Science, as I said, has tried to parameterize the volcanic particulates, and he shows that they really are important, but of course it only lasts for a very short time. Anthropomorphic or anthropogenic particulates — I guess one thing to say about that is people are not going to stand for it, they are going to reduce them. Like the discussion we had of London the other day. London is cleaner now than it has been for a thousand years, and that is going on all over the world except in the developing countries, which are pretty smoggy. But they are not going to stay smoggy as they develop economically.

ANDERSON

Putting aside the question of the relationship between change in surface temperature and changes in CO<sub>2</sub> content and focusing on projections of CO<sub>2</sub> changes in the atmosphere over the next 100 years, could you summarize for us the three major uncertainties, two or three major uncertainties in that prediction and suggest research to eliminate those uncertainties? or reduce them?

REVELLE

As Nordhaus points out, the uncertainty is basically an economic uncertainty: mainly, how fast is economic growth going to occur? and what is going to be the cost of different sources of energy — nuclear energy or bio-

mass energy versus fossil fuel energy? And that is the real cost, which includes the convenience of fossil fuel energy. Liquid fuels are absolutely essential in our modern industrial society, but primarily for transportation, and it is awfully hard to get any other source of liquid fuels than petroleum. You can make a lot out of coal and oil shale, but at a cost. You can make them sort of artificially in a big nuclear power plant, but the expense there is very high, and the uncertainty is really the uncertainty of predicting what the world is going to be like a hundred years from now from the standpoint of our industrial civilization, not really a scientific but a physical uncertainty.

ANDERSON

May I recast the question slightly: for a given release rate of  $\text{CO}_2$  from fossil fuel, could you speak to the major uncertainties, given that input and research that could be directed toward reducing the uncertainties?

REVELLE

I gave a list of those uncertainties — let me see if I can find that. The only thing you might call scientific uncertainty is the airborne fraction — that is the basic problem of the carbon cycle. The evidence today is that it is about .4, in other words 40% of all  $\text{CO}_2$  put into the atmosphere stays in the atmosphere for a considerable time. That quantity is probably going to go up as the  $\text{CO}_2$  content increases, because of what is called the buffer factor; in sea water it could go up as high as 8 in the airborne fraction. That group of uncertainties really involves better understanding of the carbon cycle, the interchange between the sea and the air, than we have now, and the effect of the biosphere on the airborne fraction. All of the other uncertainties relate to the quantity of fossil fuels that will be burned, and those pretty much overwhelm this airborne fraction.

HARE

Could I add to that? There are two others, namely, the numbers of the human population, which I think is a scientific number, but we do not know it. Secondly, peace or war.

REVELLE

Of course all bets are off if you have a nuclear war.

## CHAMEIDES

I have two questions. The first question concerns this airborne fraction. There must be some time scale associated with what you call the airborne fraction because presumably after a thousand years the airborne fraction is extremely small. So I would like to know whether you are talking about 5 years, 10 years or 100 years for that. The second question is one of clarification concerning the effect of particulates on climate. It was my understanding that the climatic impact of particulates in the atmosphere was not all that obvious whether it would be cooling or heating. Professor Fiocco told us yesterday, I thought, that the impact of volcanos on the surface temperature of the earth was not all that clear — we had a very warm winter in spite of the large volcano emissions. So is it established that the particulates lead to a cooling, or is that still an open question of itself?

## REVELLE

Well, actually a lot is known about them, but they behave in a complicated way. Particulates over the ocean increase the albedos because the albedo of the ocean is only about 5%. Particulates over the land lead to warmth, because they in fact absorb and re-radiate radiation, and they reduce the albedo, they are less reflective than the land surface itself. So it is not by any means obvious that they would actually reduce the temperature. The other question about the airborne fraction, that depends on the rate of emission of  $\text{CO}_2$  and the airborne fraction of 0.4, or rather the amount going into the ocean is about 40%. Remember I said that the entire atmosphere exchanges with the ocean in about 7 or 8 years.

## CANUTO

Just a piece of information since Professor Fiocco has brought up the cloud impact in centimeters and Prof. Bettòlo has brought out the particulates. In my Institute Hansen and two of his colleagues, are exactly working out the details for those two models, and they are working both on the volcanos and the clouds — there are a couple of people working on clouds — so I think that the next major piece of research that they are going to dedicate themselves to is precisely trying to solve this problem. I do not think the heads of NASA would be ready to bet on any direction of  $\Delta T$  as far as Chameides is concerned, but having recognized the importance of that un-

certainty, they are dedicated to that; and so I think that in the next year or so, with the care with which they usually work, we will have a rather reliable number.

ROWLAND

I want to repeat a question that I asked before and which got lost. But I will make a comment in connection with the comment that Professor Knabe made about varying organic matter, that one of the strongest point sources of methane that we have found is the city dump for the city of Irvine, where the air over that dump when we sampled it was 250 parts per million methane instead of 1.7 because of the methane that was coming off from the dump. So in the city of Long Beach they are taking the methane out of their dumps, covered biological areas, and enough methane is coming off that it is profitable to take the methane and use it to burn. But the question I just want to repeat because the answer got lost in the previous discussions. What is known about the composition of that gas?

REVELLE

There are some higher hydrocarbons. There is some pentane and I think some butane too, but I am not quite sure. It is rather small, but it is surprising how more or less pure the stuff is.

ROWLAND

Are there unsaturated hydrocarbons present?

REVELLE

Yes.



# ATMOSPHERIC CONDITIONS AFTER A NUCLEAR WAR

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## ABSTRACT

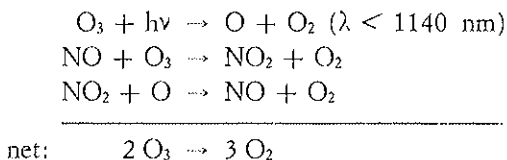
During a full scale nuclear war, the atmosphere would be loaded with huge quantities of pollutants, which are produced by fires in urban and industrial centers, cultivated lands, forests and grasslands. Especially detrimental are the meteorological effects of light absorbing airborne particles. Estimates are presented of the amounts of various types of fuels which would burn in the event of a major war and of the resulting particulate matter production. The fires could produce several hundred million tons of airborne particulate matter, by which the penetration of sunlight to the earth's surface would be reduced greatly over extended areas of the northern hemisphere, maybe even globally. This could temporarily reduce crop growth and biospheric productivity in important ways.

This situation would last for several weeks and cause very anomalous meteorological conditions. Much solar radiation would be absorbed in the atmosphere instead of at the earth's surface. The land areas and lower atmosphere would, therefore, cool and the overlying atmosphere warm, creating strong vertical thermal stability in a highly polluted atmosphere. For extended periods, worldwide weather patterns would be abnormal. The resulting cold, probably freezing, temperatures at the ground could also interfere severely with crop production during the growing season

and cause extreme conditions for large sections of the biosphere. The combination of lack of sunlight, cold temperatures and other abnormal meteorological conditions would add enormously to the already huge problems of the survivors.

## 1. INTRODUCTION

Many meteorological investigations have been devoted to the atmospheric transport and deposition of radioactive material from nuclear bomb testing. Very few studies have, however, been performed on the possible changes which may take place in the physics, chemistry and meteorology of the atmosphere as a consequence of a full scale nuclear war. Some early studies (e.g. Ayers, 1965; Batten, 1966) were too limited in scope and did not take into account the effects considered in this and an earlier study (Crutzen and Birks, 1982). The first major investigation which dealt with possible global, atmospheric and climatic effects of a nuclear war was conducted by a special committee appointed by the US National Academy of Sciences (NAS, 1975). Considerable attention was given to the global depletion of stratospheric ozone and the consequential, harmful biological effects of substantially increased penetration of ultra-violet radiation to the earth's surface. Earlier, Foley and Ruderman (1973), Johnston (1973), Johnston *et al.* (1973), and Hampson (1974) had proposed that the oxides of nitrogen (NO and NO<sub>2</sub>), which are produced in the super-heated air of the nuclear fireballs, would catalyze the destruction of ozone in the stratosphere by the set of reactions (Crutzen, 1970).



As about  $10^{32}$  molecules of NO are produced per MT of explosive energy (1 Mt = 1 megaton TNT =  $10^{15}$  calories), a global war with detonations totalling  $10^4$  Mt would produce  $50 \times 10^{12}$  g NO. This is many times more than the amount which naturally resides in the stratosphere. Large reductions in stratospheric ozone by several tens of percent, lasting for several years, were calculated as a consequence of a major nuclear war in which large weapons with yields of more than 1 Mt would be detonated.

Such large weapons cause the hot fireballs to rise into the stratosphere (NAS, 1975). A several fold increase in the penetration of ultraviolet radiation to the earth's surface would result. This was considered to be the main, long-term, global, atmospheric effect of a total nuclear war. By cursory comparison with the reported effects of major volcanic explosions, the production of dust from nuclear ground bursts was estimated to lead to rather insignificant changes in the earth's climate.

Recently, Ambio, the environmental journal of the Royal Swedish Academy of Sciences, invited an international and interdisciplinary group of scientists to analyze again the environmental effects of nuclear war (Ambio, 1982). These studies were based on a targeting scenario, describing "how a nuclear war might be fought" (Barnaby *et al.*, 1982), which is also adopted for the present study and reproduced in Table I. It reflects probable US and Soviet strategic delivery capabilities in 1985. It does not describe the most probable war and may be more catastrophic than envisioned by many military experts. One third of all nuclear explosives would be directed

TAB. I - *AMBIO Scenario.*

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|  |  |  |
|--|--|--|
| A. Total number of warheads used: 14747          |  |  |
| Total megatonnage used: 5742 Mt                  |  |  |
| Megatonnage used in Northern Hemisphere: 5569 Mt |  |  |
| Megatonnage used in Southern Hemisphere: 173 Mt  |  |  |

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|    |                  |             |
|----|------------------|-------------|
| B. | Size of warheads | Number used |
|    | 100 kt           | 939         |
|    | 200 kt           | 2930        |
|    | 300 kt           | 4410        |
|    | 500 kt           | 5692        |
|    | 1 Mt             | 769         |
|    | 10 Mt            | 7           |

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|  |               |         |
|--|---------------|---------|
| C. Numbers of warheads used for different target categories, |               |         |
| Megatons used for different target categories:               |               |         |
| Military targets   | 6620 warheads | 2960 Mt |
| Population (1124 cities)                                     | 4970 warheads | 1941 Mt |
| Industry/Energy  | 3136 warheads | 701 Mt  |
| Closing of straits<br>(14 straits)                           | 21 warheads   | 140 Mt  |

---

## D. Warheads used for different target categories:

|                    |        |  |
|--------------------|--------|--|
| Military           | 300 kt | (one 300-kt warhead per target)            |
|                    | 100 kt | (one 100-kt warhead per target)            |
|                    | 200 kt | (one 200-kt warhead per target)            |
| ICBM               |        | (two 500-kt warheads per silo)             |
| Submarine Bases    |        | (one 1-Mt warhead per base)                |
| Population         | 1 Mt   | (three 300-kt + one 100-kt per city)       |
|                    | 3 Mt   | (three 1-Mt warheads per city)             |
|                    | 10 Mt  | (ten 500-kt + five 1-Mt warheads per city) |
| Industry           | 1 Mt   | (five 200-kt warheads per site)            |
| Oil fields         | 1 Mt   | (two 500-kt warheads per site)             |
| Closing of straits | 10 Mt  | (seven 10-Mt + fourteen 500-kt warheads)   |
|                    |        | (this is total for the 14 straits)         |

## E. Military targets:

Megatonnage per target  
(average)

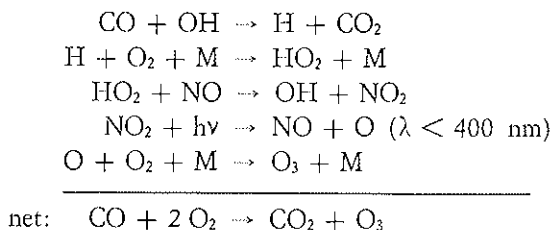
|   |                                 |              |
|---|---------------------------------|--------------|
| Air bases   | 300 kt                          | ground burst |
| Naval ports   | 300 kt                          | ground burst |
| Army bases  | 300 kt                          | ground burst |
| Command/control/radar   | 300 kt                          | ground burst |
| Early warning systems   | 100 kt                          | ground burst |
| SOSSUS  | 300 kt                          | water burst  |
| ICBM  | Two 500 kt warheads<br>per silo | ground burst |
| Energy Resources targets:                                     |                                 |              |
| Hydro electric stations                                       | 10 kt                           | airburst     |
| Other energy resources  | 10 kt                           | airburst     |
| Oilfields   | 1 Mt                            | airburst     |
| Industrial targets:   |                                 |              |
| (only large industrial complexes)                             |                                 |              |
| Oil refineries  | 1 Mt                            | airburst     |
| Chemical plants   | 1 Mt                            | airburst     |
| (heavy organics, urea/nitric acid.<br>sulfuric acid, ammonia) |                                 |              |
| Cement  | 1 Mt                            | airburst     |
| Iron ore/steel  | 1 Mt                            | airburst     |

against cities, which is totally senseless, considering the enormous death toll and the huge amount of injured survivors which it would cause (Middleton, 1982; Lewis, 1979). On the other hand, cities have been bombed extensively during the second world war, including two nuclear attacks. Furthermore, government centers, industries and military establishments are often located close to or in cities, so that city bombing seems inevitable during a nuclear war (Bracken and Shubik, 1982). The bombing of only

one major city would most likely provoke a massive retaliatory exchange involving many cities in the world. As long as there are so many weapons around, they may very well be used against cities, especially in a future world with the likelihood of nuclear proliferation. That the bombing of cities, or at least the fear of it, is included in military thinking follows clearly from the existence of elaborate evacuation plans in several countries (e.g. the USSR) and current proposals to institute them also in the U.S. The incredibility of limitation of a nuclear war in a complex military setting has been shown by Ball (1981).

For a variety of reasons, e.g. prevention of post-war superiority, the nuclear exchange would not only involve NATO and Warsaw Pact member states, but also Japan, China, India and Australia. Almost 45% (5740 Mt) of the available megatonnage worldwide (13000 Mt) would be used by the superpowers, delivered by 14750 warheads. The sizes of the warheads vary between 100 Kt and 10 Mt with an average of about 0.4 Mt. In this paper we will mainly explore the atmospheric effects of urban, industrial and forest fires, which would be started by nuclear explosions, neglecting the effects of conventional, non-nuclear weapons. We will also delete a discussion of the possible consequences of long-lasting fires in oil and especially gas fields, which could certainly be expected as a result of blowouts of production wells, but are difficult to quantify. The potential consequences of such blowouts could be very severe, as discussed by Crutzen and Birks (1982). The meteorological effects of soil-derived dust from nuclear ground bursts have likewise been disregarded in this study. Contrary to the statements of the NAS (1975), Turco *et al.* (1983) in a new study have indicated that they may not be neglected.

There is a very important difference between the nuclear arsenals which were adopted for the NAS (1975) and the AMBIO (1982) studies, reflecting rapid military developments. The NAS study assumed mainly the use of large bomb sizes, mostly with explosive yields of 1 Mt. For the Ambio Study, describing the likely strategic situation in 1985, Barnaby *et al.* (1982), on the other hand, developed a scenario with many more weapons of smaller sizes, much more in agreement with the currently available arsenals. The fireballs from these smaller bombs do not rise high into the stratosphere and much of the NO which is produced by them, will remain in the troposphere (Peterson, 1970). In this case a production of ozone is expected. This is due to reactions, again involving NO and NO<sub>2</sub> as catalysts (Crutzen, 1973), e.g.



Similar, but more lengthy, reaction chains, leading to ozone formation, occur during the oxidation of hydrocarbons, with methane oxidation playing an important global role. The production of ozone would be further enhanced by the simultaneous production of  $\text{NO}_x$ , CO and various reactive hydrocarbons by the fires and by the gas and oil well blowouts, which would occur around the world. It was shown by Crutzen and Birks (1982) that this could lead to photochemical smog formation over large parts of the Northern Hemisphere. However, for such "photochemical smog" reactions to take place, the availability of sunlight is a prerequisite. As fires do also produce large amounts of black smoke which absorbs sunlight, an analysis of the aerosol production by the fires started during the nuclear war became necessary. This analysis led to the discovery of the most serious global, environmental consequence of a major nuclear war, discussed so far. It was shown that the presence of smoke could profoundly change global meteorological conditions.

In this paper a study of the effects of smoke evolution on atmospheric and environmental conditions will be presented. Much of the necessary information for such a study is quite uncertain, so that a very wide range of estimated effects is possible. The main uncertainties of the analysis are pointed out and "reasonable" choices are made, avoiding extreme assumptions. The main purpose of this paper is once again to show the enormous potential importance of the atmospheric and environmental effects and to provide background material for further studies.

## 2. FIRES, PARTICULATE MATTER AND THEIR OPTICAL PROPERTIES

During a nuclear war, many fires would start near urban, industrial and military targets (Barnaby *et al.*, 1982). We will try to make some rough estimates of the extent of fires in various categories of combustibles, the amount of particulate matter produced thereby, and its optical properties. We will use this information to estimate the effects of the particulates on

the penetration of sunlight through the atmosphere. A rather extensive survey of the fire research literature was made for this purpose. Data were gathered for the following categories of combustible materials: construction wood, oil and gas, synthetic polymers and forest fuels. For each of these the average, percentage yield of particulate matter and its graphitic or elemental carbon (EC) content were estimated. The mechanisms of soot or EC formation in flames have been reviewed by Wagner (1980) and Rasbash and Drysdale (1982).

The aerosol particles, which are important for this study, are combustion products and are initially mainly formed in the nucleation mode with radii much below  $0.1\ \mu\text{m}$ . Through coagulation, these embryonic particles recombine rapidly to larger sizes. The atmospheric lifetime of particles with radii less than  $0.1\ \mu\text{m}$  is, therefore, relatively short, under normal conditions less than a few days. Particles with radii larger than  $3\ \mu\text{m}$  are likewise removed rather rapidly from the atmosphere, mainly by gravitational settling. In the size range between about  $0.1\ \mu\text{m}$  and  $3\ \mu\text{m}$ , the so-called accumulation mode, atmospheric aerosol particles have the longest residence time in the atmosphere. This is mainly determined by precipitation scavenging and, as a global average, may range from about one week below  $1.5\ \text{km}$ , to one month in the upper troposphere, and about one year or longer in the stratosphere (Jaenicke, 1981).

There will, however, exist large variations in the removal rates of these aerosol particles, especially of the important elemental carbon component. In a recent study, Ogren and Charlson (1983) have presented an overview of the complex processes which determine the residence time of EC in the atmosphere. These authors distinguish between externally and internally mixed EC, the external mixture consisting of particles which have not yet combined with other types of occurring aerosol, i.e. rather "fresh" EC. Externally mixed accumulation mode EC particles are not expected to be efficiently incorporated in cloud droplets because they are hydrophobic and can, therefore, not act as cloud condensation nuclei. For such particles rainout and washout should be rather inefficient (Pruppacher and Klett, 1980, p. 395-396; Ogren and Charlson, 1983). With time, externally mixed EC is converted into internally mixed EC by coagulation with other types of aerosol particles or after the condensation of compounds from the gas phase, after which they may become hygroscopic and act as condensation nuclei. The residence time of EC in the atmosphere should, therefore, be longer than the average value

applying for aerosol. A more detailed discussion about these removal processes will be given in section 5 of this paper.

Airborne particulate matter scatters and may also absorb solar radiation. It is a remarkable coincidence of nature that the optically most effective aerosol particles are also the most long-lived ones. These particles have a specific scattering of about  $4 \text{ m}^2/\text{g}$  aerosol, which is a typical value for various situations in the atmospheric environment, e.g. for forest fire smokes (Tangren, 1982; Radke *et al.*, 1978; Vines *et al.*, 1971) and urban and rural air (Waggoner *et al.*, 1981; Chylek *et al.*, 1981; Wolff *et al.*, 1979, 1981, 1982). The presence of graphitic or elemental carbon in aerosol is very important, as it leads to very efficient absorption of solar radiation. This material is only formed during flaming combustion. The specific absorption of "fresh", externally mixed, EC has been measured to range from about 5 to  $20 \text{ m}^2/\text{g}$ , with a mean value of about  $10 \text{ m}^2$  per gram EC (Chylek *et al.*, 1981; Novakov, 1979, 1982; Cadle and Groblicki, 1982). Coagulation leads to the formation of larger aerosol particles, which, in the case of externally mixed EC, would absorb sunlight less efficiently (Chylek *et al.*, 1981). For aged aerosol, the specific absorption, as determined by observations in remote regions, seems generally to be equal to  $10 \text{ m}^2/\text{g}$  EC. This value will, therefore, be adopted in this study. A theoretical explanation for this has been given by Ackerman and Toon (1981). The specific scattering ( $b_s$ ), absorption ( $b_a$ ) and extinction ( $b_e$ ) which will be adopted for an initial analysis are, therefore, given by

$$(1a) \quad b_s = 4 \text{ m}^2/\text{gram aerosol},$$

$$(1b) \quad b_a = r_{ec} \times 10 \text{ m}^2/\text{gram aerosol},$$

$$(1c) \quad b_e = b_a + b_s$$

where  $r_{ec}$  denotes the fraction of elemental carbon in the smoke particles. The radiative transfer calculation method followed in this study is only approximate. A more complete and self consistent analysis will be presented in a forthcoming paper (Crutzen *et al.*, 1984).

Information on particulate matter production in test fires has been compiled in Tables II-V. In a few instances, extinction cross sections were directly measured and used to derive the properties of the smoke particles. It is clear in all cases that available information is scanty, variable and uncertain. Because we are no experts in combustion research, we have checked our analysis with several combustion specialists and have gotten



TAB. II - *Literature survey on characteristics of aerosol produced by burning of wood.*

| Ref. nr.  | Type                                  | Aerosol yield                                  | Elemental C    | m <sup>2</sup> /g fuel<br>(extinction) |
|-----------|---------------------------------------|--|----------------|--|
| 1.        | Fireplace, softwood                   | 9 g / kg                                       | 33% of aerosol |  |
|           | Fireplace, hardwood                   | 10 g / kg                                      | 8% of aerosol  |  |
| 2.        | Residential wood                      |  | 13% of aerosol |  |
| 3.        | Laboratory test fires<br>free burning |  | 50% soot       | 0.023                                  |
|           | ventilation controlled                |  |                | 0.15                                   |
| 4.        | Laboratory test fires<br>hardwood     | 0.085-0.16%                                    |                |  |
|           | fibreboard                            | 0.75%  |                |  |
| 5.        | Laboratory test fires                 | 1-2.5% (flaming)<br>3.1-16.5%<br>(non-flaming) |                |  |
| 6.        | Laboratory test fires                 |  |                | 0.01                                   |
| 7.        | Laboratory test fires                 | 0.2-0.6%                                       |                |  |
| "Average" |                                       | 1%   | 20%            | (0.06)                                 |

References: 1 (Muhlbaier Dasch, 1982), 2 (DeCesar and Cooper, 1983), 3 (Rasbash and Pratt, 1979, and personal communication D.J. Rasbash), 4 (Hilado and Machado, 1978), 5 (Bankston *et al.*, 1981), 6 (Tewarson, 1982), 7 (Seader and Einhorn, 1976).

the impression so far that our estimates are quite reasonable. More studies are, however, required.

Table II containing data on wood burning combines information from burning in fireplaces and from test fires of cellulosic materials, which are typically used in building construction. For this category of materials, we compromise to derive an average aerosol yield of 1% of the fuel burned, containing about 20% EC. References to the studies considered here have been listed in the Table captions. In the same way the information for the other categories of fires has been compiled in Tables III-V. In the derivation of the average quantities, we emphasised the importance of the flaming phase for the optical (light absorption) properties of the aerosol. Smoldering burning will produce larger particles, because of the greater probability of coagulation of embryonic particles from the slowly burning material (Mulholland and Ohlemiller, 1982). For the flaming burn-

TAB. III - *Literature survey on characteristics of aerosol produced in oil gas burning.*

| Ref. nr.  | Type                         | Elemental C           | m <sup>2</sup> /g fuel<br>(extinction) |
|-----------|------------------------------|-----------------------|--|
| 1.        | Residual oil in burner       | 31% of aerosol carbon |  |
| 2.        | Diesel engine                | 80% of aerosol        |  |
|           | Gas furnace                  | 90% of aerosol carbon |  |
| 3.        | Light oil in burner          | 40-70% of aerosol     |  |
|           | Natural gas furnace          | 40-70% of aerosol     |  |
| 4.        | Light oil in burner          | 40% of aerosol carbon |  |
| 5.        | Oils, rubber                 | 100% soot             | 0.7 - 1.2                              |
| 6.        | Oil slick                    | 2-6% of fuel burned   |  |
| 7.        | Natural gas diffusion flames | all emissions as soot | 3                                      |
|           | Heavy fuel oil » »           | all emissions as soot | 2                                      |
| 8.        | Aliphatic oils               | 3-10% of fuel burned  |  |
| "Average" |                              | 5% of fuel burned     | (0.7)                                  |

Note that references 1-4 all refer to clean burning in household equipment and are not representative for mass fires. References: 1 (Cooper and Watson, 1979), 2 (Muhlbaier Dasch and Williams, 1982), 3 (Nolan, 1979), 4 (Wolff *et al.*, 1981), 5 (Rasbash and Pratt, 1979; Rasbash, private communication), 6 (Day *et al.*, 1979), 7 (Maraval, 1972), 8 (Rubber and Plastics Research Association of Great Britain, letter to authors).

ing of plastics we derived rather similar, average properties as for oil and gas burning, so that these two categories will be combined (compare Tables III and IV). For each of the categories of combustibles, the average extinction coefficients have likewise been calculated from the derived information on aerosol yield and EC content, using formulae (1a)-(1c). The derived quantities have been printed within parentheses on the last lines of Tables III-V. We note that, compared to the measured values, the calculated extinctions are on the low side for fossil fuel and synthetic polymer and "in the middle" of the range for wood burning.

Large uncertainties also exist in the category vegetation and forest fires. The values compiled in Table V are lower than used by Crutzen and Birks (1982). Uncertainties mainly arise from difficulties in the sampling of forest fire plumes and the complex nature of forest fires in which different phases of burning (flaming and smoldering) occur simultaneously in a variety of combustible materials. This makes the interpretation of forest fire plume data very difficult. We consider some of the ship-

TAB. IV - Literature survey on characteristics of aerosol produced by burning of plastics.

| Ref. nr.  | Type  | Aerosol                  | Elemental C   | m <sup>2</sup> /g fuel<br>(extinction) |
|-----------|---|--------------------------|---------------|--|
| 1.        | Plastics<br>Rubber  |                          | 100% soot     | 0.2 - 1.6<br>1.0                       |
| 2.        | Various plastics  | 5-50% soot               | 2-40% of fuel |  |
| 3.        | Polyethylene, styrene<br>PVC (flaming)<br>Polyurethane<br>(flaming) | 1.2-3.2%<br>9%           |               |  |
| 4.        | Plastics  | 6-20%                    |               |  |
| 5.        | Plastics  | 3-5 %                    | 100% soot     |  |
| 6.        | Plastics  | 11-20%                   | 75% soot      |  |
| 7.        | Plastics  |                          |               | 0.3 - 1.2                              |
| 8.        | Automobile<br>components  | 5%                       |               |  |
| 9.        | Plastics  |                          | 60-100%       |  |
| 10.       | Polystyrene   | 3-10% soot               |               |  |
| 11.       | Polyethylene<br>Polyisoprene<br>Polystyrene                         | 5-8.3%<br>19.4%<br>21.0% |               |  |
| "Average" |   | 5%                       | 60%           | (0.5)                                  |

References: 1 (Rashash and Pratt, 1979, and D.J. Rashash, personal communication), 2 (Morikawa, 1980), 3 (Bankston *et al.*, 1981), 4 (Hilado and Machado, 1978), 5 (J.E. Snell, personal communication), 6 (Tewarson *et al.*, 1981), 7 (Tewarson, 1982), 8 (EPA, 1978), 9 (Seader and Ou, 1977), 10 (Rubber Plastics Research Association of Great Britain, letter to authors).

board measurements by Andreae (1983) in the tropical Atlantic, which were clearly influenced by biomass burning effluents from the African and South American continents, to be of particular significance.

For all categories the exact determination of the elemental carbon content is a difficult physico-chemical problem. This may seem surprising as soot is so easily observable with the eye. The role of soot in atmospheric optics and climate is now attracting substantial attention (Novakov, 1979; Wolff and Klimish, 1982). Because of its radiative properties, deliberate weather modification with soot particles has been proposed and discussed (Gray *et al.*, 1976; Chen and Orville, 1977).

TAB. V - *Literature survey on characteristics of aerosol produced by vegetation fires.*

| Ref. nr.  | Type                                      | Aerosol/fuel | Elemental C           |
|-----------|---|--------------|-----------------------|
| 1.        | Slash burns                               |              | 10 % of aerosol       |
| 2.        | Vegetation burns                          |              | 7.1% of all aerosol C |
| 3.        | Forest Fires                              |              | 10 % of aerosol       |
| 4.        | Prescribed forest fires                   | 4%           |                       |
| 5.        | Prescribed forest fires                   | 2%           | 25 % "soot"           |
| 6.        | High intensity forest fire,<br>prescribed | 0.44%        |                       |
|           | Low intensity forest fire,<br>prescribed  | 2.4%         |                       |
| 7.        | Agricultural burning                      |              | 9 % of aerosol        |
| 8.        | Forest wildfires                          |              |                       |
|           | 60% flaming                               | 10 kg/ton    |                       |
|           | 40% smoldering                            | 60 kg/ton    |                       |
| 9.        | Forest wildfires                          | 70 kg/ton    |                       |
| 10.       | Forest wildfires                          |              | 4 % of aerosol        |
| 11.       | Laboratory test fires                     |              |                       |
|           | flaming                                   |              | 15 % of aerosol       |
|           | non-flaming                               |              | 2.5% of aerosol       |
| 12.       | Mid-Atlantic air samples                  |              | 7 % of aerosol        |
| 13.       | Slash burns                               |              | 7.9% of aerosol       |
| "Average" |   | 4%           | 8%                    |

References: 1 (DeCesar and Cooper, 1983), 2 (Cooper and Watson, 1979), 3 (Macias *et al.*, 1981), 4 (Radke *et al.*, 1978), 5 (Vines *et al.*, 1971), 6 (Evans *et al.*, 1977), 7 (Cass *et al.*, 1982), 8 (Wade, 1980), 9 (Ward *et al.*, 1976), 10 (Ouimette and Flagon, 1982), 11 (Patterson and McMahon, 1983), 12 (M.O. Andreae, 1983 and private communication), 13 (Shah, 1981).

Finally we note that the data which are compiled in Tables II-V are mostly based on simple laboratory tests with single specimen of typical fuel types. The applicability of these data to mass fires is debatable (Powell *et al.*, 1979). In fact, according to Rasbash and Drysdale (1982), the effect of the environments into which the fire volatiles are released is probably more important than the nature of the combustibles. Lack of ventilation enhances smoke production, as can clearly be seen from the data of Rasbash and Pratt (1979), listed in Table II. As shown in Tables II-IV, burning of unoxidized fossil fuels and plastics yields much more

smoke and soot than the burning of half oxidized wood (Rasbash and Drysdale, 1982). It is also instructive to note that per gram of fuel, forest fires produce about 4 times more aerosol than the burning of wood in fireplaces and laboratory tests, which might be the result of more limited supply of oxygen in forest fires. For this reason, the acceptance of the derived average aerosol optical properties of Tables II-IV for the remainder of this study may well imply a considerable underestimation of the aerosol and soot production and of the absorption and extinction of sunlight in the atmosphere by mass fires.

### 3. QUANTITIES OF VARIOUS MATERIALS BURNED

#### 3.1 *Forest fires*

Temperate and boreal forests occupy a total area of  $24 \times 10^6$  km<sup>2</sup>. Crutzen and Birks (1982) guessed that forest fires following a nuclear war might destroy a total area of  $10^6$  km<sup>2</sup>. This is 55 times larger than the area which is annually subjected to wildfires in the US (excluding Alaska). For the temperate and boreal forests the area which is annually affected by wild-fires is 5-10% of one million km<sup>2</sup>. The available statistics of the US Forest Service (Ward *et al.*, 1976) give a forest wildfire area of 0.18 million km<sup>2</sup> in the 1930's in the US, about ten times higher than at present. This reduction is of course due to the effective fire fighting and prevention programs which were instituted in the US since the 30's.

For the Ambio Scenario it may be calculated that about 22% of the nuclear explosions would occur in forested regions (Galbally *et al.*, 1983). With maybe millions of ignitions starting simultaneously over large areas effective fire fighting would be clearly impossible following a nuclear war. Especially during the summer season in large tracts of woodlands the probability of fire spread is substantial. During August probabilities are larger than 50% for the occurrence of "actionable" or "critical" fire spread conditions in the Western half of the US (Schroeder and Chandler, 1966). Under "actionable" conditions fires would still spread, if not fought; under "critical conditions" effective fire fighting is impossible. In a related study Huschke (1966) estimated that for half of the time, as much as 50% of all US timber lands are medium or highly flammable during the summer months.

Only a few estimates have been made of the forest fire spread from nuclear detonations. Hill (1961) quotes from earlier US Forest Service studies (not available to the author) minimum forest fire areas of 500, 1000, and 2100 km<sup>2</sup> for 1, 3 and 10 Mt, respectively. These areas correspond to fire occurrence at all points where the radiant heat pulse from nuclear detonations exceeds 15 cal/cm<sup>2</sup>. Maximum spread areas which are listed by Hill (1961) are at least a factor of ten higher.

The deductions of forest fire spreads are extremely difficult and uncertain, depending critically on meteorological conditions and therefore seasonally dependent. It is not straightforward to extrapolate the above fire spread areas for the Ambio scenario, as in some areas there will be dense targeting and considerable overlap between potential fire areas. In an earlier study a forest fire area of 10<sup>6</sup> km<sup>2</sup> (Crutzen and Birks, 1982) was assumed. This estimate has been attacked both for being much too small and much too high by various forest experts. All recognize the seasonal dependence of the estimate and one forest expert even suggested that 5-10 million km<sup>2</sup> of forest might burn in Alaska and Siberia during the summer. A thorough, global analysis is necessary. This should also include estimations of long-lasting fires, as much forest area would be destroyed by radioactivity (Woodwell, 1982) and by post-war climatic changes. For this study we will assume a total forest fire area of 10<sup>6</sup> km<sup>2</sup>, but will also give results for a case in which forest fires are neglected.

With an area of 10<sup>6</sup> km<sup>2</sup> and average biomass density of 20 kg/m<sup>2</sup>,  $4 \times 10^{15}$  gram of biomass would burn as a consequence of a nuclear war. This assumes that 20% of all available fuel in the forest fire area, mostly leaves, duff, small twigs, branches and bark would burn, which is a reasonable estimate for normal forest fires. It may be an underestimate for any wild fires started by nuclear explosions, as blast effects will break larger size materials and pile much of it up on the forest floor. Furthermore, in this study no account was taken of the aerosol production by fires which might take place in organic forest soils or peat bogs (Shostakovitch, 1925), and other plant communities than forests, such as brushlands and agricultural lands.

### 3.2 *Urban and industrial fires*

The estimation of the areas which would be destroyed by urban and industrial fires is likewise a difficult task, as the results would vary from city to city. In order to reach some quantitative estimates, we prefer

to extrapolate here from the nuclear fire experiences of Nagasaki and Hiroshima. For Nagasaki the completely burned-out area covered 7 km<sup>2</sup> due to a 22 Kt weapon. At Hiroshima a 12 Kt weapon caused the burnout of 13 km<sup>2</sup> (Hill, 1961; Ambio, 1982). This can be translated in a total burnout for radiant heat pulses larger than 20 cal/cm<sup>2</sup> in Nagasaki and 7 cal/cm<sup>2</sup> in Hiroshima in the initial flash (Hill, 1961; Glasstone and Dolan, 1977). The difference in these threshold values is due to a combination of topographic and constructional factors. Parts of Nagasaki were protected from ignitions by high hills, while the building density in Nagasaki was appreciably lower than in Hiroshima (Ishikawa and Swain, 1981). At a radiant pulse of 20 cal/cm<sup>2</sup> even heavy fabric, such as draperies and furnishings, will catch fire. Thinner fuels such as dried leaves and newspapers will ignite at about 5 cal/cm<sup>2</sup>. Between 5 and 20 cal/cm<sup>2</sup> potential fuels such as books, industrial trash and Kraft corrugated board will ignite (Martin and Broido, 1963).

Adopting a conservative criterion of 20 cal/cm<sup>2</sup> for burnout, the average nuclear weapon of 400 Kt, as adopted in the Ambio scenario, would destroy an area of about 150 km<sup>2</sup> by fires. We may note that this area of destruction is about a hundred times larger than that covered by the initial fireball. With a total use of 1940 Mt of nuclear explosives against cities, the total burned area over the entire earth would be almost 0.8 million km<sup>2</sup>. This estimate does not take into account that industrial and military targeting, which was counted as a separate category in the Ambio study, would likewise start fires in many urban areas. It also neglects firespread, which may be substantial, as the experience in Hiroshima showed.

We may compare this estimate of global burnout with that which may be derived from information in the OTA (1979) study. According to this study for a 1 Mt burst on Detroit, the main fire area would cover 180 km<sup>2</sup>. For the Ambio scenario this would extrapolate to 0.35 million km<sup>2</sup>.

For the following discussion we use an average of 0.5 million km<sup>2</sup> for the total urban area, which would be attacked by fires. This is about 30% of the combined area of all cities in the world with more than 100,000 inhabitants. An area of this size is ten to forty thousand times larger than that burned during the Hamburg firestorm of July, 27-28, 1943 (Ebert, 1963; Caidin, 1960).

Data on fuel load densities in urban areas are scarce. In German compilations the following typical values for fuel loads per m<sup>2</sup> of floor

area are given: 40 kg for offices, 125 kg for libraries, 50 kg for laboratories, 60 kg for chemical factories and a wide range 12-120 kg for various other uses. Compilations for the US (FEMA, 1982; Culver, 1976) give values of 50-100 kg/m<sup>2</sup> for residential buildings, 50-200 kg/m<sup>2</sup> for offices, up to 150 kg/m<sup>2</sup> for industries and 100-400 kg/m<sup>2</sup> for storage spaces. Floor area fire loads for apartment buildings seem to be of the order of 25 kg/m<sup>2</sup> in the U.K. (Rasbash, 1967) and 50 kg/m<sup>2</sup> in Japan (Morikawa, private communication). Furniture mass loadings in homes in the UK may range from 10-14 kg/m<sup>2</sup> in bedrooms to 14-22 kg/m<sup>2</sup> floor space in sitting rooms (Rubber and Plastics Research Association of Great Britain, letter to the authors). For pre-second world war city apartments in Germany an average fire load density of 110 kg/m<sup>2</sup> floor area may apply. In modern buildings this may be 40 kg/m<sup>2</sup> (Schmitt, 1954). The fire loads in high-rise buildings may be larger than 1000 kg/m<sup>2</sup> as an analysis for office buildings in the U.S. has shown (Culver, 1976).

The fire loads per unit ground area in cities are of course very variable. For a modern German city center a reported value is 130 kg/m<sup>2</sup>; in an older city 330 kg/m<sup>2</sup> may be more appropriate (Schmitt, 1954). The fire load in the Hammerbrook section of Hamburg prior to the firestorm of July, 1943, was 300 kg/m<sup>2</sup> (Ebert, 1963). In the central parts of some older cities fire load densities may, therefore, be very high. In their evaluation of the potential behavior of large urban fires for three model American cities, Larson and Small (1982) adopted total areal fire loads of almost 240-640 kg/m<sup>2</sup> for the city centers out to 1-2 km radius, 70-190 kg/m<sup>2</sup> for the inner belt out to 3-6 km and 18-50 kg/m<sup>2</sup> for the outer belt out to 12 km. Their analysis leads to overall areal fire load densities of 270, 45 and 23 kg/m<sup>2</sup> for cities in the Eastern, Middle and Western US, respectively. Considering the overall population distribution, the higher values are more representative for the case of an all-out nuclear war. The effects of blast on fire behavior must also be considered, but is unknown (Wiersma and Martin, 1973). This may lead to extinction or enhancement of fires. For this reason, Larson and Small (1982) performed two sets of model calculations. For one set it was assumed that all material in the cities would burn; in the alternative case it was assumed that blast effects would bury most combustible material in the inner parts of the city so well that little of it would burn. The latter possibility seems doubtful, at least for US cities, when we consider that only 25 years ago the cities of Washington and San Francisco contained as much as 96-99% combustible construction (Broido, 1960).



For the present calculations we will adopt a value of  $40 \text{ kg/m}^2$  for the fire load density in urban areas. This may not be too far off from a reasonable value if city centers would be preferentially targeted and blast limited most of the fires in the central parts. However, it could be an underestimate, if this is not the case. We will also assume that only half of the buildings or half of the available fire load of  $40 \text{ kg/m}^2$  would actually burn, i.e.  $20 \text{ kg/m}^2$  (OTA, 1979). Altogether, in the urban area of  $0.5 \text{ million km}^2$  at least  $10^{16}$  gram of fuel would be consumed by fires. Most of this material will be wood in constructions and furniture, but it will also contain an appreciable fraction of synthetic organic polymers (plastics), which produce aerosol and soot much more efficiently than wood.

For the purpose of the present study, we assume the aerosol produced by the burning of plastics to have similar properties to those produced from oil and gas fires. These materials are all stored in large quantities in urban areas. The annual world-wide production of synthetic organics is about  $6 \times 10^{13} \text{ g}$  (U.N., 1981). According to Marland and Rotty (1983) about  $2 \times 10^{14} \text{ g}$  or 4% of the global fossil fuel production is not immediately burned, but converted to various longlived materials. About half of this material is asphalt. Polymeric materials are becoming increasingly common and may constitute as much as 10-20% of all combustible materials in German buildings (Verband der Sachversicherer e.V., personal communication). This percentage will probably increase substantially in the future (Anonymous, 1975). Lacking a more thorough analysis, we guess that about  $10^{15} \text{ g}$  of polymeric synthetic materials have accumulated world-wide. This is based on an average lifetime of about 20 years.

The global fossil fuel storage is about equivalent to 3-5 months of consumption. To this must be added the energy stored for domestic heating and for industry, and in military stock-piles. The total may amount to  $2 \times 10^{15} \text{ g}$ . Large amounts of asphalt have accumulated in cities and part of this will also burn vigorously, as e.g. during the Hamburg firestorm (Caidin, 1960). As this material is longlived, the amount of asphalt which may have accumulated globally may be about  $3 \times 10^{15} \text{ g}$ .

Altogether, a total of about  $6 \times 10^{15} \text{ g}$  of synthetic polymers, fossil fuels and asphalt may have accumulated worldwide. Especially, as oil storage facilities and refineries are likely targets, it seems reasonable to assume that  $10^{15} \text{ g}$  of material in these categories would burn.

We repeat that in this paper we have not considered the consequences of the fires which could start in coal dumps or due to blowouts in oil and

gas production wells, because these are difficult to quantify. The latter is, however, a serious possibility, as testified by several military documents (Marriott, 1974/1975; Judd, 1975; Wall, 1976/1977; Simpson, 1976).

#### 4. DARKNESS PRODUCTION POTENTIAL OF THE AMBIO SCENARIO

The information on the quantities of combusted materials, and on aerosol and elemental carbon production, which is collected in Tables II-V, has been combined in Table VI to derive the state of the atmosphere during the nuclear war. We assume that the war would last for only a few days; the aerosol particles would also be given off to the atmosphere in such a short time. Most fire produced aerosol would initially be located between 30°N and 60°N, where most of the nuclear targets are located. If the nuclear explosions would occur over a period of three days, the fire plumes produced on the West and East coast of the US and over Europe (including the USSR) could cover most of the 30-60°N latitude belt, except the Pacific Ocean. This is based on an average westerly wind speed of 20 m/s in the middle and upper troposphere (Oort and Rasmussen, 1971). Spread in South-North direction within the latitude zone should

TAB. VI - *Compilation of optical depths over 60% of the 30-60°N latitude belt ( $6 \times 10^{13} \text{ m}^2$ ), immediately following a nuclear war according to the Ambio scenario. The quantities  $d_s$ ,  $d_a$  and  $d_{\text{ext}}$  are the estimated average optical depths for scattering, absorption and total extinction, respectively, calculated for overhead sun conditions. Quantities within parentheses neglect smoke production by forest fires.*

| Category                             | Fuel<br>(burned (g)) | Aerosol<br>produced (g) | Elemental<br>Carbon<br>produced (g) | $d_s$         | $d_a$         | $d_{\text{ext}}$ |
|--------------------------------------|----------------------|-------------------------|-------------------------------------|---------------|---------------|------------------|
| Cities/Industries                    |                      |                         |                                     |               |               |                  |
| Wood                                 | $1.0 \times 10^{16}$ | $1.0 \times 10^{14}$    | $2.0 \times 10^{13}$                | 6.6           | 2.0           | 8.6              |
| Oil, asphalt,<br>polymers            | $1.0 \times 10^{15}$ | $0.5 \times 10^{14}$    | $3.5 \times 10^{13}$                | 3.3           | 5.9           | 9.2              |
| Forest fires ( $10^6 \text{ km}^2$ ) | $4.0 \times 10^{15}$ | $1.6 \times 10^{14}$    | $1.3 \times 10^{13}$                | 10.7          | 2.2           | 12.9             |
| Total                                | $1.5 \times 10^{16}$ | $3.1 \times 10^{14}$    | $6.8 \times 10^{13}$                | 20.6<br>(9.9) | 10.1<br>(7.9) | 30.7<br>(17.8)   |

occur very rapidly, because altogether about 15,000 nuclear detonations would occur. The area which would be initially covered by smoke would, therefore, be equal to  $6 \times 10^{13} \text{ m}^2$ .

The average optical depth for this aerosol-covered part of the earth can for each category of combustibles be calculated from the formulae

$$(2a) \quad d_s = F \times b_s / 6 \times 10^{13}$$

$$(2b) \quad d_a = F \times b_a / 6 \times 10^{13}$$

$$(2c) \quad d_{\text{ext}} = d_s + d_a$$

where  $b_a$  and  $b_s$  are defined by equations 1a and 1b, and  $F$  is the quantity of aerosol produced. The symbols  $d_s$ ,  $d_a$  and  $d_{\text{ext}}$  are the optical depths for scattering, absorption and total extinction, respectively. These are shown for each of the categories of fires in Table VI. The sums of these quantities are so large that, for a few days, very little sunlight could reach the smoke covered part of the earth. In section 6 we estimate that the transmission of sunlight to the earth's surface might be less than  $10^{-5}$  for several days. These conditions are caused by the production of  $2.3 \times 10^{14} \text{ g}$  of aerosol, of which about  $6 \times 10^{13} \text{ g}$  would consist of elemental carbon.

Darkening of the sky and large reductions in the total amounts of sunlight reaching the surface over extended areas have been documented for large forest fires. Descriptions of such observations can be found in Crutzen and Birks (1982). Effects of forest fires in Western Canada in 1950 were clearly observable in Europe (Smith, 1950; Wexler, 1950). If we extrapolate these relatively small events to the huge extent of burning in the case of a nuclear war, the afore described enormous effects become entirely plausible.

It may be noted that this large quantity of aerosol is produced by the burning of one million  $\text{km}^2$  which covers only one percent of the surface of the continents. Much of the material produced during the most intense periods of fires would be deposited at high levels in the troposphere (and maybe lower stratosphere). During the Hamburg firestorm the smoke columns may have reached 13 km (Caidin, 1960; Ebert, 1963). The high rising effluents contain most of the light absorbing aerosol. The particulate matter, which is formed by smoldering burning and which does not contain elemental carbon, will remain much closer to the ground. This aerosol would substantially reduce visibility and could, together with the many other air pollutants, cause bad health problems for many of the survivors of the war.

We emphasize that the described situation would be appropriate only for the first few days during or following the nuclear war. In the following section we will analyse how later the aerosol might influence other parts of the earth. The effects of rainout will be taken into account.

## 5. PRECIPITATION SCAVENGING

We have noted that the lifetime of airborne particulate matter between  $0.1 \mu\text{m}$  and  $3 \mu\text{m}$  is mainly determined by precipitation scavenging, leading to average residence times of about one week in the lower and one month or longer in the upper troposphere and stratosphere. This range of values will be used in the following analysis. Here we will first discuss the possible loss of aerosol in the convection clouds which may be stimulated by the fires. Scavenging taking place in the rising convective column of the superheated air of the fireball will not be considered. This is justified by the fact that the initial area of the fireball is only about one percent of the total fire area.

Precipitation efficiencies (precipitation/condensation) of naturally occurring convective clouds are quite variable, but may average about 50% (Slinn, 1982). Removal of aerosol may, however, be more efficient (Hobbs and Molenkamp, personal communications). Nothing is known about the rainout efficiencies of the "fumulus" clouds which are stimulated by the buoyancy of the fires. However, not all fires will cause such convective cloud formation.

The following arguments may indicate that precipitation scavenging of fresh EC in "fumulus" clouds may not be too important.

a) Following Galbally *et al.* (1983) we may roughly estimate the volume of the plume of a city fire by assuming a width of 5 km, a typical duration of the fire of 12 hours and a mean zonal wind velocity of 20 m/s. For an assumed vertical injection column of 7.5 km, the fire plume volume would be  $3 \times 10^{13} \text{ m}^3$ . For the 15,000 fires as envisaged in the Ambio scenario, the volume of air initially filled with smoke may thus be of the order of  $4.5 \times 10^{17} \text{ m}^3$ , containing about  $2 \times 10^{17} \text{ kg}$  of air. The heated air rising up from the lower troposphere into the plume might at most have contained about  $10^{18} \text{ g}$  of water vapor, if entrainment is neglected. This is the amount of water which at most can rain out in the fire induced convective storms. The  $10^{16} \text{ g}$  of water vapor which are created by the burning of the combustibles are negligible compared to this.

b) Eagan *et al.* (1974) observed a production of  $6 \times 10^{10}$  cloud condensation nuclei (CCN) per gram of forest fuel consumed. This can only represent a few percent of all fire generated aerosol. Most of this aerosol, in which we are particularly interested, is produced with mean radii less than  $0.1 \mu\text{m}$  (Ward *et al.*, 1976), so that  $6 \times 10^{10}$  CCN in this size range would represent a mass of  $2 \times 10^{-4}$  g. One gram of forest fuel produces, however, a much larger total of  $2.7 \times 10^{-2}$  g of particulates (Ward *et al.*, 1976). On the average about 22% of the aerosol produced during the flaming combustion of various combustibles consists of EC (see Table VI). For forest fuels the EC content is 8%. It can not be expected that EC would be preferentially used as CCN, as fresh soot particles are hydrophobic (Ogren and Charlson, 1983), and in any case the CCN could only be a minor fraction of all EC produced by the fires.

c) The global mass fires would consume  $10^{16}$  g of combustibles, mostly wood, so that  $N_d = 6 \times 10^{26}$  cloud condensation nuclei would be created by the fires. If all of these were activated, the average droplet size  $r_d$  may be determined from the equation

$$N_d \times \frac{4}{3} \pi r_d^3 \rho_d = G$$

where  $\rho_d = 1 \text{ g/cm}^3$ ,  $N_d = 6 \times 10^{26}$  and  $G = 10^{18}$  g water.

It follows that  $r_d = 7.5 \mu\text{m}$  for an average droplet concentration of  $n_d = 1000/\text{cm}^3$ . The average separation between droplets would be  $800 \mu\text{m}$ . In comparison Eagan *et al.* (1974) measured  $r_d = 4 \mu\text{m}$  and  $n_d = 3700 \text{ cm}^{-3}$  in the plume of a forest fire. Under these conditions, the time needed for precipitation to form by collision and coalescence will be prohibitively long. As the average fall velocity of a droplet of  $7.5 \mu\text{m}$  radius is  $0.2 \text{ cm/s}$ , it follows that in one hour such a droplet can only grow to at most two times its original size by collision and coalescence. A typical microscale turbulence length is about  $1000 \mu\text{m}$ , compared to an average droplet radius of  $7.5 \mu\text{m}$ , making turbulent shear and inertial coagulation very inefficient processes (Pruppacher and Klett, 1980, pp. 373-375 and 506-507).

d) It follows from the above discussion that efficient precipitation can develop in the "fumulus" clouds only if a small fraction of the cloud condensation nuclei will be activated. However, in this case the scavenging efficiency for the fire generated aerosol particles in the size range  $0.05 - 1 \mu\text{m}$  (the "Greenfield gap") is negligible (Pruppacher and Klett, 1980,

pp. 395-396). The low efficiency of aerosol scavenging in the "Greenfield gap" has, however, been questioned following observations on aerosol scavenging by precipitation falling through plumes from coal power plants and a Kraft paper mill (Radke *et al.*, 1980; Slinn, 1982). These measurements and their interpretation are still debated. As a possible explanation for the observations it was proposed by Radke *et al.* (1980) that the particles became dry when measured, while in the atmosphere they had deliquesced into larger particles. This nucleation scavenging mechanism may be very important for hygroscopic aerosol, including aged, internally mixed soot particles, which have become hygroscopic by absorption of suitable compounds from the gas phase or coalescence with more hygroscopic aerosol. For fresh soot particles, which are hydrophobic, the "Greenfield gap" may well be intact (e.g. Covert and Heintzenberg, 1983). Although it has long been known that "black rains" may accompany large forest fires (Plummer, 1912) and these were also reported in connection with major city bombings (e.g. Hamburg, Caidin, 1960; Nagasaki and Hiroshima, Ishikawa and Swain, 1981), the effectiveness of aerosol removal by rain is difficult to quantify. "Black" rains may also be due to downdraft effects and washout or rainout of large, partly burnt aerosol particles which rapidly coagulate with raindrops. About 20% of the aerosol produced by forest fires is found in the 1-5  $\mu\text{m}$  size range and 10% is larger than 5  $\mu\text{m}$  (Ward *et al.*, 1976), so that substantial production of supermicron particles may be expected for all fires. For very intense, large forest fires, it is clear from world-wide reports that that precipitation scavenging can not cleanse the atmosphere efficiently enough to prevent major obscurations of the sun over transcontinental distances (Plummer, 1912; Shostakowitch, 1925; Wexler, 1950).

The observations by Radke *et al.* (1982) of efficient removal of aerosol particles produced by the TITAN satellite launch (P.V. Hobbs, personal communication) may not be applicable, as the aerosol from the TITAN launch must have been strongly hygroscopic because of the presence of high concentrations of the combustion product HCl, which with ambient  $\text{NH}_3$  will produce yield  $\text{NH}_4\text{Cl}$  aerosol.

Based on the previous arguments, we will neglect the prompt removal of aerosol in "fumulus" clouds, but recognize that the validity of this assumption is based on a very simple, mostly theoretical, analysis of the very complex phenomenon of mass fires, about which there exists very little observational information. Although more information can be gained by observations of major forest wildfires, even these do not simulate the

special features of fires in urban and industrial centers in which enormous amounts of combustibles are set on fire simultaneously over a large area and in which the fireball rise may induce huge and complex convective circulation systems, which may reach into the stratosphere. Therefore, despite the arguments presented in favor of only a relatively small removal efficiency of the soot particles by "fumulus" clouds, there remains the feeling of a possible lack of essential information on this issue. In the following we will note that precipitation scavenging is also the most critical factor determining the residence time of aerosol in the atmosphere and that knowledge about this is quite uncertain.

## 6. ATMOSPHERIC DISPERSION, RAINOUT AND SUNLIGHT TRANSMISSION

We have roughly estimated that the  $2.3 \times 10^{14}$  g of particulate matter would initially cover an area of  $6 \times 10^{13}$  m<sup>2</sup> and occupy a volume of  $4.5 \times 10^{17}$  m<sup>3</sup>. This implies an average particulate concentration of  $4.4\text{--}6.7 \times 10^{-4}$  g/m<sup>3</sup> in the early smoke clouds. Following the initial phase, the aerosol particles will spread out over larger areas, and be gradually removed by rainfall.

For the treatment of spread and rainout of the particles we must in this study assume similar behavior as during normal atmospheric conditions. This is probably not valid, as much sunlight absorption would take place in the atmosphere and not at the earth's surface. This would lead to profound and global changes in many meteorological processes. For this study, however, it is impossible to treat these problems satisfactorily and we must rely on a simple model, based on current experience.

The average residence times against rainout and washout for  $0.1\text{--}3$   $\mu$ m size particles range from about 10 days in the lower to 30 days in the upper troposphere and to more than one year in the stratosphere (Jaenicke, 1981). There will of course be substantial variations in the rainout removal rates, which may vary from 3 days in rainy to much more than one week in dry climatic regions (Ogren and Charlson, 1983). These variations can not be treated with the simple model which is at our disposal. We will, therefore, perform calculations for the first month following the war, assuming various characteristics scavenging times ( $t_r$ ) of 10 and 30 days, and also negligible rainout. The latter applies to that fraction of the aerosol which would reach the stratosphere. We will indicate later that there is a real

possibility that this may occur to the differential heating of the smoke clouds.

The horizontal spread over area  $A(t)$  of the aerosol clouds with time  $(t)$ , expressed in  $m^2$ , can be roughly described by the formula

$$(3) \quad A(t) = 6 \times 10^{13} + 4 \times 10^{13} [1 - \exp(-t/t_a)] + 6 \times 10^{10} \sqrt{t}$$

The terms on the right hand side describe the area of initial coverage, and the spreads in East-West, and in South-North directions, respectively. The parameter  $t_a$  is chosen to be 10 days and corresponds to the time which is needed to fill the gap in the aerosol cloud cover which would initially be located over the Pacific. Given an average zonal wind shear of about 10 m/s between lower and upper troposphere (Oort and Rasmussen, 1971), the gap of 6000 km may be filled in about a week. The North-South spread of the cloud outside the 30-60°N latitude belt is simulated by a horizontal eddy diffusion model with an average exchange coefficient  $K_{yy}$  of  $10^6 m^2/s$  (Hidalgo and Crutzen, 1977). Figure 1 gives the percentage coverage of the earth by the smoke layers, as calculated with formula (3).

Although coagulation of aerosol particles affects the transfer of

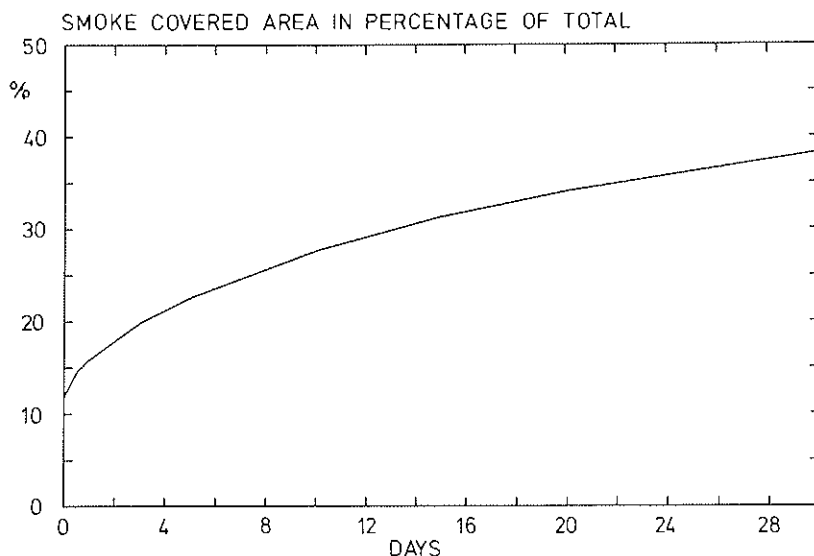


FIG. 1. Estimated percentage coverage of the earth's surface by smoke clouds as a function of time (in days).



radiation through the smoke clouds, observations in remote areas have generally established a specific absorption of  $10 \text{ m}^2/\text{g}$  EC for aged, internally-mixed elemental carbon. For this reason, the following, approximate formulae for the optical depths for scattering and absorption at time  $t$  may be used:

$$(4a) \quad d_s(t) = d_s(o) \frac{A(o)}{A(t)} \exp(-t/t_r)$$

$$(4b) \quad d_a(t) = d_a(o) \frac{A(o)}{A(t)} \exp(-t/t_r)$$

$$(4c) \quad d_e(t) = d_s(t) + d_a(t)$$

In these formulae,  $t_r$  denotes the average, characteristic rainout time of the aerosol particles, while the initial depths are given in Table VI.

An approximate method to calculate transmission of sunlight through the atmosphere via an effective optical depth of the atmosphere taking into account both scattering and absorption has been derived by Sagan and Pollack (1967). Although their method is mainly valid for large optical depths, we will use it also in this study. For small optical depths an upper limit for the average transmission of sunlight to the earth surface could be derived by the formula:

$$(5) \quad T = \exp(-2 d_a).$$

The appearance of the factor 2 in this formula simulates the globally averaged zenith angle of the sun.

Sagan and Pollack (1967) derived an effective optical depth ( $d_{\text{eff}}$ ) with the following formulae:

$$(6) \quad d_{\text{eff}} = \sqrt{3} u (1 - \omega_o) d_e,$$

whereby  $\omega_o$  (the single scattering albedo) and  $u$  are given by

$$(7) \quad \omega_o = \frac{d_s}{d_s + d_a}$$

$$(8) \quad u^2 = \frac{1 - \omega_o + 2 \beta \omega_o}{1 - \omega_o}$$

The parameter  $\beta$  is a measure of the fraction of radiation which is scattered backwards. For the present calculations  $\beta$  may be set equal to 0.15 (Twomey, 1977, p. 226).

The transmission, reflection and absorption of the solar radiation may finally be calculated by the formulae:

$$(9) \quad T = \frac{4u}{(u+1)^2 \exp(d_{\text{eff}}) - (u-1)^2 \exp(-d_{\text{eff}})}$$

$$(10) \quad R = \frac{(u+1)(u-1) [\exp(d_{\text{eff}}) - \exp(-d_{\text{eff}})]}{(u+1)^2 \exp(d_{\text{eff}}) - (u-1)^2 \exp(-d_{\text{eff}})}$$

$$(11) \quad A = 1 - T - R$$

The calculated transmissions of solar radiation to the ground are shown in Figure 2 for the cases  $t_r = 10$  days, 30 days and no rainout at all. When

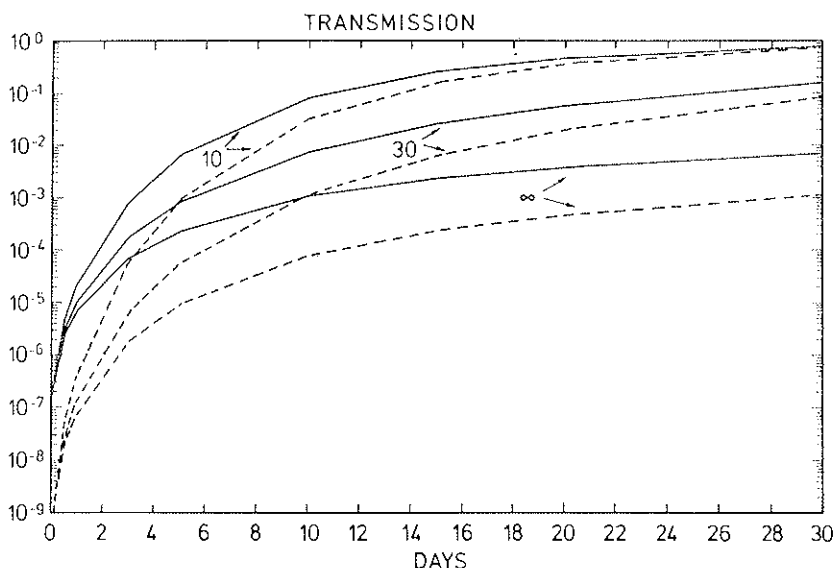


FIG. 2. Calculated transmissions of sunlight to the earth's surface under the smoke clouds for three characteristic rainout removal times of the smoke (10, 30,  $\infty$  days). The dashed curves take into account the burning of one million  $\text{km}^2$  of forests; the full lines neglect forest fires.

the effects of the burning of 1 million km<sup>2</sup> of forests are considered, we note that even for the relatively fast rainout case with  $t_r = 10$  days, the penetration of radiation to the earth's surface remains below 1% of normal for about 7 days and below 10% for 12 days. The transmission calculated for day 30 is in this case still only about 70%. With a rainout time equal to 30 days, light levels would remain below 1% for 14 days and below 10% for 30 days. On day 30, the transmission of sunlight is only 10% of normal. By this time, the aerosol layer would cover about 70% of the northern hemisphere. With no rainout at all, the transmission of sunlight would remain below 0.2% for an entire month. It is clear that these results may describe only average conditions. In reality the smoke cloud cover could be rather patchy, randomly causing the appearance of dark and more normal daylight conditions. Figure 2 also contains the calculated transmissions, if forest fires are neglected. In this case the effective optical depth is reduced by about 30%. Large reductions in sunlight transmissions remain.

The results of the calculations are clearly very sensitive to the adopted rainout scavenging rates and this is probably the most uncertain aspect of our analysis. Conditions could become especially severe, and spread rapidly over the globe if a substantial fraction of the aerosol would reach the stratosphere, or if changes in the static stability of the atmosphere or physical properties of the clouds would prolong the average residence times of aerosol particles to much longer than normal. It may be argued that this might indeed occur. For instance, the atmospheric heating rate in the upper sunlit parts of the smoke layers during the first days of their existence may be calculated from the elemental carbon concentration of  $1.5 \times 10^{-4}$  g/m<sup>3</sup> and a mass absorption cross section of elemental carbon of 10 m<sup>2</sup>/g to be as high as 50 K per hour. This would strongly favor the rapid upward convection of smoke, probably into the stratosphere (Galbally *et al.*, 1983; Crutzen and Birks, 1982). Furthermore, the higher air temperatures which would result, hinder condensation processes and promote cloud evaporation.

In fact, it is quite possible that the initial fireballs of low-altitude nuclear bursts could drag large amounts of vaporized carbon (and other oxidizable materials, such as aluminium) into the upper atmosphere. We have not included this process in our numerical calculations but, because of its potential importance, we provide a few comments on its nature here. We have seen that fire loadings in the inner parts of cities may be several hundred kilogram per square meter. If much of these combustibles would

vaporize within the fireball (see Glasstone and Dolan, 1977; Gilmore, 1974), for a 0.4 Mt explosion, the ratio between the moles of carbon and atmospheric oxygen could be in the range of 10-100. After stabilization of the cloud near the tropopause between 7 and 13 km, the nuclear cloud radius would be about 5 km. Entrainment would have decreased the C/O<sub>2</sub> ratio to  $5 \times 10^{-3}$ . However, oxidation of elemental carbon effectively stops at 1500 K. The C to O<sub>2</sub> ratio at that instant would be several percent and inhomogeneities in the composition of the clouds may lead to incomplete oxidation, EC formation and its deposition in the upper troposphere or lower stratosphere. As of the order of  $10^{15}$  g of combustible materials could be confined in fireballs, the production of EC by this means and its direct deposition in the upper atmosphere could be very important.

## 7. BIOLOGICAL AND METEOROLOGICAL CONSEQUENCES

For different rainout rates we have calculated widely different transmission of solar radiation through the atmosphere. For slow rainout rates, the transmission may remain below 10% for a whole month (see Figure 2), which means that sunlight transmission would be less than 1%, if twice the amount of aerosol were to be dumped in the atmosphere. Because of the uncertain analysis of the amounts of fuels burnt and particulate matter formed from different materials, and considering also the simplicity of the model adopted in this study, this possibility may not be discounted. A prolonged stay of aerosol particles in the atmosphere would occur if much particulate matter rapidly reached the stratosphere because of the intense solar heating of the smoke clouds.

A reduction in sunlight to much below one percent could create severe biospheric conditions. Phytoplankton and herbivorous zooplankton in the oceans could die, if conditions of at most one percent sunlight penetration would last, e.g., for about one month in July and August and three months in January (Milne and McKay, 1982). If a war would take place in the growing season, agricultural production would be much reduced because of lack of sunlight. Much cultivated land might actually burn before that. Survivors of the nuclear holocaust could, therefore, suffer much from both famine and adverse atmospheric conditions.

The atmospheric, vertical temperature profile and many other meteorological conditions would change profoundly. Under normal conditions, most of the solar radiation, which is not scattered back to space, is absorbed at

the earth's surface. This leads to the observed decrease of temperatures with height in the troposphere. Under the immediate post war conditions, the surface is no longer heated by solar radiation below the smoke clouds and land surfaces are bound to cool. This occurs rapidly (Hunt, 1976). As an example of this, the decrease of insolation due to the arrival in Washington, D.C., of smoke layers from Canadian forest fires in late September, 1950, caused surface temperatures to drop by 2-4°C (Wexler, 1950).

Various types of models may be applied to estimate the meteorological effects of a nuclear war. Detailed one-dimensional model calculations, which take into account aerosol coagulation, convection, condensation and radiative transfer of solar and terrestrial radiation, have been performed by Turco *et al.* (1983). The effects of soil derived, submicron dust particles which are formed by ground bursts and deposited high in the atmosphere, were also considered. For conditions closely corresponding to the Ambio scenario, Turco *et al.* (1983) calculated a rapid cooling by about 35°C, resulting in freezing conditions over the continents which would last for several weeks to months. For most locations and times such freezing conditions, together with the lack of sunlight, would be catastrophic to many plant and animal species, as well as entire ecosystems. Such conditions would rapidly develop over land. The much larger heat capacity of the ocean surface layers would sustain much more normal temperatures over the oceans and in coastal areas.

It is difficult to predict the meteorological behavior of the atmosphere under such conditions, for which we need detailed three-dimensional models. We may, however, guess that in the low atmosphere winds would blow from the continents to the much warmer oceans. Upward motions develop over the oceans, accompanied by fog and precipitation, especially over coastal waters. This could provide the most efficient removal mechanism for the aerosol in the atmosphere. A return flow would occur aloft, carrying water vapor to the continents, which would precipitate as snow. Over the cold lands extensive areas could also be covered with supercooled fogs, which would be very damaging to vegetation. Also here the aerosol may be removed from the lower atmosphere. However, much light absorbing smoke would probably remain far above this ocean-land circulation system and its removal by precipitation scavenging might well be very inefficient.

The plausibility of the results of Turco *et al.* (1983) can be demonstrated with simple radiative equilibrium models, in which we assume that all smoke is evenly distributed above the 750 mb level in the atmosphere, the remaining layer closest to the ground being smokefree (see Figure 3).

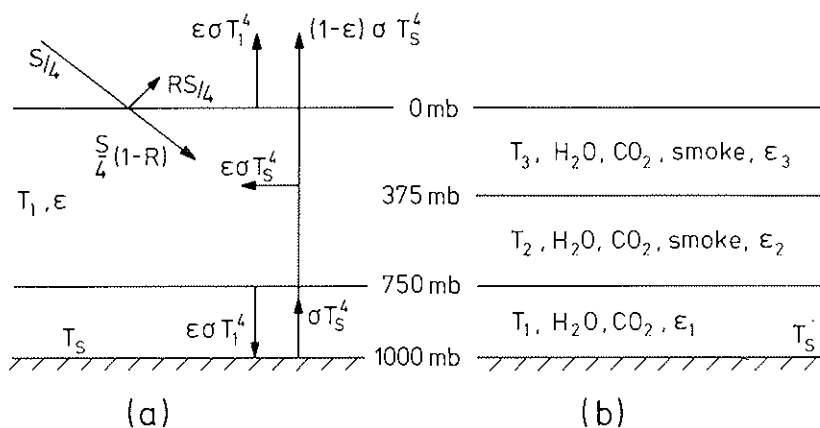


Fig. 3. Assumed partition of atmosphere in layers for two radiative equilibrium models; a) infrared transfer by atmospheric gases neglected; b) infrared transfer by  $H_2O$  and  $CO_2$  taken into account.

The assumption about the location of the smoke is quite arbitrary, but soot probably reaches the greatest heights. In the simplest demonstration we neglect the effect of clouds and of infrared radiation by the atmospheric gases  $CO_2$  and  $H_2O$  and consider only the effect of the smoke on the transfer of solar and infrared radiation. The layer between the ground and 750 mb is, therefore, assumed to be totally transparent to all radiation. The surface and smoke layer temperatures are  $T_s$  and  $T_1$ , respectively. The smoke layer is assumed so opaque in the visible that most solar radiation is absorbed by the black smoke. In the infrared, however, the specific absorption is about ten times smaller (Chylek *et al.*, 1981; Roessler and Faxvog, 1979), so that we take the IR emissivity ( $\epsilon$ ) to be equal to 0.1. The radiative equilibria for the surface and smoke layer for average conditions are given by the formulae (see Figure 3):

$$(12) \quad \epsilon \sigma T_1^4 = \sigma T_s^4$$

$$(13) \quad (1 - R) S/4 + \epsilon \sigma T_s^4 = 2 \epsilon \sigma T_1^4$$

with  $S$  = solar constant ( $1360 \text{ W/m}^2$ ),  $\sigma$  = Stefan-Boltzmann constant ( $5.7 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$ ) and  $R$  the reflectivity of the smoke layer, which equals about 0.1 according to formula (10).

Solving equations (12) and (13) we obtain

$$T_1 = 413 \text{ K and } T_s = 232 \text{ K}$$

The ground temperature without the presence of smoke is calculated from the formula

$$(14) \quad \sigma T_1^4 = (1 - R) S/4$$

If here we take also  $R = 0.1$ , a typical value for the earth's surface, we obtain  $T_s = 273 \text{ K}$ . The presence of the smoke layer causes, therefore, a cooling of the surface by about  $40^\circ\text{C}$ , in good agreement with the results of Turco *et al.* (1983).

A more realistic, but still simple, radiative equilibrium model may be developed by taking into account also the effects of infrared radiation absorption by water vapor and carbon dioxide. Absorption of solar radiation by atmospheric gases is neglected. For this case we divide the atmosphere in three layers: a cloud-free one between 1000 mb and 750 mb, and two layers containing equal amounts of smoke above the 750 mb level (see Figure 3). In this case the transfer of solar radiation by the aerosol layers is treated with the method of Sagan and Pollack (1967), as described before. The specific scattering and absorption of smoke were taken equal to  $4 \text{ m}^2/\text{g}$  and  $2.2 \text{ m}^2/\text{g}$  respectively. The radiative properties of smoke in the infrared were based on the data by Roessler and Faxvog (1980) and Shettle and Fenn (1979), adopting an elemental carbon content of 22% (see Table VI). The emissivities of water vapor and carbon dioxide were mostly based on the works of Ramanathan (1976) and Rodgers and Walshaw (1966). The effects of clouds were still neglected. More details about the model are given in the appendix. The results of the calculations are presented in Figure 4, in which the calculated radiative equilibrium temperatures for the ground ( $T_s$ ), the smokefree 1000-750 mb layer ( $T_1$ ) and the two smoke layers between 750 and 375 mb ( $T_2$ ) and above 375 mb ( $T_3$ ) are plotted as functions of the mass of smoke per unit area. For small optical depths of the smoke, the results are sensitive to the assumed albedo of the earth's surface. For this reason results are shown for ground reflectivities of 0.3 and 0.5. The latter value would apply for dirty snow with a soot to ice ratio of about  $10^{-5}$  (Chylek *et al.*, 1984), which would apply for the immediate post nuclear war conditions. For small optical depths a sharp temperature discontinuity is calculated at the surface of the earth. This is typical for radiative equilibrium model results, which can not take

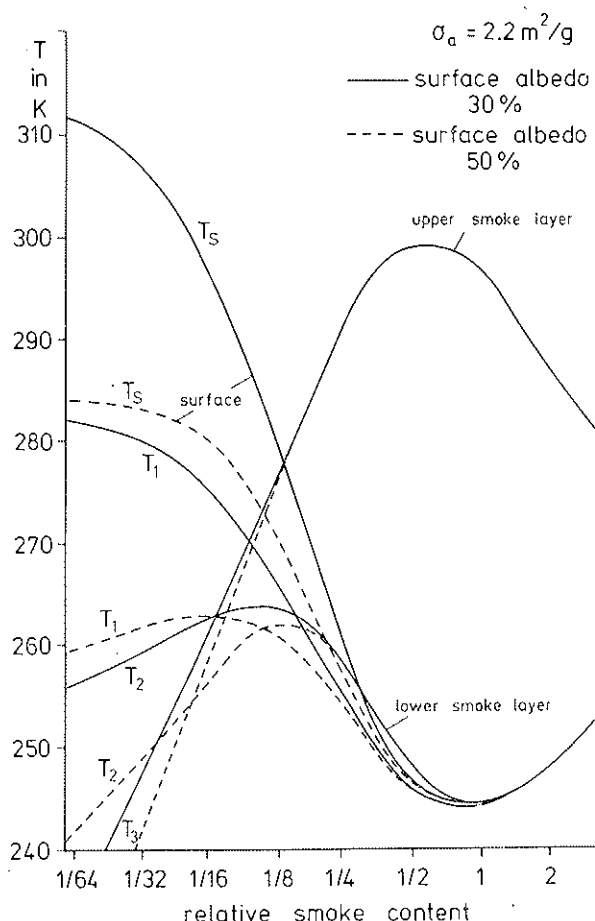


FIG. 4. Calculated temperature at the earth's surface ( $T_s$ ) and in three atmospheric layers ( $T_1$ ,  $T_2$  and  $T_3$ ) as function of the atmospheric smoke content. A relative smoke content of unity corresponds to 1.2 g of smoke per  $\text{m}^2$  surface area. Two sets of calculations are presented for hypothetical surface albedos of 30% and 50%.

into account the transfer of sensible and latent energy from surface to atmosphere.

The model results show a large cooling by about  $50^\circ\text{C}$  of the ground and the lower atmosphere due to the introduction of smoke up to an average coverage of  $1.2 \text{ g/m}^2$ , which accidentally corresponds to the uniform distribution of 310 million tons of smoke (Table VI) over the northern hemisphere. For larger smoke coverage ground temperatures



actually increase slightly as the smoke no longer influences the short wave radiation field, but reduces the escape of infrared radiation to space. The upper smoke layer would heat up to temperatures which are normally found at the earth's surface. The entire temperature profile is thereby turned upside down and an enormous inversion develops over the entire depth of the troposphere, particularly over the continents. This reduces convection, vertical mixing and precipitation. Under such conditions fire produced air pollutants would remain airborne much longer than under natural conditions (Crutzen and Birks, 1982).

In order to indicate the sensitivity of the model to changes in the optical properties of the aerosol, Figure 5 shows results obtained with the same model, but for two times smaller smoke absorption cross sections ( $1.1 \text{ m}^2/\text{g}$  aerosol) in the visible. We see that the results differ only in details from those shown in Figure 4. Similar results were also obtained for an absorption cross section of  $0.6 \text{ m}^2/\text{g}$  aerosol. These lower values apply for aerosol with appreciably lower EC content.

The sensitivity of the results to the ground reflectivity may be of particular importance, as we may expect extensive cloud cover and snow-fall to develop over the continents. This would accelerate the cooling of the earth's surface and substantially delay and maybe even prevent a return to normal climatic conditions.

Because of the simplicity of the model, the results obtained with it should not be overinterpreted. Figure 4 suggests, however, that even ten times less smoke than calculated in Table VI, could still lead to  $20^\circ\text{C}$  colder continental surface temperatures.

The simple climate equilibrium models presented above provide, therefore, the essentials of the results of the more elaborate and accurate model of Turco *et al.* (1983). However, even this model is clearly limited as it is one-dimensional and averages globally over horizontal surfaces. To estimate the meteorological effects of a nuclear war it is necessary to use interactive multi-dimensional, dynamical models of the atmosphere. Simplified computations with such models have already been carried out at three research centers in the US and USSR. Some preliminary calculations with two-dimensional (McCracken, 1983) and three-dimensional climate models (Alexandrov, 1983; Covey *et al.*, 1984) support the findings derived with the simpler models and point to the possibility that winter conditions may occur in July especially over North America, the Soviet Union, China and large parts of India.

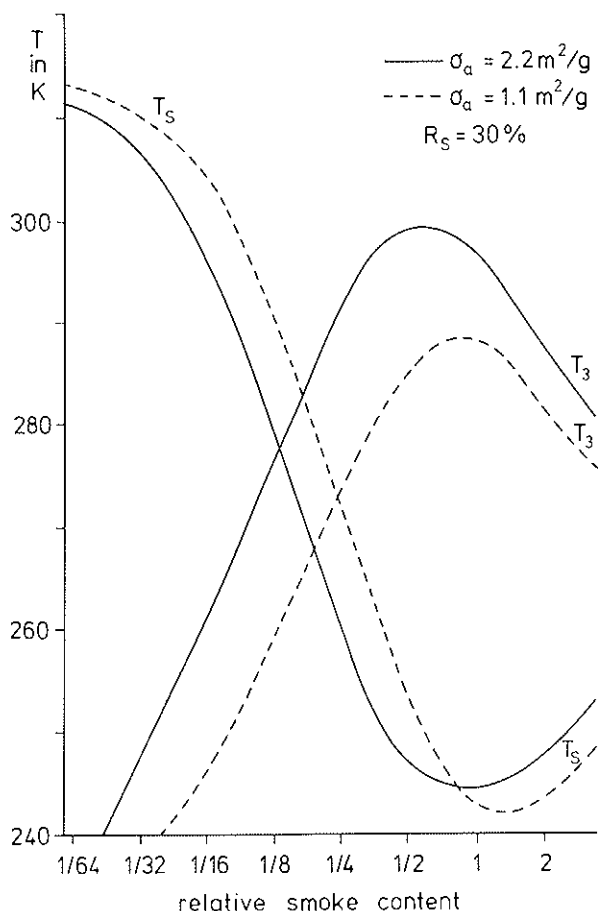


FIG. 5. Calculated temperatures in top smoke layer ( $T_3$ ) and at the earth's surface ( $T_s$ ) for specific absorption cross sections of 1.1 and 2.2  $\text{m}^2/\text{g}$  aerosol in the visible. Assumed albedo at the earth's surface 30%.

## 8. ADDITIONAL ATMOSPHERIC EFFECTS (BRIEF INDICATIONS)

a) For the immediate period following the nuclear war, the atmosphere would become loaded with many unusual pollutants such as hydrogen chloride which is produced by the burning of polyvinyl-chloride (PVC), which material is used extensively in modern buildings. During the first months following the war, the removal of  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and other fire effluents may lead to precipitation with a pH of only about 3. Over

land a dirty, supercooled drizzle may become established, which, together with other air pollutants, would be detrimental to biosphere and survivors.

b) Through nuclear explosions and fires there will also be a temporary strongly enhanced production of NO. We estimate that the total may amount to about  $10^{14}$  gram of NO. In the dark atmosphere NO will be mainly converted to NO<sub>2</sub>, which is a relatively strong absorber of solar radiation. We estimate that the optical depth caused by the fire and fireball produced NO<sub>2</sub> may be close to half, reducing the average penetration of sunlight to the ground by another factor of almost three for wavelengths below 500 nm.

c) If a substantial amount of the dark aerosol would reach altitudes above 25 km, the formation of ozone by the photodissociation of molecular oxygen would be much suppressed, as the active solar radiation below 240 nm would be strongly absorbed by the soot particles with a specific absorption cross section of maybe 20-30 m<sup>2</sup>/g EC. Also, not only the smoke could reach the stratosphere, but also gaseous (e.g. NO<sub>x</sub>, H<sub>2</sub>O and HCl), and maybe particulate compounds, which destroy ozone catalytically. The higher than normal temperatures which would result because of absorption of solar radiation by soot in the stratosphere, will also strongly enhance ozone loss reactions. Severe ozone depletions may, therefore, take place. The effects of enhanced UV-B (290-320 nm) solar radiation fluxes on the biosphere can be substantial and have been studied especially in connection with the concurrence of non-melanoma skin cancer in the white race. A 1% reduction in total ozone will on the average lead to a 2% increase in the UV-B radiation flux, so that there is an optical amplification factor of two. A statistical analysis of the skin cancer incidence in the US indicates an additional biological amplification factor of about two, so that a reduction in the total ozone by about 1% would lead to a 4% increase in non-melanoma skin cancer (Scotto *et al.*, 1982). Although for humans the UV-B problem is small in comparison to the afore described much more serious environmental consequences of a nuclear war, other parts of the biosphere (e.g. the marine phytoplankton communities) are very susceptible to increased UV fluxes (NAS, 1982). It should be noted that the total solar radiation at ground level could very well be smaller than normal (due to the presence of soot in the atmosphere), while at the same time the UV-B component of the solar flux is larger. This is due to the strong sensitivity of UV-B radiation levels to changes in total ozone.

d) The deposition of the aerosol on the earth's surface may cause

additional environmental and climatic stress. Crutzen and Birks (1982) pointed out the possibility of enhanced snowmelting in permanent glaciers. A recent study by Chylek *et al.* (1984) on the albedo of soot-contaminated snow may be used to obtain an idea of its potential importance. If  $10^{14}$  g EC is deposited in the northern hemisphere over a period of one month, the average EC content in precipitation would be about  $10^{-5}$ . Such a concentration of soot in snow would advance complete snowmelt by about one month. Alexandrov (1983) has already pointed to the risk of melting of snow and glaciers, leading to continental flooding due to the occurrence of above freezing air temperatures at high altitudes.

e) It is also quite possible that fallout of the large amounts of dark aerosol will lead to a substantial reduction in photosynthesis in the upper layers of the oceans and lakes. Under normal conditions, filter-feeding zooplankton very actively remove small-sized mineral and organic particles in a matter of weeks from the euphotic layer to the deep sea through their excretions (Delany, 1967; Alldredge and Madin, 1982; Degens and Ittekkott, 1983; Deuser *et al.*, 1983 a,b). After the darkness period following a nuclear war, this biological cleansing mechanism may be much disturbed, so that oceanic productivity may remain reduced over considerable time, even after the clearing of the atmosphere. Another negative factor contributing to this may be that fire produced aerosols contain large amounts of harmful pollutants, e.g. trace metals (Hardy and Crecelius, 1981) and radioactive material.

f) Even after the initial fires have stopped burning, during the years following the nuclear war frequent fires would occur in the forested areas which were destroyed by fires, cold temperatures and radioactive fallout. It is well known that forest fires may burn the same area several times over in intense fires of dead and very flammable forest materials (Plummer, 1912). The forest area damage by radioactivity alone may be three times larger than caused by the immediate fires (Galbally *et al.*, 1983; Woodwell, 1982).

g) Although large quantities of reactive hydrocarbons which are produced by the fires would remain available after the atmosphere is cleansed from smoke, the production of ozone by photochemical reactions is dependent on the availability of sufficient quantities of the  $\text{NO}_x$  gases. Because these gases or their reaction products, may be absorbed on the smoke particles, tropospheric ozone production might not occur to the extent estimated by Crutzen and Birks (1982). High ozone concentra-

tions could, however, appear at the earth's surface due to much enhanced downward transport of ozone from the stratosphere in smoke-free regions, which could compensate for the upward motions which are stimulated by the solar heating of the black smoke clouds.

## 9. CONCLUSIONS

The very serious environmental effects of a total nuclear war as presented by Crutzen and Birks (1982) and evaluated further in this and other very recent papers (Turco *et al.*, 1983; Covey *et al.*, 1984; McCracken, 1983; Alexandrov, 1983) are surprisingly new scientific discoveries. In the event of a war, it is quite likely that for weeks sunlight will be much reduced over extended areas of the Northern Hemisphere by the production of several hundred million tons of long-lived aerosol which scatters, and most importantly, absorbs sunlight. This is possible because of the burning of huge amounts of combustibles in cities and industries. The meteorological and ecological consequences of such atmospheric aerosol loading could be severe. The continents would cool and the overlying atmosphere warm, effectively wiping out the troposphere and creating very stable thermal conditions in the lower atmosphere. Above the smoke clouds the atmosphere would become much more destabilized. A combination of cold temperatures and darkness would strongly diminish agricultural and biological productivity, adding enormously to the problems of the survivors of the war. Important ecosystems, including tropical and subtropical forests, might become endangered and many plant and animal species might disappear from the earth. We note that we are here dealing with global (or at least hemispherical) effects which could also affect nations which would not be directly involved in the war. The environmental effects have been treated by Ehrlich *et al.* (1983) and especially by Harwell (1984).

We have demonstrated our arguments on the basis of the Ambio (1982) war scenario, using much simplified rainout, aerosol physics and radiative equilibrium models. Our analysis of the amounts of burned materials and smoke production is likewise uncertain and no doubt can be much improved upon, but we have tried to avoid extreme assumptions. It is very hard to carry out sensitivity analyses in this new research field with so many uncertainties. It is quite possible to forward arguments for a much less severe impact of a nuclear war. For instance, one may propose

much more efficient rainout of aerosol. Worse impacts are also possible. We left out the burning of coal dumps and the consequences of long lasting fires in gas and oil wells, and forests, many of which might become especially vulnerable to fires due to damage by darkness, freezing and radioactive fallout damage (see Galbally *et al.*, 1983; Woodwell, 1982; Ehrlich *et al.*, 1983). We also neglected the albedo effects of soil derived dust in our radiative transfer calculations. The numerical results of this study should, therefore, not be taken too exactly. However, it is hard to discount the possibility that for most survivors of a nuclear war and life on earth as a whole, meteorological and climatic conditions could become extremely hostile. The Ambio war scenario employs 40% of the entire nuclear weapons arsenals of the world, about equally aimed at industrial/urban military targets. Smoke production is, however, far from proportional to total weapon use. For instance, an analysis of the USSR population distribution and industrial capacity showed that the 50 largest cities contained 33% of the urban population and 40% of the industrial capacity. For the largest 300 cities the corresponding numbers increased only to 60% and 65%, respectively (Kemp, 1974). As a consequence, a nuclear war in which "only" 10% of the nuclear arsenals were used against population and industrial centers, could still yield half of the smoke derived for the Ambio scenario. Referring to the results of Figure 4, this could still lead to a lowering of the continental surface temperatures by 40°C. Turco *et al.* (1983) have concluded that a "small" 100 Mt nuclear war, mainly aimed at major cities, could cause severe climatic perturbations.

Our findings have, therefore, clear military implications. They indicate that a one-sided attack by one of the superpowers might well lead to the destruction of the attacking side itself and many other nations because of worldwide destruction of life support systems and environment, as a consequence of large scale, severe disturbances of the atmosphere due to smoke and dust emissions. It is important that these effects are better quantified and studied with more appropriate models. We hope that this paper will lead to the involvement of other scientists to improve the simple analyses presented in this paper and to participate in studies of the atmospheric, biological and ecological consequences of nuclear war, so that all governments can be thoroughly informed of them.

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## DISCUSSION

MARINI-BETTÒLO

I think that your model proposed can be also applied to the movement of the particulates in general also through space.

CRUTZEN

Yes. I think one of the major drawbacks with a model like this is that it is really based on too much experience with normal conditions, and when you get a situation like this with an enormous stability in the lower atmosphere, basically the troposphere suddenly is gone and becomes stratosphere. I think we have to revise any model which we have developed so far, and there are several reasons to believe that the situation could be worse than I pictured here. The high stability of the lowest layers of the atmosphere may mean that aerosol will remain in the atmosphere much longer than we are used to under normal conditions. It is also very easy to calculate the heating rates which one would get in the dust or in the smoke clouds when they are heated by the sun. I did that and you get 30°C per hour. That means that these clouds are just not going to lie there, nice and stable, they are going to move upwards; so I think it is a very serious possibility that the smoke clouds will come up in very high levels in the atmosphere and can be transported globally. So even the Southern Hemisphere might not be safe from conditions which are indicated here.

MARINI-BETTÒLO

You indicate the limits to the use of these models, but that because you have high concentrations of soot and particulates all over. If you use the same model to not so high concentrations, as it happens, for instance in a sand storm, and so on, it would it apply better?

CRUTZEN

Yes, it would be more applicable, but I have never developed a model for a particular situation like that. The models which I have developed are for global dispersions, say, of fluorocarbons, or of stratospheric aerosol, normal situations which we could test with observations in the atmosphere.

CANUTO

Just a clarification. The blast area of bombs does not increase linearly with the megatonnage of the bomb. It increases with the power of two-thirds if I am correct. In other words, 100 one-megaton bombs do more damage than one bomb of 100 megatons. How does one then scale your result if you want to make it worse; in other words you use .4 megatons — and you want to compare your result with the one of Brian Toon who has not used the same number of megatons. In other words, it is difficult to scale your number.

CRUTZEN

I think that on the average — I have to look up the numbers, but actually the average size of the bombs is 0.5 megatons — mine was 0.4. So we are not so far off.

CANUTO

Did the blast area come in any way in your computations?

CRUTZEN

No, the blast area I neglected. Everything is determined by the heat radiation, and this is based on experiences from the past. So — I think I have been on the conservative side there.

MALONE

I would like to congratulate Dr. Crutzen on one of the most impressive papers that I have heard in the last 43 years. With regard to its policy implications, it stands certainly in a class all by itself. I would simply underscore Dr. Crutzen's emphasis on the conservativeness of his estimates. Having looked at thousands of vertical temperature profiles, it is clear, I believe, that the residence time will be of about an order of magnitude difference between the stratosphere rather than the troposphere, and also the lapse rates, would no longer apply. So as you say, it is just an entirely different atmosphere. This would inhibit the precipitation and the fallout, so that I just really wanted to underscore the conservative nature of your calculations.

I have three questions. It was not quite clear to me whether you took the whole globe or just the Northern Hemisphere into account. When you calculated



the spread of the smoke cloud, soot cloud, was it just the Northern Hemisphere, or was it the globe?

CRUTZEN

No. The few explosions in the Southern Hemisphere I neglected in this study, so I took the targets in the Northern Hemisphere and assumed that they were initially between  $30^{\circ}$  north and  $60^{\circ}$  north. Then they started spreading out over the Northern Hemisphere, but in 30 days according to this model did not reach the Southern Hemisphere. In a real case I doubt very much whether that would be the case, probably it would reach the Southern Hemisphere, because the sooty smoke would absorb so much solar energy that the heated atmosphere would move upward and southward much faster than is normally the case.

MALONE

My second question is: did you speculate at all on the likely consequences of the baroclinicity which would be established between the marine and the continental areas — that would probably be quite large.

CRUTZEN

I can speculate about it, and my guess is that firstly the calculations seem to indicate that freezing temperatures over land may very well occur. On the other hand, over the oceans, because of the high thermal capacity of the surface waters, the ground or the near-surface temperatures would be higher; so what probably would occur is that there would be an uprising motion over oceanic regions, compensated by sort of high pressure régime, over land areas. How far those circulation systems will extend into the troposphere is very much dependent on where the soot layers will be. If they are very low, then I can imagine that one gets soot out of the circulation. If they are high up, then I think the soot layers, independent of where they are — over the land or over the ocean — will start setting up some sort of circulation of their own. I do not see how we can estimate that reasonably at the moment. The other thing which one has to look at is the possibility that a land-sea breeze situation may be set up between oceans and lands. There will still be humidity brought into the land areas and there will be, I think, developing a rather shallow circulation. And with freezing temperatures near the ground,

I think one will develop cold fog — super-cool fog which of course in itself may mean an enormous hazard to vegetation. This is a thing we have not discussed so far, but that could be extremely hazardous for land vegetation.

MALONE

The third question: I was not quite able to determine how long the diminution in the radiation would inhibit photosynthesis. Would it be a matter of days, weeks?

CRUTZEN

The 2% level seems to be the compensation point for many plants, and now it becomes a very large function of the rain-out times which one applies to the models. If a ten-day rain-out time is applied, then already after two weeks most blank communities may be above the 2% compensation point. If a 30-day applies, or longer, then we have the low compensation points conditions for an extended period of time, and that would mean that simply many ecosystems are consuming themselves and will shrink. Agricultural productivity most likely one can forget about in a situation like this.

CANUTO

Could you invert your computations applied to the tertiary, 75 million years ago, to the disappearance of dinosaurs? In this case we do know that something happened but we do not know the megatons.

CRUTZEN

Yes. Of course this sort of calculations and the models which are applied here by Sagan and Toon were firstly developed for the dust storms on Mars. Low temperatures were discovered as soon as the dust started blowing. That was one point; but they later applied it also for the extinction of dinosaurs.

# ATMOSPHERIC ACIDITY

A. LIBERTI

*Chemistry Department*  
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Atmospheric acidity is one of the atmospheric events to which great attention has been paid namely in the last decade when it has been realized that anthropic activity was able to affect substantial parts of the global atmosphere. The increase of the concentration of carbon dioxide from approximately 300 ppm by the turn of the century to a level of about 340 ppm at present, the haze formed over industrialized areas, easily recognized from aircraft and satellite observations, and the long range transport of air pollutants as well as the effects of the acidification of the precipitation are now well documented. It is therefore of great importance to evaluate the causes which determine atmospheric acidity, how it can be estimated and its impact upon the environment.

It has been suggested [1] that the atmosphere-hydrosphere-biosphere system with a present day atmosphere, which is 20% oxygen and 79% nitrogen, and a world ocean with a pH of 8 and an alkalinity of 2,3  $\mu\text{eq/l}$  is determined by a set of gigantic coupled acid-base and redox titrations.

The volatile acids from the earth's interior ( $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$  and others) are neutralized by bases from the rocks and the reduced species formed are oxidized by oxygen. The system is however in a dynamic equilibrium upon which man's activity can have a relevant influence on a global as well as a local scale. The large amounts of atmospheric contaminants released by fuel combustion, industrial production and the extensive use of chemicals determine high fluxes of acidic precursors which contribute to alter atmospheric status.

Air pollutants are generally emitted near the surface or from stacks up to 100-200 m high. The initial concentration is rapidly reduced by atmospheric turbulence and thermal instability. Most pollutants stay within

the lower part of the troposphere and will therefore be more or less evenly distributed within the mixing layer. These emissions, through photochemical and chemical reactions lead to an increase in the total acidity of the atmosphere and consequently an increase in fluxes of acidity to the earth's surface occurs through rainfall of increased acid content at a lower pH (wet deposition) and through absorption and fallout of gases and aerosols (dry deposition).

The mean residence time of pollutants depends upon various factors such as the presence of specific components of the atmosphere, atmospheric stability and precipitation frequency.

In order to handle the problem of atmospheric acidity it is envisaged to consider the emission sources of air pollutants, the reactions occurring in the atmosphere, the modification of the cycles of the atmospheric elements and the impact on the environment.

### *Emission of air pollutants*

Most of the air pollutants are connected with the use of fossil fuels for heat and energy production, including motorized traffic and the emissions from industrial processes and large scale use of many industrial products e.g. fertilizers, solvents, pesticides, freons.

The main emission products from industrialized and densely populated areas are carbon dioxide, sulphur dioxide and nitrogen oxides, the last two species being the main precursors to acid precipitation after conversion to sulphuric and nitric acids.

Important in this connection is the formation of photochemical oxidants, which occur by photolysis of nitrogen dioxide in the presence of reactive hydrocarbons. The main "natural" ionic constituent in aerosols and precipitation is ammonium, which is emitted as ammonia from soil and animal manure.

The haze which can be seen in fair weather is mainly due to sub-micron ammonium sulphate particles. This aerosol also contains soot, agglomerates of very small carbon particles with adsorbed high molecular weight organic compounds and appreciable amounts of certain trace elements, e.g. lead, zinc, iron, nickel, cadmium etc.

The understanding of the chemical oxidation of the primary pollutants  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{HCl}$  is the most interesting aspect of atmospheric acidity and efforts have been made to describe the fate of these species from their sources to sink [2].

### *Sulphur dioxide*

It is well known that  $\text{SO}_2$  is a water soluble gas and its oxidation occurs in an oxygen saturated solution namely in the presence of ion metals, which may act as catalysts. A first order rate constant for its conversion to "sulphate" has been assigned; the conversion process in the atmosphere leads however to several oxidation products  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  ( $\text{NH}_4$ ) $_2\text{SO}_4$  etc. so that the evaluation of the mechanism and rates of the heterogeneous paths of  $\text{SO}_2$  oxidation within the troposphere have a great interest for atmospheric scientists.

The overall process of oxidation of  $\text{SO}_2$  is a complex function of gas phase photochemical oxidation reactions leading to condensable vapours and the catalytic and non-catalytic oxidation on wetted aerosol surfaces. Though to a different extent according to local and meteorological conditions all reactions might occur simultaneously in the troposphere and it is practically impossible to discriminate various processes which might influence each other, it is customary to examine separately homogeneous and heterogeneous reactions.

A thorough investigation of possible atmospheric homogeneous oxidation reaction has been carried out by Calvert *et al.* [3] and possible atmospheric processes in the gas phase are listed in table I.

These reactions might be grouped according to three main and distinct mechanisms:

a) Direct photo-oxidation involving the reactions of excited  $\text{SO}_2$  molecules produced, following the adsorption of solar U.V. radiation in the first and second adsorption bands of  $\text{SO}_2$ .

b) Oxidation of  $\text{SO}_2$  by reactive intermediates, e.g. atoms or free radicals, which are generated photochemically.

c) Oxidation of  $\text{SO}_2$  by reactive intermediates generated in thermal reactions, e.g. ozone-olefin reactions.

The direct photo-oxidation of  $\text{SO}_2$  by way of the electronically excited states of  $\text{SO}_2$  is relatively unimportant for most conditions which occur within the troposphere.  $\text{SO}_2$  molecules adsorb UV radiation quite strongly in the near UV region but the energy involved is insufficient to break the O-S-O bond. Though a number of reactions of electronically excited molecules have been reported, in ambient air the net oxidation of  $\text{SO}_2$  does not occur at an appreciable rate as the excited states are quenched to the ground state by  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  [4].

TABLE I - *Possible atmospheric gas phase SO<sub>2</sub> oxidation processes.*

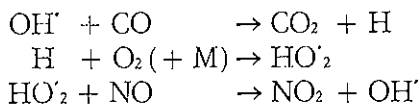
| Initial Steps                 |  |
|-------------------------------|--|
| (1)                           | $\text{SO}_2 + h\nu (2400-3400 \text{ \AA}) \rightarrow \text{SO}_2^*$   |
| (2)                           | $\text{SO}_2^* + \text{O}_2 \rightarrow (\text{SO}_4)$   |
| (3)                           | $\text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$   |
| (4)                           | $\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}$  |
| (5)                           | $\text{SO}_2 + \text{NO}_3 \rightarrow \text{SO}_3 + \text{NO}_2$  |
| (6)                           | $\text{SO}_2 + \text{N}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{N}_2\text{O}_4$                            |
| (7)                           | $\text{SO}_2 + \text{CH}_3\text{O}_2^* \rightarrow \text{SO}_3 + \text{CH}_3\text{O}^*$                        |
| (8)                           | $\text{SO}_2 + \text{HO}_2^* \rightarrow \text{SO}_3 + \text{OH}^*$  |
| (9)                           | $\text{SO}_2 + \text{OH}^* + \text{M} \rightarrow \text{HSO}_3 + \text{M}$                                     |
| Possible Subsequent Reactions |  |
| (10)                          | $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ |
| (11)                          | $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{nucleus}$  |
| (12)                          | $\text{HSO}_3^* + \text{OH}^* \rightarrow \text{H}_2\text{SO}_4$   |
| (13)                          | $\text{HSO}_3^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{SO}_3$                                    |
| (14)                          | $\text{HSO}_3^* + \text{HSO}_3^* \rightarrow \text{H}_2\text{S}_2\text{O}_6$                                   |
| (15)                          | $\text{HSO}_3^* + \text{H}_2\text{O} \rightarrow \text{HSO}_3(\text{H}_2\text{O})$                             |
| (16)                          | $\text{HSO}_3^* + \text{O}_2 \rightarrow \text{HSO}_5^*$   |
| (17)                          | $\text{HSO}_5^* + \text{H}_2\text{O} \rightarrow \text{HSO}_5(\text{H}_2\text{O})$                             |

Several authors have been able to show experimentally that natural air containing trace amounts of SO<sub>2</sub>, exposed to sunlight, is photochemically oxidized and that the rate of SO<sub>2</sub> oxidation was a complex function of the trace gas composition of the air mixture (NO, NO<sub>2</sub> - hydrocarbons level and composition).

The oxidation of SO<sub>2</sub> within the natural troposphere is therefore expected to occur largely through reactions 7,8 and 9 of table I.

The main mechanism is through radicals which might be formed in various ways such as from ozone photodissociation and from the reaction

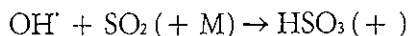
of oxygen atoms,  $O(^1D_2)$  with  $H_2O$ . These reactions can be followed by a series of fast elementary steps in which  $OH^\cdot$  and  $HO_2^\cdot$  radicals are inter-converted



Radicals are removed by reaction with each other, which may lead to oxidising products such as  $HO_2^\cdot + HO_2^\cdot \rightarrow H_2O_2$ , or to acid gases  $OH^\cdot + NO_2 (+ M) \rightarrow HNO_3 (+ M)$ .

Other pollutant species, namely organic vapours and  $NO_x$ , play an important role, the former being oxidized through peroxy radicals,  $RO_2^\cdot$ , to aldehydes including formaldehyde, which is photochemically active, the latter in converting the unreactive  $RO_2^\cdot$  and  $HO_2^\cdot$  to reactive  $RO^\cdot$  and  $OH^\cdot$  radicals and in removing  $OH^\cdot$  radicals as  $HNO_3$ .

The fundamental reaction is thus



$HSO_3^\cdot$  radical is rapidly converted to  $H_2SO_4$  aerosol. It has to be stressed that, though in polluted air  $OH$ -initiated oxidation is the dominant process, other thermal reactions, such as the one between  $O_3$  and olefinic hydrocarbons leading to reactive intermediates may occur. Also thermal ozone-olefin reactions can promote  $SO_2$  oxidation at a rate which may be significant in the atmosphere; as high olefin concentrations are required, this process seems to be only of importance near large sources of these hydrocarbons. Homogeneous gas-phase oxidation of  $H_2S$  and organic sulphides by free radical species appears to be the dominant process and  $SO_2$  is the most important oxidation product.

In conclusion the homogeneous photochemically initiated free radical reactions are the most significant mechanism for conversion of  $SO_2$  to sulphate in the lower atmosphere. According to Eggleton and Cox [5] in the western European summer,  $SO_2$  oxidation rates in sunlight are expected to be between 0.5% and 5%  $hr^{-1}$ , depending on the degree of pollution of the atmosphere, with the lower figure relating to clean air. In winter-time, rates in sunlight are expected to be a factor of 2 slower and, due to the reduced hours of sunlight, the overall removal rate of  $SO_2$  by photochemical reactions is slower by an even greater amount.

### *Liquid phase oxidation reactions*

Oxidation of  $\text{SO}_2$  in liquid phase can occur in clouds, fogs and in rain droplets in the absence and in the presence of catalysts and of ammonia with formation of sulphate; ammonium sulphate in rainwater has been however always detected.  $\text{SO}_2$  conversion to sulphate in clean water is a slow process but is known to be accelerated in the presence of ammonia. Oxidation of  $\text{SO}_2$  can also occur through an uncatalyzed mechanism which involves ozone as the oxidizing agent as well as by means of dissolved hydrogen peroxide, originating from gas phase photochemical reactions. The former mechanism is very sensitive to pH, becoming dominant in an alkaline regime whereas the latter, which is rather insensitive to pH, prevails under acid conditions; it depends on hydrogen peroxide in the atmosphere and therefore on photochemical activity which has a noticeable seasonal variation.

Oxidation of  $\text{SO}_2$  in droplets, which contain various products, detectable in the atmosphere, is the measurement accepted as being real as it approaches atmospheric conditions. Studies upon the oxidation of  $\text{SO}_2$  in droplets, which contain soot particles, definitely show the effect of carbonaceous material in performing the conversion to  $\text{SO}_4^{2-}$ . This process seems to be of relevant importance in polluted areas. As far as liquid phase oxidation of  $\text{SO}_2$  is concerned, it seems that the uncatalyzed oxidation of  $\text{SO}_2$  by ozone or hydrogen peroxide is probably the dominant mechanism in the droplet phase.

### *Reaction on the surface of particles*

Atmospheric particles as well as any solid material interact with atmospheric  $\text{SO}_2$ , the interaction being characterized by two processes.

### *Adsorption and conversion to sulphate*

The extent of both processes depends upon the nature and composition of the materials considered and is affected by a variety of factors, the more relevant being humidity and surface reaction. The adsorption process occurs in two steps; in the first one, which is very fast, a second step intervenes which might be due to the slow diffusion of  $\text{SO}_2$  in the solid phase [6]. The conversion to sulphate takes place rapidly on an



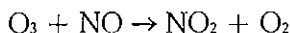
alkaline dust whereas no oxidation has been observed on neutral or acid material unless the material exhibits a catalytic effect as there has been observed in soot the presence of manganese salts and other metal salt aerosols; humidity has in both cases an important role, a higher sulphate conversion being observed at higher humidities.

These results show the same trend of those obtained for  $\text{SO}_2$  in the liquid phase.

### *Nitrogen oxides*

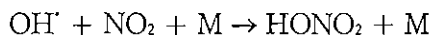
The tropospheric nitrogen cycle has been strongly affected by emission of nitrogen oxides mainly due to the oxidation of nitrogen in the air during combustion processes. About 50% comes from motorized traffic and most of the remainder from power stations and space heating. Oxidation of NO to nitrogen dioxide is reported in chemical smog but a variety of reactions can occur in gas phase involving in addition to NO and  $\text{NO}_2$ , higher oxides  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  as well as nitrous HONO, nitric and peroxy-nitric acid.

Chemical oxidation of NO to  $\text{NO}_2$  occurs rapidly through reaction with ozone as well as in daylight with photochemically generated peroxy radicals ( $\text{HO}$ ,  $\text{CH}_3\text{O}_2$  ecc.) according to this reaction

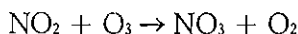


The net conversion of NO to  $\text{NO}_2$  is limited to the photodissociation of  $\text{NO}_2$  ( $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ). As atomic oxygen rapidly recombines with oxygen to yield ozone, a photostationary state is reached, which governs the concentration of NO,  $\text{NO}_2$  and  $\text{O}_3$ , the ratio between the two nitrogen oxides being determined by the light intensity.

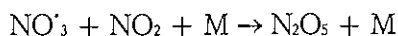
Oxidation of  $\text{NO}_2$  leads to the formation of nitric acid, which can be formed through two different mechanisms. In daylight photochemically generated OH react with  $\text{NO}_2$  according to the following reaction



Oxidation can occur through the reaction with ozone



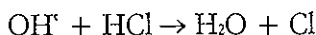
Nitrogen pentoxide, is formed in the reversible reaction with  $\text{NO}_2$ ,



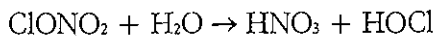
which reacts with water to form  $\text{HNO}_3$ . In day-time the removal of  $\text{NO}_3$  either through the reaction with  $\text{NO}$  to form  $\text{NO}_2$  or through photolysis reduce the efficiency of this reaction. At nighttime the rate of oxidation of  $\text{NO}_2$  by  $\text{O}_3$  is of the same magnitude as the daytime rate for the reaction with  $\text{OH}$  radicals.

### *Hydrogen Chloride*

Noticeable amounts of hydrogen chloride can be found in the emission namely due to incineration and combustion process of chlorine containing materials.  $\text{HCl}$  is quite stable towards oxidising agents and on account of its solubility can be incorporated into the rain or can be adsorbed by dry deposition. It can undergo an oxidation process similar to that of  $\text{SO}_2$  with  $\text{OH}$  radicals to yield chlorine atoms



Atomic chlorine by reaction with hydrogen containing gases reforms  $\text{HCl}$  again whereas by reacting with ozone yields  $\text{ClO}$  radical which is further converted to chlorine nitrate,  $\text{ClONO}_2$ , which is a stable species. This compound can photodissociate to release chlorine atoms and can also react with water and hydrolyze



According to this reaction in addition to the same strong acid input an oxidizing species is produced.

### *Acidity formation in the atmosphere*

A review of the main reactions occurring in the atmosphere emphasize the various processes which lead to the formation of species, which can alter the relative ionic equilibrium.

Sulphate aerosol production, which is by far the most important process, changes however noticeably under different atmospheric conditions

and the various mechanisms may occur to a different extent. Factors affecting these changes are the concentration of photochemically produced gaseous species, temperature and aerosol acidity and size distribution. It is found that, in general,  $\text{H}_2\text{SO}_4$  condensation and  $\text{H}_2\text{O}_2$  oxidation on the wetted aerosol can be dominant pathways to sulfate aerosol formation under daytime conditions. Under summer daytime conditions sulfate formation is higher and  $\text{H}_2\text{SO}_4$  condensation can be the more important mechanism. Under winter daytime conditions sulfate formation is lower and  $\text{H}_2\text{O}_2$  oxidation can be the prevailing mechanism. Under nighttime conditions, the rate of sulfate aerosol formation is lower and catalytic and noncatalytic oxidation mechanisms on the wetted aerosol surface become the major sulfate formation mechanisms. In particular, catalytic oxidation by soot, iron and manganese appear to be the most important pathways under nighttime conditions.

The changes in the relative importance of sulfate aerosol formation mechanisms under different atmospheric conditions is shown in Fig. 1.

The soot mechanism appears to be the major sulfate aerosol formation mechanism which is not directly or indirectly related to photo-

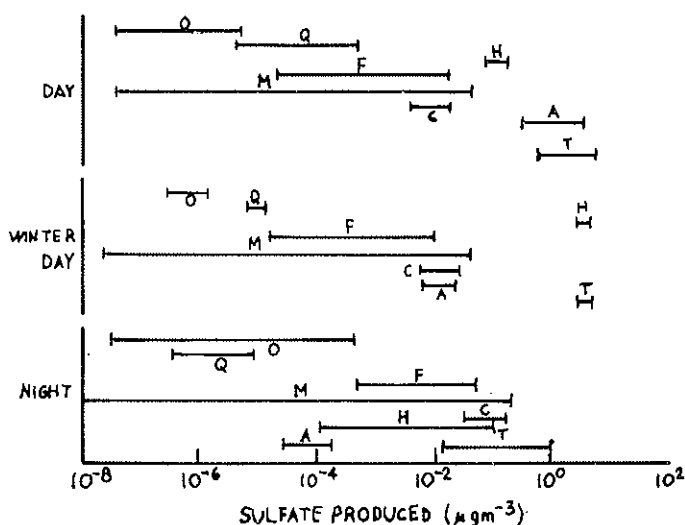


FIG. 1. Relative importance of various urban sulphate aerosol production mechanisms: T = total sulfate; A =  $\text{H}_2\text{SO}_4$  condensation; H =  $\text{H}_2\text{O}_2$  oxidation; O = uncatalyzed oxygen oxidation; Q =  $\text{O}_3$  oxidation; F = iron catalyzed oxidation; M = manganese catalyzed oxidation; C = soot catalyzed oxidation.

chemical activity. The increase in soot has a negligible effect under summer daytime conditions with photochemical reactions. But under conditions of higher particle acidity (low  $\text{NH}_3$ ) and reduced photochemical activity (low  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ ) soot catalysis could be a competitive pathway to sulfate formation under daytime conditions.

The variety of reactions which have been described indicate the large number of chemical species which enter in the troposphere and which may have an impact upon the environment. It is necessary to emphasize that all species are in a dynamic equilibrium for the meteorological turbulence so that in some cases redox and acid-base reactions occur with the formation of stable compounds with high formation constants but nevertheless the reagent species are detectable in the atmosphere. A typical example is the evaluation of the atmospheric aerosol where besides the presence of ammonium sulphates, free ammonia and sulphuric acid may coexist.

In an ambient aerosol strong acids may exist in the gaseous state ( $\text{HNO}_3$ ,  $\text{HCl}$ ), in the form of aqueous droplets ( $\text{H}_2\text{SO}_4$ ), or as species adsorbed at particle surfaces. Their fate can be foreseen by considering the reactions these acids may undergo, which are outlined in table II.

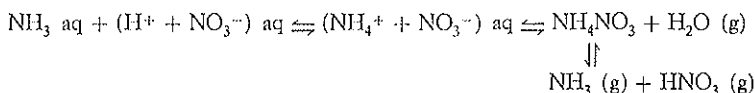
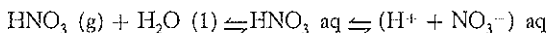
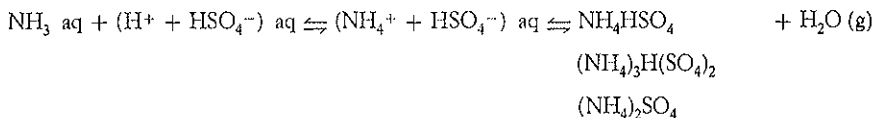
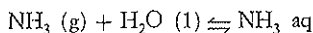
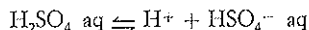
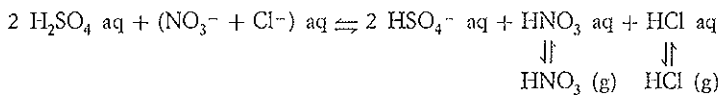
The main reaction is the neutralization with ammonia, which is the major reactant. In case of thermodynamic equilibrium temperature and partial pressure of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and volatile acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ) it would be possible to describe the  $\text{NH}_3$ -acid-ammonium salt system according to Gibbs phase rule, but in ambient air for the various meteorological factors affecting equilibrium this aim is not feasible.

Also a heterogeneous strong acid salt reaction leading to volatile acids is possible; as an example a loss of hydrochloric acid from marine aerosol particles can be observed in combination with  $\text{NO}_2$  and  $\text{SO}_2$  conversion. The third route of the conversion products of  $\text{SO}_2$  and  $\text{NO}_x$  is their transport to the earth's surface. It is important to notice that  $\text{H}_2\text{SO}_4$  and ammonium salts of strong acids are products of a gas to particle (droplets) conversion and as such are present in the fine particle mode ( $0.05 - 2 \mu\text{m}$ ) of ambient aerosols. Particulate matter of this mode behaves physically different from coarse particles ( $> 2 \mu\text{m}$ ) on one hand and gaseous atmospheric trace constituents ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ) on the other. Fine particles exhibit low gravitational settling and brownian mobility and have therefore the highest overall residence time in ambient air compared to the other components.

The removal of these species from the atmosphere can take place

TABLE II - *Fate of atmospheric strong acids.*

## 1) Reaction with ammonia

2) Conversion of nitrates and chlorides during heterogeneous  $\text{H}_2\text{SO}_4$  formation:

## 3) Transport of strong acids and their salts to the earth's surface by dry and wet deposition.

through their deposition in rain and for direct deposition of gases and particles into natural surfaces. For the two groups of processes the collective terms wet and dry deposition have been applied. Wet deposition is transfer of a certain species from the atmosphere to the earth's surface within or on the surface of rain, snow or hail; it is therefore an indirect process where precipitations act as a vector. Dry deposition is the direct transfer with the absorption of gases and particles by natural surfaces (vegetation, soil material, water). Wet and dry deposition are largely independent of each other although rain-wetted surfaces affect rates of dry deposition.

*Wet deposition*

The general picture for acid and basic components which are known to take part in rain acid base chemistry is summarized in fig. 2.

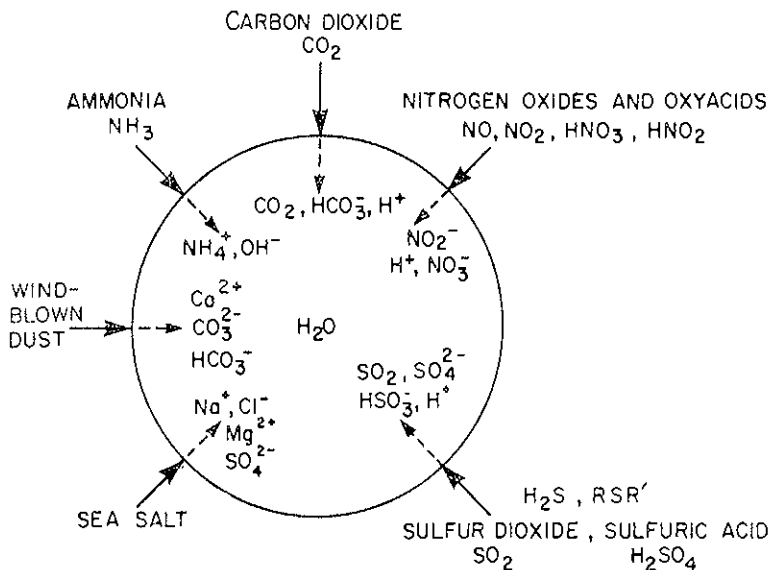


FIG. 2. Acid and basic components of the rain.

For a consideration of wet deposition mechanism it is useful to make a distinction between processes transferring material to cloud droplets before they begin their descent as a raindrop, known collectively as rain-out and processes transferring material to falling raindrops known as wash-out. There are five mechanisms [8] by which particulate and gaseous compounds may be captured by cloud or rain drop: diffusiophoresis, brownian diffusion, impact and interception, solution and oxidation of gaseous species (notably  $\text{SO}_2$  and  $\text{NO}_2$ ) and the cloud condensation nuclei (CCN) pathway.

These processes are outlined in Fig. 3.

Quantification in the contribution to sulphur and nitrogen in rain by the above processes has been summarized in table III.

Equilibrium concentrations of gas phase  $\text{SO}_2$  and dissolved sulphur species in the same oxidation state ( $\text{SO}_2$ ,  $\text{HSO}_3^-$ ) are reached in a few seconds for droplets smaller than  $100\text{ }\mu\text{m}$  diameter. However, for the time scales involved in rainout, oxidation of S(IV) to S(VI) dominates this mechanism for the accumulation of S by cloud droplets. The oxidation may proceed through the variety of mechanisms previously described ranging from catalytic reactions in solution often assisted by the presence of  $\text{NH}_3$ ,

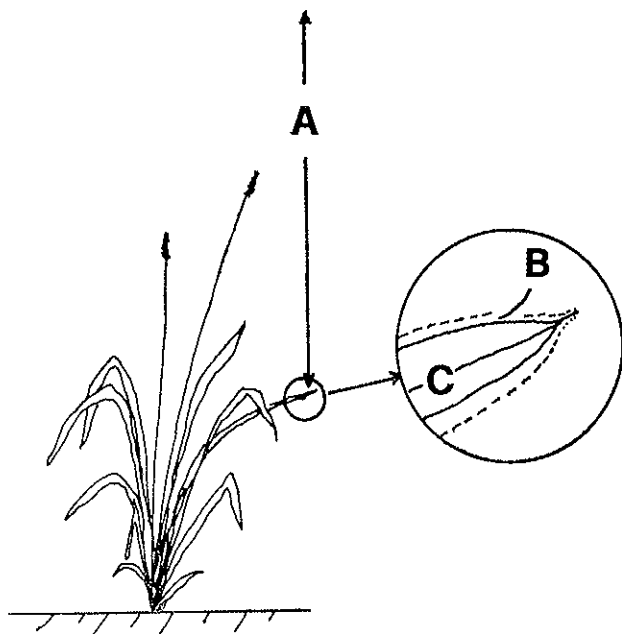


FIG. 3. The main wet deposition processes.

to more effective reactions involving  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^\cdot$  and  $\text{O}_3$ .  $\text{NO}_2$  is converted to  $\text{HNO}_3$ , both in solution and in gas phase, which then reacts with atmospheric ammonia forming  $\text{NH}_4\text{NO}_3$  aerosol contributing to the CCN pathway.

Sulphur and nitrogen containing aerosols play a major role in the production of cloud water droplets as they form a dominant fraction of the particles, suitable for condensation of water vapour. The aerosol contains sulphur and nitrogen compounds in the concentration range from  $0.04 \mu\text{g m}^{-1}$  to  $80 \mu\text{g m}^{-1}$ . Sulphur and nitrogen are present in a variety of compounds, though sulphur is almost invariably present in its most oxidised  $\text{S}^{\text{VI}}$  state. The major compounds are  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{NO}_3$ . The hygroscopic nature of sulphur- and nitrogen-containing aerosols enhances their efficiency as CCN, and this, with their ubiquitous presence in both polluted and clean air, makes this pathway for removal an important one, although it is difficult to quantify directly.

TABLE III - *Processes contributing to the sulphur and nitrogen in rain.*

| PROCESS                                     | SULPHUR  |  | NITROGEN  |   |
|---|--|--|---|---|
|   | Range of concentrations in rain at ground level<br>$\mu\text{g g}^{-1} \text{SO}_4^{2-}$ | Note (1)   | Range of concentrations in rain at ground level<br>$\mu\text{g g}^{-1} \text{NO}_3^-$ | Note (2)  |
|   |  | Average contribution to wet-deposited sulphur<br>% |   | Average contribution to wet-deposited nitrogen<br>% |
| Diffusiophoresis                            | $10^{-2} - 10^{-1}$  | 2.5  | $10^{-3} - 10^{-2}$   | 2.5   |
| Brownian Diffusion                          | $10^{-2} - 10^{-1}$  | 2.5  | $10^{-3} - 10^{-2}$   | 2.5   |
| Impaction and Interception                  | $10^{-1} - 1.0$  | 10   | $10^{-2} - 10^{-1}$   |   |
| Solution and Oxidation of Gaseous 'Species' | 0.5 - 3.0  | 20   | $10^{-2} - 0.4$   | 15 - 25 (3)   |
| Cloud Condensation Nucleus Pathway          | 2.0 - 20.0   | 65   | $10^{-1} - 5.0$   | 60 - 70   |
| (5)   | (4)  |  | (4)   |   |

## NOTES

(1) Considering rain with geometric mean  $\text{SO}_4^{2-}$  concentration of  $3.5 \mu\text{g g}^{-1}$  (weighted for rain quantity).

(2) Considering rain with geometric mean  $\text{NO}_3^-$  concentration of  $0.5 \mu\text{g g}^{-1}$  (weighted for rain quantity).

(3) Uncertainty in this component necessarily leads to uncertainty in other components.

(4) Lower limits of range deduced from average contribution and range of concentrations measured.

(5) This table considers the whole wet deposition pathway, no distinction between RAINOUT and WASHOUT.

*Dry deposition*

The mechanisms by which gaseous and particulate pollutants are transported to and dry deposited on natural surfaces are examined in order to enable prediction of deposition rate for a variety of surfaces in a range of atmospheric conditions.



The process of dry deposition for gases and particles has three stages which are outlined in Fig. 4. The first one is the transport from the free atmosphere to the laminar boundary layer of air close to the surfaces of objects. The second one is the transport through this layer and in the third the gas or particles must be absorbed and captured or otherwise entrained by the surface. As various species are transported to successive stages in this process the number of individual mechanisms influencing rates of transport increases and rates of transport for different materials diverge.

For gases and particles small enough for gravitational settling to be unimportant (this is the case for particles with diameters  $< 5 \mu\text{m}$ , which have terminal velocities less than  $0.5 \text{ mm s}^{-1}$ ), transport in the free atmosphere is effected by turbulent diffusion. Rates of turbulent diffusion exceed molecular diffusion rates by several orders of magnitude so that for the free atmosphere, molecular diffusion may be ignored. The turbulence is generated by frictional forces at the earth's surface, close to which rates of turbulent diffusion may be estimated from mean vertical gradients in wind velocity and air temperature.

The very shallow ( $\sim 1 \mu\text{m}$ ) layer of air in contact with the surfaces, where stream lines for air-flow are approximately parallel to the surface and turbulence is suppressed by the viscosity of the air, is known as the laminar boundary layer. The thickness of this layer is determined by physical characteristics of the object (size, shape and surface structure) and by the velocity of air outside the laminar boundary layer. Although gases and small particles are transported by the same mechanism and at about the same rates in the free atmosphere, their transport through the laminar boundary layer differs considerably. Gases must diffuse through this layer by molecular diffusion, the concentration gradient and diffusion coefficient for the gas in question controlling the rate of transfer.

Particles smaller than  $0.1 \mu\text{m}$  diameter are able to diffuse through the laminar boundary layer by Brownian diffusion, the efficiency of the mechanism increasing as particle size decreases below  $0.1 \mu\text{m}$ . In general, rates of Brownian diffusion, which are small even by comparison with molecular diffusion, and do not therefore, represent an efficient process for the transport of sulphur and nitrogen containing particles across the laminar boundary layer. Another mechanism for transport of particles through this layer is inertial impaction. For this process the particle must

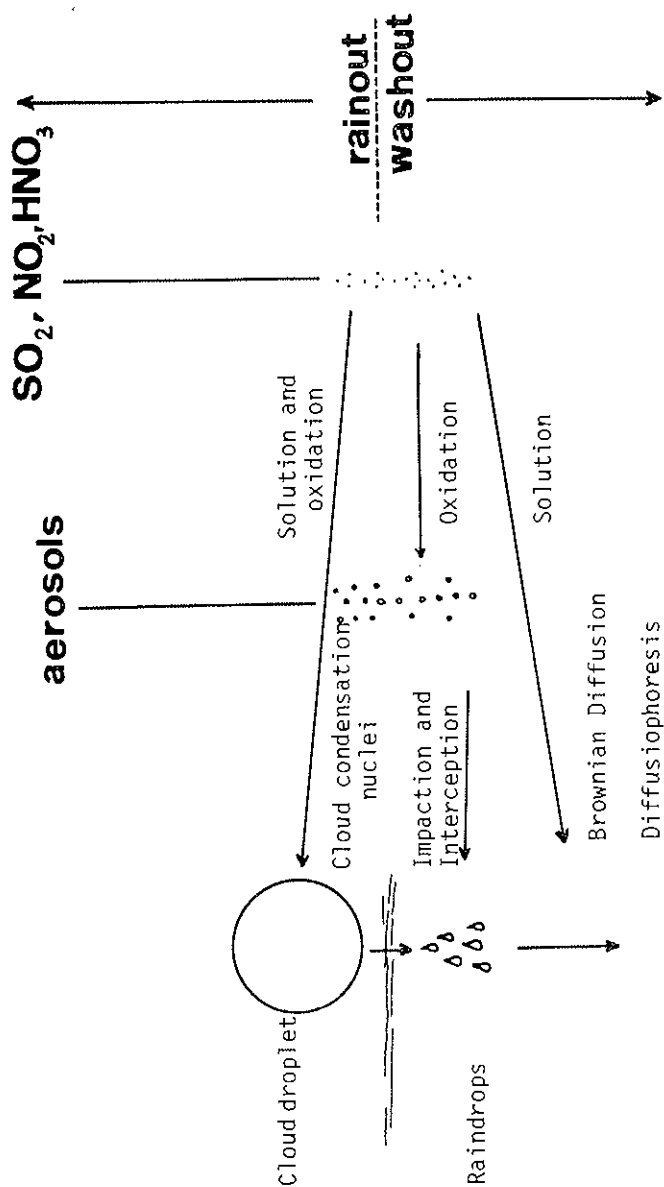


FIG. 4. The dry deposition process: A free atmosphere; B laminar boundary layer; C plant surface.

have sufficient momentum when reaching the laminar boundary layer to penetrate the layer of relatively still air and be captured by the surface.

Having reached the surface, the mechanism for dry deposition now enters its most complex phase as here gases behave in a manner entirely dependent on the chemical and physical affinity of the gas for the surface in question. For active gases like  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{HNO}_3$  (gas) and a uniform surface like water the relative simplicity of the system lends itself to theoretical treatment. For more complex surface like a canopy of vegetation a wide range of materials are simultaneously presented to the gas molecules: the epicuticular wax covering on leaf surfaces, a matrix of cell wall material and intercellular fluids lining the sub-stomatal cavity, surfaces of dead tissues and in many cases a second canopy of vegetation and the soil surface.

Surface properties also strongly influence the capture of particles, though the small fraction of sulphur and nitrogen containing particles that are captured by the surface are in a size range for which bounce-off and re-suspension are very unlikely.

## EVALUATION OF ATMOSPHERIC ACIDITY

On account of the various reactions which may occur in the atmosphere it is a challenging activity for the analytical chemistry to succeed in evaluating the chemical composition of the atmosphere in order to obtain a real representative picture. As all components are in a dynamic equilibrium and in most cases at levels not directly measurable, it is required to obtain the real concentration of a certain species and prevent artifacts which might take place along the sampling. The speciation of atmospheric acids is a major difficulty because these compounds must be detected simultaneously with their precursors ( $\text{SO}_2$ ,  $\text{NO}_x$ ) neutralizing agents ( $\text{NH}_3$ ) and ammonium salt particles (ammonium sulphates and nitrate). It is therefore necessary to combine a selected detection system with an appropriate sampling and sample pretreatment procedure in order to obtain a detailed insight into the complex acid-base-salt system.

Most of the interaction responsible for artifacts can be prevented by replacing the traditional sampling system, consisting in the filtration and in the selective collection of reactive trace gases with the combination of diffusion separation and filtration; this aim is reached by making use of denuders. The air under investigation is drawn through a denuder,

which is a tube the inner walls of which are coated with a suitable trapping agent for trace gases.

During the laminar flow of air through the tube the gas molecules diffuse to the tube walls, which are actually acting as irreversible sink, while the particles larger than  $0.01\text{ }\mu\text{m}$  in diameter proceed unaffected because their diffusion coefficients are several orders of magnitude lower than those of gaseous species. In addition to an effective gas particle separation this procedure offers the possibility to determine selectively reactive gases by analyzing directly the sorbed species.

Flow limitations which require a long sampling time have been overcome by the use of recently developed annular denuders, consisting of two coaxial glass cylinders. This system can operate at high flowrate and by combining denuders with selective adsorbers, as is shown in fig. 5, it is possible to sample simultaneously  $\text{SO}_2$  (tetrachloromercurate coating),  $\text{HCl}$  and  $\text{HNO}_3$  (sodium carbonate coating) and  $\text{NH}_3$  (oxalic acid coating) [9].

### *Impact of atmospheric acidity upon the environment*

The mechanisms relative to acid deposition make it possible to draw some conclusion regarding the uptake of gases and particles and the impact atmospheric acidity may have upon the environment. The following items will be considered:

- Water acidification.
- Chemical modifications of precipitation in contact with soil and vegetation.
- Effect on architectural structures and monuments.

### WATER ACIDIFICATION

Though water acidification is one of the most important aspects, one would certainly not expect significant changes in water acidity in all exposed areas. The effect is highly dependent on bedrock geology and the nature of the overburden. No acidification of fresh water is to be expected in areas with appreciable amounts of calcareous rocks. The most well known susceptible areas are those with shallow overburden and quartz-bearing bedrock. Acidification can occur in catchments with highly weathered sandy soils with low neutralization capacities.

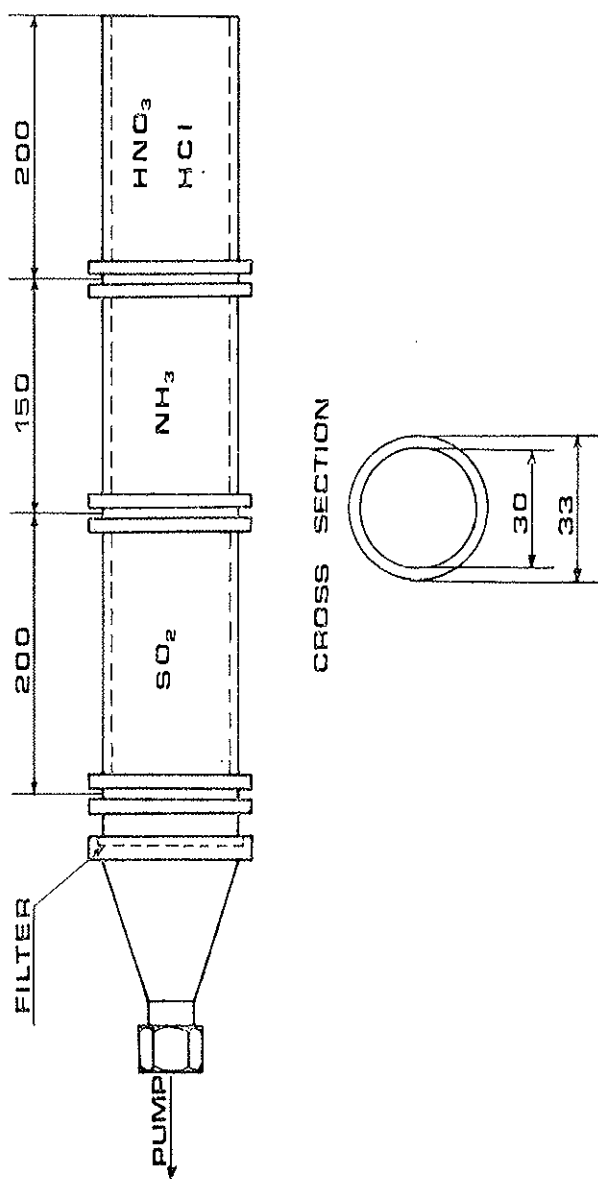


FIG. 5. Scheme of a multistage annular denuder for the simultaneous sampling of  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{NH}_3$ .

The alkalinity or better the acid neutralization capacity is the key in estimating the sensitivity of fresh water to acidification.

There is a convincing evidence of a decrease in pH in fresh waters during recent decades. Though it is difficult to quantify the change, acidification of fresh water observed in several areas corresponds well with the changes in the composition of precipitations.

High acidity affects aquatic life in two ways by altering the tolerance of individual species and through changes in the dynamic of seasonal succession and interactions between species.

A conspicuous phenomenon in many acid lakes and rivers is the heavy growth of filamentous algae and mosses. The ratio of chlorophyll to carbon is low in an acid system demonstrating that much of the algae is photosynthetically inactive. A reduced efficiency of carbon assimilation per unit of chlorophyll is observed with a reduction in productivity. Algae accumulation at low pH is probably due to reduced grazing activity by invertebrates and less decomposition. It has been shown that decomposition of organic matter is reduced in acid lakes and that organic detritus is accumulating on lake bottoms often covered by dense felts of fungal hyphae.

The mineralization of water organisms, which are specialized to decompose into slowly degradable compounds, is retarded in acid water and heterogeneous matter may accumulate on lake bottoms increasing the rate of moss formation. The dense gelatinous fungal mats reduce the oxygen available for aerobic degradation. Respiration i.e. oxygen consumption is decreased and also a reduced recycling of phosphorus, which is of a great importance for lake productivity, is observed.

Consequently a change in the invertebrate species which are important links between primary producers and fish in the aquatic food chain occurs with a serious impact on the energy flow.

There is also a change in the benthic invertebrates which constitute an important group of fish food animals and are a quite sensitive pH indicator. Below pH 4.5 no crustaceans, snails and mussels are found and no important fresh water fish can live.

There are several factors however which are related to water acidity (low  $\text{Ca}^{++}$ , high content of heavy metals and aluminium) and other abiotic factors (temperature, transparency) which mask or enhance the pH effect. It now seems proven that aluminium is a real toxic agent in lakewater in acidified catchments, this metal being leached in high amounts from soils under acidification. Aluminium buffer system replaces the normal bicarbonate buffer system when lakes are acidified and Al concentrations

have led to heavy fish mortality with an Al toxicity having a maximum around pH 5.

#### CHEMICAL MODIFICATIONS OF PRECIPITATION IN CONTACT WITH SOIL AND VEGETATION

Only a small fraction of the precipitation falls normally directly into rivers and lakes (often 5-10%). The main part is affected by a number of processes in the catchment resulting in a runoff composition which may be very different from that of the precipitation. The first change in the composition occurs as the precipitation passes the canopy of the vegetation.

Plant stomata represent the major sink for  $\text{SO}_2$  as well for other acid components, other sinks being cuticular surfaces and soil surface. Particles and adsorbed gases accumulated in the tree crowns may be washed off by the precipitation.

The effectivity of forests in scavenging and retaining atmospheric components has ecological significance and this may imply that forests are particularly at risk from atmospheric pollutants.

In addition the runoff should be considered with respect to effects of vegetation and ion exchange. The roots take up various cations and release  $\text{H}^+$ , resulting in a soil acidification.

Cation exchange is one of the most important processes we have to consider. Soil particles have normally a negatively charged surface and therefore a layer of cations close to the surface. These cations may be interchanged with those in the solution. Thus when a dilute solution of neutral salts percolates through acid soils, the leachate becomes acid because of exchange of other cations with hydrogen ions.

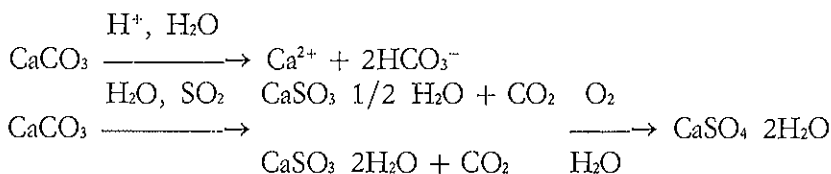
Under the influence of a continuous acid load, soils pass through three phases: In the first phase they retain the whole acidity and load the seepage water with basicity (calcium and magnesium ions released from the cation exchangers). They pass then over in the second phase where part of the acidity deposited is changed into cation acids (manganese and aluminium ions) which leave the soil with the seepage water by determining the weathering of the soil; the other part of the acidity is accumulated in the solid soil phase, partly as aluminium sulfate. In the third phase this accumulated acidity is lost and leaves the system with the seepage water. In this phase the acid load to the hydrosphere increases strongly. The risk existing for the hydrosphere can hardly be overestimated.

## EFFECTS ON ARCHITECTURAL STRUCTURES AND MONUMENTS

The common masonry materials as limestones, marble, sandstones basalt and granite as well as artificial materials as brick, concrete and mortar are composed primarily of carbonate and silicate mineral. The natural weathering of these materials, due mainly to atmospheric  $\text{CO}_2$ , increases at an alarming rate due to atmospheric acidity and acid precipitation.

It has been postulated [10] that silicate minerals as feldspar exposed to atmospheric agents undergo hydration and decay through the polarization and the ensuing dissociation of the water dipole into  $\text{H}^+$  and  $\text{OH}^-$  due to the attractive forces of the free valencies. In this interaction the oxygens are converted to hydroxyl groups and part of the potassium is removed in solution. A partial or total cationic ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ) depletion decomposes the feldspar. Since the neutral water now reaches an increased pH, introduction of acids neutralizes these alkali and facilitates a further decay of these minerals.

Calcite and dolomite are the common carbonate materials of sedimentary (limestone, sandstone) and metamorphic (marble) rocks used as building stones. These materials are highly susceptible to attack by acid deposition and by the presence of atmospheric  $\text{SO}_2$  according to the following reactions:



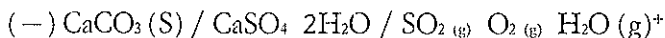
Atmospheric acidity is responsible for the attack in the presence of humidity whereas the  $\text{SO}_2$  reaction continues to occur in the presence of liquid water as well as water vapours. The calcium sulfate that forms is less preserved when the structures are exposed to direct rainfall. In protected regions  $\text{SO}_2$  continues its attack almost continuously and the gypsum obtained from this reaction forms crusts on protected surfaces. As a consequence most ancient buildings in the industrialized countries have a black appearance in some areas and a clean aspect in others. The black appearance is due to gypsum crusts, which have incorporated soot in the process of crystallization whereas the areas directly showered with the



acid precipitation are largely clean. The condensed water vapours in a shaded area keep the building from drying and once the crust has formed it continues to grow inwardly for not having been washed away by driving rain. These crusts of weathering are much less permeable to water than is the marble itself but do not behave as a protective coating as the transport of  $\text{SO}_2$  along the water films corrodes the marble behind the crust rendering these regions highly friable. The rate of decay in these areas is accelerated with regard to marble in unprotected areas.

The main reaction responsible for marble decay and damage to monuments is therefore the sulphation which occurs on the surface of these materials. Oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  occurs by catalytic action due to surface impurities such as  $\text{Fe}_2\text{O}_3$ , soot, colloidal deposits,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  already formed, humidity and also to sulphur oxidising bacteria.

The mechanism of sulphation has been explained [11] by means of an electrochemical process described by a galvanic cell formed between  $\text{CaCO}_3$  acting as a negative pole and the corrosive environment ( $\text{SO}_2 + \text{air} + \text{water vapour}$ ) active as the electrolyte.



According to this mechanism the rate determining step for the second stage of the sulphation of  $\text{CaCO}_3$  is a solid state diffusion in which the diffusion species could be  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ .

Decay of stone can take place through efflorescences which are encrustations formed at the surface; they produce discoloration at the facades of buildings and upon repeated crystallization and hydration, they mechanically disintegrate the stone.

They may be formed as a result of attack of chemically active gases on masonry material and atmospheric acidity is thus responsible for this effect.

Damage to stone occurs also for the corrosion of metallic bars used for anchoring blocks of stone with each other and with the structural framework. Oxidation of iron produces the mineral limonite ( $\text{FeO} \cdot \text{OH}$ ) which has greater volume than the parent iron. This volume increment generates stresses sufficient to disintegrate the stone. The presence of  $\text{SO}_2$  and other acid components decidedly accelerates the decay phenomenon.

The net effect of the entire deterioration process is to alter physical and chemical properties so that the weathering stone becomes even more susceptible to atmospheric attack.

## CONCLUSIONS

The origin of atmospheric acidity has been analyzed through various reactions which occur in the atmosphere. Though natural phenomena such as volcanic eruptions, forest fires and the breakdown of organic substances by bacteria can produce the acid compounds of sulphur and nitrogen which mainly cause acid rain to form, it is believed that to the main sources of pollution such as thermal power stations, district heating, motor vehicles (particularly foundries and smelteries, industries and households emitting sulphur dioxide and oxides of nitrogen, should be attributed the origin of atmospheric acidity. This event is however related also to a variety of reactions involving a large number of human activities.

The impact of atmospheric acidity upon the environment occurs through wet deposition by returning to the surface dissolved in rain, or through dry deposition by depositing directly on structures and crops.

Acid rain alters the pH of lakes and rivers when it falls directly into them, causing their biological death. When absorbed by soils it leaches out the natural base minerals such as potassium, calcium and magnesium, and drains them into the subsoil, thus removing a major source of mineral nutrients for plants and trees. The damage continues when the rainwater reaches the water table, and often carries a load of dissolved toxic metals, such as aluminium, which may arrest the growth of aquatic organisms or kill them outright by destroying in some areas any aquatic life. In soil the dissolving of toxic metals may cause the roots of trees to rot away. Besides the death of lakes and forests and rotting of stonework, the damage to architectural structures and monuments should also be considered.

The size of these problems and the impact which atmospheric acidity may have upon mankind are a challenge for all scientists in these areas.

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## DISCUSSION

BROSSET

We have discussed the term "total acid deposition" because the total impact of acidic material is, as you pointed out very beautifully, due to the gas phase, to the liquid phase and also to the solid phase. We have been working with these problems in Scandinavia for many years and we were really interested to get a rather detailed picture of the acidity, discriminating between strong acids in the precipitation and weak acids, and examining all the details we could get from the analysis of the material. Now we have started to consider the problem in more general terms. For example there are two components: hydrogen ion and ammonium ion. Ammonium does not represent the final neutralization of the hydrogen ion with ammonia, because the reaction is reversible and depends on the ammonium present in the air. And you know very well that plants can just use their ammonium ion and release their hydrogen ion. So the total acidification is the impact or the deposition of hydrogen and ammonium ion together. Now concerning the particles we have still the hydrogen ion, and of course you can identify the different species analyzing a filter. The gas phase is a little more complicated because the acid present in the gas phase is nitric acid, but there are also precursors of acids like sulphur dioxide.

I have just put forward these points because I think we should consider, as our Chairman has said, acid rain as a part of the total acid deposition.

LIBERTI

I believe that the term acid precipitation, which is widely used, is to a certain extent quite misleading in describing this atmospheric event. It gives rise to a feeling that the environment may get some damage from the rain, only when its pH is lower than 5 and no detectable effects are observed in the absence of rain. This is definitely incorrect as in most areas there is in the atmosphere a measurable concentration of acid components which determine an atmospheric acidity. The lack of suitable analytical methods has prevented so far the measuring of this important parameter. It is difficult to say if the damage to the environment is due mainly to the adsorption of gaseous components from the atmosphere, to acid deposition or to acid rain, but definitively all causes contribute to a certain extent.

It must be added that rain acidity might have different sources; it might be due to the solution of acid components of the atmosphere as well as to the formation of the rain itself in the clouds; in some cases the pH of the rain remains constant and sometimes changes towards higher values.

I think that deterioration of the environment due to atmospheric acidity is a general phenomenon which appears to a larger extent in those areas where there is either a high and direct input of anthropogenic activities or a consistent transport over a long range.

CANUTO

Is there any sign of deterioration of monuments in Sicily? If it rains it is not very often, as you say. In Rome, where there are great monuments about 2000 years old — and others only 300 years old, which means they are made of different material — is there any example of deterioration of monuments that you have seen over the last 40 years — due to this dry deposition that you are talking about?

LIBERTI

When damages to forest and buildings in specific areas are observed, very likely a variety of factors occur simultaneously. As an example not all pine forests are decaying, but there are areas like in the coast of Tuscany in Italy and Southern France where damages are very considerable.

In my opinion atmospheric acidity always plays an important role, but additional factors should be mentioned. Tensioactive agents present in the sea are found in the aerosols and certainly their presence increases the wettability of the plants and their sensitivity to toxic agents.

MARINI-BETTOLO

Thank you, Professor Liberti. I think that an important point has been cleared. We should not generally speak about *acid rains* but better of *acid deposition*.

LIBERTI

I believe it is more correct to talk about *atmospheric acidity* to describe this effect on the environment.

## MARINI-BETTÒLO

I agree, and even the rain should be considered the scavenger of acidity as well as the snow. As the snow accumulates on the soil the effects of acid deposition appear when the snow melts.

## BROSSET

What happens in snow, in fact, if the snow is falling, is that there will be in snow the different salts, mainly ammonium sulphate salts — and where there are temperature changes, of course there will be in the system a freezing point depression, so finally during the season everything of these particles will be collected just over the soil, down there, and now when the melting period comes, you have the shock, and the shock, especially when the snow is lying on a frozen lake, can kill all the fish population in a few days.

## KNABE

I would like to comment on one item: the dying forest close to the seashore. According to what was here reported it may be due to a combination of sea aerosol and tensioactive agents now largely present in the environment.

They could remove the coat of waxes on the leaf surface, and so then the sea salt could penetrate into the cells and could kill the cells. I just wanted to know if this has been cleared in your country, or is it still in discussion? The other point: you mentioned quite rightly that  $\text{NH}_4^+$  is no really neutralizing agent. In the soil it will be transformed into  $\text{NO}_3^-$ , and nitric acid will contribute to acidity. The measurement of total acidity by just titrating the amount of acidity is a questionable thing. You have to determine the species of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the precipitation and add it to the acidity, so you have to do more than titrating... Well, I have a question: what happens on the surface of leaves or other material in dry deposition of acids? Maybe if you have a coat of  $\text{SO}_2$  which is then transformed into sulphuric acid, will this sulphuric acid be a permanent coat on the leaves and can nitric acid then be added to this?

I mean we have some examples which we really cannot interpret and it would be very interesting to know what happens on the surface of the leaves during long dry periods.

## LIBERTI

Thank you for your suggestion. The problem of the decay of forests close to the seashore takes place in several areas, and according to some scientists this event has been attributed to tensioactive agents. I strongly support that surfactant agents are not poisonous for the plants but contribute to dissolve the protecting oil layer of the leaves and leave the stomata opened for a fast adsorption of any toxic substance. I do not believe in a toxic action of sodium chloride, as all pines along the seashore have always been exposed to such substance and damages have been observed only in some cases.

What has been definitely established in these areas is the presence of small concentrations of strong acids such as nitric and hydrochloric acids. It is difficult to state, however, in the present state of scientific knowledge, if these species are directly responsible for the decay of the pines.

## BROSSET

You pointed out a very important thing; that is what happens really on the needles and the leaves when we have an acid deposition in the system. Probably when you have a fall through a needle tree, it will be much more acid than the rainfall itself. If you have a leaf tree, it is usually more alkaline. Does something happen? But exactly what happens I do not think we really understand.

## MARINI-BETTÒLO

Do you have any evidence of the influence of acid deposition on the mobilization of some of these ions in the soil? That is, after acid deposition is there an increase of these soluble ions in the soil or not? For instance the effect on selenium in the soil, mainly, in Norway.

## LAG

The first question: we do not know too much about that, but we have an increase of aluminium ion in fresh water which is harmful for a fish.

As for selenium it is very small quantities of this element that we get from the South Sea. I mentioned the differences from the coast to the inland, there we have comparatively more material.

# EFFECTS ON SOILS OF CHEMICAL EVENTS IN THE ATMOSPHERE

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## 1. INTRODUCTION

Once a basic understanding of plant nutrition was reached, there arose among the scientists an interest in the relationship between atmospherical chemistry and soil chemistry. At the very early stages attention was focused on nitrogen. This element had often proved to be a minimum factor — to use Liebig's term (Liebig, 1840).

It was soon shown that electrical discharge could result in binding atmospherical nitrogen to oxygen. This reaction principle was technically introduced in Norway at the beginning of this century in connection with the production of nitrate after Birkeland-Eyde's method (La Société Norvégienne . . . 1957). Before the problem of industrialized production of fixed nitrogen was solved, scientists were largely concerned with the amounts of this material added to the soil by precipitation. Comparatively comprehensive investigations were carried out at many places in the world (Eriksson, 1952). Even if the analysis methods were rather primitive, the results of the registrations were of great value. The results showed that the allowance of nitrogen from the atmosphere were small in comparison to the required amount in order to obtain large crops for most of the cultivated plants.

Likewise, contributions of other elements by precipitation were studied. Because the concentration of many elements was so sparse, it caused difficulties in analyses.

At an early stage it was proved that small particles derived from volcanic eruptions and from sand storms in deserts could be transported



a long way by global air currents. Such findings helped the understanding of important circulation processes in the atmosphere.

## 2. NUCLEAR EXPLOSIONS IN THE ATMOSPHERE

The nuclear bombs over Hiroshima and Nagasaki, and the later atmospherical detonations created a new type of soil problems. Radioactive elements in the air came with time into the soil, were later taken up by the plants and thus became dangerous in animal and human nutrition.

Throughout the world comprehensive investigations on quantities of radioactive fall-out took place. Because most of these registrations were carried out by military authorities only few of the results have been published. Investigations started to find out how to prevent or diminish the injurious effects. For example, other compounds were added to the soil to reduce the uptake of radioactive elements in plants. The results from this type of investigations were published to a greater extent.

After the decision that nuclear explosions in the atmosphere should come to an end, the interest for these problems ceased.

## 3. INVESTIGATIONS OF CHEMICAL PRECIPITATION - THE GEOPHYSICAL YEAR 1957-1958

Great improvements in analytical techniques during the last fifty years have made it possible to start the investigation of problems previously thought to be practically impossible. The new methods resulted in quicker and more reliable analyses of chemical composition. Some trace elements, which earlier could only be determined semi-quantitatively, were now presented by exact data.

In the 1940's Swedish scientists took up the question of the chemical composition of the precipitation. A number of stations were established in order to collect samples. In Scandinavia we have a close cooperation for many agricultural scientific tasks. As the precipitation amount varies much more in Norway than in Sweden the question of establishing such stations in Norway was raised. In autumn 1954 sample collection was started at three places in Norway.

The establishment of the geophysical year 1957-1958 gave the

impetus for a great intensification of these precipitation investigations. The number of Norwegian stations was increased from 3 to 12.

#### 4. INCREASING INTEREST IN ATMOSPHERICAL POLLUTION

As pollution with radioactive elements ceased, the allowances to the atmosphere from polluting material from industry and from common consumption in the urbane society increased. Many interesting discussions have taken place on whether the climate has been affected. The significance of changes of ozone, carbon dioxide, and dust has been researched.

Atmospherical pollution can have a direct influence on soil chemical conditions. Some gases formed by burning the fossil materials coal and oil, will go over to acids in the atmosphere. Acids from atmospherical pollution are added to the soil surface with precipitation. Recently extensive investigations related to damage caused by acid precipitation have taken place and in parts great injury has been observed. Other types of pollution as well as acids take place.

In many countries, both in Europe and America, data have been published from large projects. A number of textbooks have been written, and new journals have been established.

#### 5. SOME SOIL CHEMICAL INVESTIGATIONS IN NORWAY

##### a) *Geographical variations in the contents of elements in uncultivated soils*

The analyses of precipitation water from 12 different stations in Norway showed great geographical variations (Låg, 1963). For example, the quantities of Na and Cl added to the soil surface were respectively 111 and 191 times higher at Lista than at Vågåmo. We had expected great variations, but the differences were even higher. As the analytical material increased, so did the interest to reveal if the chemical differences could be traced back to the soil.

Almost at the same time as we planned the chemical investigation of precipitation, we started a simple systematical registration of the forest soils. It began with investigations in the field, but from 1960 to 1964 also sampling of humus from the three counties: Nord-Trøndelag,

Oppland, and Buskerud, for laboratory analyses was included. A comparison of the investigations of precipitation and humus gave very interesting results.

The analytical figures for the humus samples in Nord-Trøndelag showed that the exchangeable sodium and magnesium decreased strongly from the coast towards inland (Låg, 1962). The concentration of calcium had a corresponding increase. The analysis of the samples taken in Oppland and Buskerud confirmed these tendencies. A similar distribution as in sodium and magnesium was found for the three halogenes: chloride, bromine, and iodine (Låg and Steinnes, 1976). We were somewhat surprised to find a rather similar geographical distribution pattern for selenium as for the mentioned typical sea-salt elements (Låg and Steinnes, 1974, 1978). As far as I know, this is the first time such relationship between the amount of soil selenium, precipitation, and distance from the sea has been pointed out.

In earlier times the precipitation water was supposed to be almost as pure as distilled water. We are now aware that from the sea-waves drops come into the atmosphere and, in that way, sea-salts are included in the precipitation. The influence of the sea-water on the precipitation is greatest near the coast. It is supposed that some elements, to a certain extent, may evaporate directly from the sea-water and be transported by the air currents into the inland areas.

Attempts to find out how fast the content of sea-water salts decreases from the coast towards inland have been made. A distance corresponding to a 50% reduction is called "sea-salt decrease index". Preliminary figures for West-Norway show 50-100 km for some elements.

#### *b) Pollution from industry and ordinary public activities*

Many various types of industrial activities result in pollution of the atmosphere. The furnaces at the earlier mines were sources of pollution. Modern electrochemical industry brought other types of problems. Fluorine exhausted from aluminum factories has caused great damage in the vicinity. Some of these factories emit organic components that may be dangerous to health. Smoke from ferrosilicium, ferromanganese, and ferrochrome factories is really noticeable. Many factories which refine heavy metals spread polluting material.

More restrictive orders from the government with regard to combustion techniques have given improvements.

Cities and other densely populated regions have problems in getting rid of municipal waste. With the increase in oil prices a special interest for building incineration plants in order to exploit the waste material as a source of energy arose. But with present combustion techniques, great amounts of polluting material escape through the chimneys.

Common oil and coal combustions add pollution to the atmosphere. Sulphuric acid is a main factor in acid precipitation. Both industrial production and ordinary consumption are responsible for this type of pollution. In addition to sulphuric acid we also find some nitric acid in the precipitation. Both sulphur and nitrogen are vital plant nutrition elements. As a rule the plants will find sulphur enough in the soil but lack sufficient nitrogen sources. Many other elements are included in the incinerating gases.

In Norway comprehensive investigations of acid precipitation effects have taken place (Overrein, Scip and Tollan, 1980). Fish death caused by such influences in some districts in southern Norway has been proved. The soil material in this region is often shallow, coarse grained and derived from bedrock rich in silisium. The buffer capacity is therefore low and the acid effect of the precipitation will quickly be noticed. On the other hand, there has so far not been proved any decrease in the growth of the forest. In this connection we must remember that the acid precipitation also contributes with the nutrient element nitrogen.

We suppose that most of the sulphuric acid in the precipitation is transported with the global air streams. Approximately 10% come from inland sources. External air currents deliver many other elements. Micro-polluting organic material that may cause cancer has been determined in very small concentrations. Whether the amounts in which they appear in the precipitation in Norway have any influence is unknown.

Investigations of soil samples have showed that lead, cadmium, arsenic, and to a small degree selenium have been brought with external air streams (Låg and Steinnes, 1978; Steinnes, 1978).

From our own road traffic the soil is contaminated through the atmosphere. But the lead quantities are lesser here than in countries with a more comprehensive car traffic.

Locally some industrial factories are responsible for a strong soil pollution.

Possible influence of ozone on vegetation has been discussed in later years.

### c) *The uptake of elements in plants*

To a certain extent the plants may take up pollution elements directly from the air. The harmful fluorine components from the aluminum factories may to a great extent appear as a cover on the green plants. This type of consequence is only present as long as the pollution persists, contrary to effects from elements added to the soil.

Litter material from the vegetation returns to the soil and many compounds may again be taken up by the plants. In this way a circulation process continues between the soil and the vegetation. Whether the plants have been food for animals or humans before the remnants are integrated to the soil, making the circulation chain longer, has in principle no importance.

Many elements in the waste are essential in plant nutrition. Other elements are unnecessary for the plants but are needed for animals and humans. It is therefore favourable for these organisms that the elements are taken up by the vegetation when the plant material is meant for nutrition. Some elements are unnecessary both for plants and other organisms; but they are not harmful in adequate proportions. Other elements, again, are poisonous for plants and animals as well as for human beings. The plant species vary greatly with regard to the uptake of the various elements. If the soils are contaminated with poisonous elements which are easily taken up by the plants it may have a catastrophic result. With great concentrations the plants will die. If the quantities are not so high the plants may grow up, but may have such a concentration of toxic substances that it is dangerous to use the plant products in nutrition.

Until now the elements lead, cadmium, mercury, and arsenic have been mostly discussed as pollution elements. Of these the correlation between the content in soil and plant seems to be highest for cadmium.

With time we expect that other elements will be strongly involved when pollution is under consideration.

### d) *Geomedical consequences*

With the expression geomedicine we understand the science dealing with the influence of ordinary environmental factors on the geographical distribution of problems of human and animal health (Låg, 1980).

During the last half of the nineteenth century relationships between iodine deficiency and goitre were described (Underwood, 1977). A

relationship between phosphorus deficiency in the soil and osteomalacia in cattle was mentioned in Norway (Vogt, 1888). These are typical, old examples of deficiencies of geomедical character.

The discovery of relationships between atmospheric and soil chemistry opened new possibilities for explanations of geomедical causes. Earlier, cases of goitre were often ascribed to the fact that people used too little salt-water fish in their diet. Recent investigations have shown, however, that in inland districts with low precipitation, the soil as well as the vegetation has a low iodine content (Låg, 1972). Whether the differences in the bromine content, which also was found, has any influence, is unknown.

Magnesium is essential for both plants and animal organisms. Grass tetany has caused difficulties in animal husbandry and the reason seems in many cases to be magnesium deficiency. In an agricultural experiment station in Smøla, western Norway, nearly every plant nutrient has been proved missing except magnesium and chlorine. We suppose that the soil is amply supplied by these elements through precipitation.

In human medicine magnesium has with time received greater attention, i.e. in relation to cardiovascular diseases. For example, it is mentioned that the relationship between magnesium and calcium may have an interference. Differences in climate chemistry giving variation in magnesium concentrations may have medical consequences.

Selenium is an element which for some time has captured great medical interest (see e.g. Spallholz *et al.*, 1981). About fifty years ago it was pointed out that a dangerous disease in animals, discovered in the USA in the last century, was caused by selenium toxicity (Underwood, 1977). Lately investigations have been particularly concentrated on selenium deficiency.

When the soil selenium decrease from the coast to the inland was proved, it was easy to understand that muscle degeneration in domestic animals due to selenium deficiency (Mikkelsen and Hansen, 1967, 1968) was concentrated in the valleys with low precipitation in the eastern part of Norway. Our neighbour country Finland, with a mostly typical continental climate, has from an early stage taken up the problem by adding selenium to the cattle fodder. In Finland, and in other Scandinavian countries as well, there is now a discussion on the possibilities of adding a selenium compound to commercial fertilizers to increase the selenium content in the plants.

A number of medical doctors are working intensively on the problems

of cancer, multiple sclerosis, and cardiovascular diseases which may perhaps be traced to selenium deficiency. In China the so-called Keshan disease has received a lot of attention in recent years. Selenium compounds are used for preventing this endemic disease (Chen *et al.*, 1981).

In many parts of the world deficiency of selenium and deficiency of iodine are found in the same regions. Often the soils in such places are comparatively young. Quaternary glaciation is the reason for a short time for soil formation in large areas. In mountain areas with dissected landscapes erosion processes may lead to young soil profiles. Where soil formation has gone on for only a short period, the accumulation of selenium and iodine may be scarce. However, we should be aware that special concentration of selenium compounds in the bedrock may result in a high content in the soils in districts generally poor in the element.

Pollution elements in the atmosphere may result in changes in the soil with geomедical consequences. It has been reported that acid precipitation may be responsible for changes in soil and fresh-water causing such health problems as fish death.

Many other polluting compounds in addition to acids are transported long distances with the air currents. Analyses of soil samples from southern Norway have shown an increase in many undesired elements. Of course a very great accumulation of such material has not yet taken place.

From local sources poisonous elements have been spread through the atmosphere to the soil. Close to a zinc factory in Odda, western Norway, great concentrations of heavy metals in the soil and plants have been proved. The content of cadmium for example, is so high that warnings have been issued against substantial dependence upon food plants grown in the vicinity of the factory (Låg, 1975).

At Modum Blåfargeverk cobalt was produced from an ore with arsenic content. The factory was abandoned at the end of the last century. Soil and plant analysis showed a greater arsenic content than normal (Låg, 1978). Most probably the concentrations in the plants were much higher as long as the factory was driven. Comparison with preliminary figures given by FAO and WHO (1974) for acceptable limits for man show that it should not be dangerous now to use the plant products for nutrition.

Near abandoned furnaces an accumulation of copper has been found in the soil in Røros, mercury in Kongsberg, and nickel in Evje. In the

neighbourhood of a ferrochrome factory in Hardanger a great enrichment in the soil has been proved.

Incineration plants for municipal waste may lead to considerable soil pollution (Låg, 1982). Little has been done to evaluate such injury possibilities, but with the combustion technique and the gas discharges used nowadays, the natural content of some dangerous elements in the soil in the neighbourhood may be doubled during a relatively short period of time.

Because the injurious consequences of soil pollution may remain for an extremely long time, due to the circulation processes, special care should be taken into consideration in order to avoid unnecessary problems.



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## DISCUSSION

MARINI-BETTÒLO

Thank you, Professor Låg. I have another question. You have mentioned a very important factor, that influences very much also the effect of acid deposition. The poor buffering properties of your soil. Which are mainly, granitic.

LÅG

That is quite right, we have granite, gneiss and so on, compared with limestone and dolomite and such things; you have plenty of carbonates. We are in a worse situation in my country.

BROSSET

Thank you, Professor Marini-Bettòlo. I would just follow up your question about the mobilization of ions.

Now the problem is not only that there is acidification of soil, it is the acidification of ground water, and in the ground water there is a clear mobilization of aluminum ions, which is chemically quite normal. But what is a pity is that there are leakages, which means that we have dissolving and precipitating aluminum, and I am not an expert in that region but my colleagues who are studying just the forest damages tell me that there may be some deposition of aluminum hydroxide on the fine roots of the trees. There is another thing that I can tell you, that on the Swedish west coast, most of the beaches, when the households are using their own water, in copper tubes, they get their hair green now, because the acidity of water dissolves copper from the tube and young children have got stomach diseases. So that is similar to a catastrophe.

SALATI

I just want to add a comment on this new word that the scientists are introducing: *a geomedicine*. It will probably lead to a better knowledge of these diseases and of great ecological problems. In Brazil we have developed a research program in a central part of the Amazon, trying to understand a

little more about the immunology deficiency of the human being. And after several years of research it was found that there is zinc deficiency in the water and in the food in general. And this lack of zinc may raise a problem in the immunology of the internal human body.

LAG

That is very interesting to hear. I think that we have pointed to this type of problems, very complicated problems, so complicated that we must have specialists from different branches brought together in order to try to solve them. We must have medical doctors, we must have veterinarians, we must have physiologists, biologists and chemists etc. it is necessary to bring together persons with quite different backgrounds in order to go farther in what I think is a very important question. The Kashan disease in China was studied quite anxiously on now for a few years, and now seems to have got a practical solution. I do not think it is only selenium deficiency; maybe there are other factors too, but to help the population many are using selenium. Now we have some information, and it is very positive to read here how they have been able to help the population since they have results, where it may be possible to come to a positive conclusion.

BROSSET

Regarding this selenium I have heard different opinions. One is that it is acting as an antagonistic agent, immobilizing for instance mercury. It may immobilize also cadmium, because the selenites in question are quite insoluble. We know that in lakes where we have higher selenium content there is less mercury in the fish. This is of course not conclusive, but that may be an idea.

LAG

Yes, it is right that selenium has some antagonistic effects on other poisoning elements, and also I can mention interference with vitamin E, so that a combination of selenium and vitamin E can give quite a good result. The fact is that we know too little about it, but in other ways this is a question for further research.

## MARINI-BETTÒLO

I think that selenium has a very complicated task in biogeochemical work. In small quantities it is necessary to build up some enzymes, which are necessary to animal metabolism. When it is in higher quantities, it can cause big drawbacks in the animal feed, and so on. So we must look at that as a quantitative phenomenon and not only as the presence of selenium itself.

## HARE

I am sure Professor Låg knows this, but it is worth making the comment that of course the distribution of a very large number of diseases displays what is quite obviously non-random geographical distribution. There are concentrations of goiter obviously in iodine-deficient areas where the water supply is local. I can off-hand remember a dozen or more such diseases which display similar geographical inequalities, some of which are so far inexplicable, and in some jurisdictions there has been a similar geochemical mapping of those species that are known to be effective in a human physiological sense. British Columbia, for example, has been handled in this fashion in my own country.

There is a fascinating experimental possibility that has emerged there. There is one region of the province where there are two populations of human beings: those who derive their water from wells and those who derive their water from piped water supply which comes from a very long way off by pipeline. And one of my British Columbian friends is talking about taking these two populations and looking at the statistics of their health, of the incidence of deficiency disease in their health. I am sure that Norway and Sweden have done this kind of work. Is this the case? Have you parallel mapping of the geochemistry and the geomedicine?

## LAG

Yes, that was very interesting to hear. I can mention then that we had in our Academy a symposium and we issued a book: *Geomedical Aspects in Present and Future Research*. That was arranged in 1978, and now in March next year we shall have a new symposium on the possibility of connecting geomedical work to geochemical mapping in the far North, north of the Polar circle; that is a mapping going on in Finland, Sweden and Norway and there is also some small activity in Denmark. So in 1984 we shall have a new

arrangement dealing very likely with your type of work and we should like very much to have good connections with scientists in Canada and USA.

Let me also add that selenium is comparatively a dangerous element in that way, that it is poison, toxic, and there is not a great difference between the necessary and the toxic dose. That makes it quite difficult to deal with these problems i.e. to add selenium in concentrats for animals. So has been done in Finland and Norway for quite a long time. But you see in the inland part of Norway with continental climate, we have much less of selenium than in the coastal area, so we must be somewhat more careful about this business because we could run the risk of giving too much. And exactly now there is being discussed in some countries the possibility of adding selenium to artificial fertilizers. I think in a few months the question will be settled. Certainly they have technical equipment all arranged, so perhaps next summer such fertilizers with selenium will be used.

#### CRUTZEN

I asked the word when I had not heard about Finland yet. You mentioned Finland in the last minutes of your talk, but there is a very interesting region in eastern Finland where the average life span is remarkably low and heart disease plays a role, and I know that some years ago the World Health Organization, instituted a major study there; and I wonder what came out of that, or if this study is still ongoing.

#### ROWLAND

A comment on the question of selenium distribution versus sulphur distribution. Although they are in the same column in the periodic table, the chemistry of sulphur and selenium is probably quite different. In rain water I think specifically that the action of peroxide on  $\text{SO}_2$  is to oxidize it, but the action on selenium-4 is to reduce it. So that the probability of having sulphur and selenium behave the same in rain water, I think, is very low; but also when one thinks of the possible antagonism of selenium it's behaving as a reduced selenide rather than as being oxidized to selenate. I think the chemistry of selenium has to be considered quite separately from that of sulphur. Even selenium has been suggested as a possible tracer for sulphur in the eastern United States.

#### IV.

### EFFECTS ON LIFE OF CHEMICAL EVENTS IN THE ATMOSPHERE

# EFFECTS OF CHEMICAL AIR POLLUTION ON FORESTS AND OTHER VEGETATION

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## 1. INTRODUCTION OR WHAT IS AT STAKE?

What is at stake at present? Much more than we imagine. Chemical air pollution can no longer be ignored. Its detrimental effects on vegetation can be observed all over Europe and in large parts of North America (Plate 1-4). Sick trees may be found also around the industrial areas in Asia, Africa and Latin America, and until now nobody has really discovered the change in soil types and ground vegetation in the tropics.

So, what is at stake?

Autotrophic vegetation as a whole has rendered possible the development of animals on earth, of consumers and predators at the higher levels in the food chains of ecosystems. More than 100,000 species of animals, most of them insects, depend on the producers' life. Mankind cannot survive without green plants and their capability of building up carbohydrates from just water and carbon dioxide in the chloroplasts of leaves by the use of solar energy. Agriculture and horticulture have made use of this capacity since prehistoric ages and forestry has developed from the uncontrolled use of firewood and timber for houses, ships, tools, and furniture to a planned production of renewable raw materials.

Vegetation has covered the ground except where it was prevented by permanent frost or dryness. It has enabled and enforced soil formation and prevented or reduced soil erosion by running water or deflation by wind. From many points of view, forests are the most developed form of vegetation. Their dominant plants, the trees, extend their roots deeper into the ground than herbs, grasses or shrubs; they grow much

higher, thus creating especially in the tropics several storeys, one above the other which are the habitat of innumerable insects, birds, and other animals. They have the greatest capacity to produce their own climate, which is less windy and more balanced than that of open plains. Forests reduce the extremes in water flow, both dryness and floods.

They prevent avalanches in the mountains, and within generations people in Austria and Switzerland have protected their "Bannwald" against any destruction. Finally, forests and other vegetation are indispensable for our pleasure, for outdoor recreation, and for our health by filtering poisonous gases and cancerogenic dust from the atmosphere. Now, that is at stake by chemical air pollution. Why and how?

## 2. THE DOUBLE ATTACK OF AIR POLLUTION ON VEGETATION

Vegetation is affected by air pollution on at least two different pathways:

- Direct effects on overground plant parts
- Indirect effects on plants by soil changes and by impact on roots.

One might add a third way:

- Changed disposition of host plants to parasites and lowered resistance to abiotic stress — frost, heat, wind, e.g.

### 2.1. *Direct effects of air pollutants on overground plant parts*

Plant leaves are surrounded by their skin, which consists of epidermic cells, mostly without chloroplasts, and a thin cork layer, the cuticula, which protects them against water loss and contact with toxic dust and gases (Fig. 1). Only marginal amounts of air pollutants can penetrate an intact leaf surface; however, acid droplets, for instance, below pH 3.4 or certain heavy metals like cadmium can cause stipples after having overcome the barrier. Most gases find their way into the plant through small natural openings, the stomata which usually are located on the lower leaf surface. Stomata open in the morning and usually close at night thus controlling CO<sub>2</sub> uptake and the rate of photosynthesis as well as stomatal transpiration, that is, water loss. Toxic gases have a chance to enter the leaf via the same stomata which are opened for



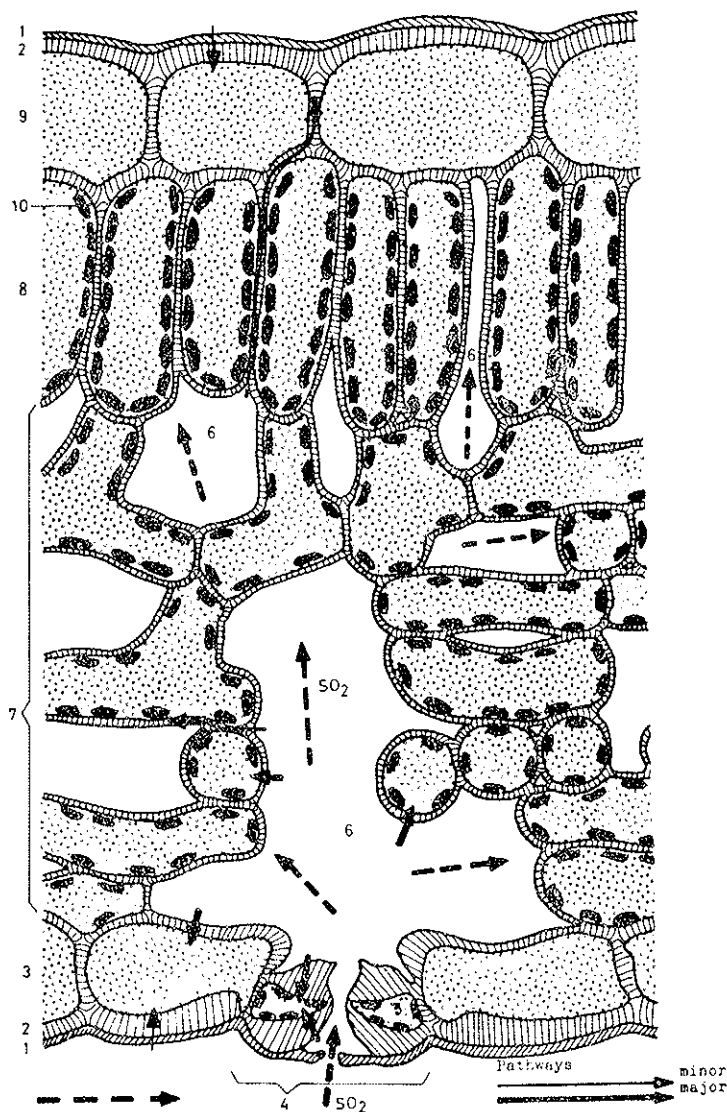


FIG. 1. Simplified scheme of uptake and distribution of  $\text{SO}_2$  in a green plant leaf. Broken arrow: Distribution of gaseous  $\text{SO}_2$ . Solid arrow: Diffusion of dissolved  $\text{H}^+$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{3-}$  (from Knabe, 1976. Design of cells redrawn from Nultsch, 1971).

- |                    |  |
|--------------------|--|
| 1) Cuticle         | 6) Intercellular space                         |
| 2) Cell wall       | 7) Spongy parenchyma                           |
| 3) Lower epidermis | 8) Palisade parenchyma                         |
| 4) Stomata         | 9) Upper epidermis                             |
| 5) Guard cell      | 10) Chloroplasts (other cell contents omitted) |

the necessary gas exchange. Water soluble gases like  $\text{SO}_2$  are then dissolved in the water-soaked cell walls and transported by the flowing water or just by diffusion to the cell interior, reaching the protoplasm and the green chloroplasts.  $\text{SO}_2$  and other pollutants interfere with plant metabolism in various aspects, the results perhaps being reversible depression of photosynthesis or irreversible necrosis of tissue. If larger parts of the plant are killed, the plant may die. Another possible effect is the contamination of fruits and fodder, which makes it hazardous for consumption by animals and men.

## *2.2. Indirect effects on plants by soil changes and by impact on roots*

Plants usually root in those soils which are appropriate to their demands with regard to soil reaction, nutrient, water, and air content. These conditions can be changed by air pollution. The soil may either become more acidic by deposition of acid gases, dust, and rain or be made more alkaline by basic dust around lime quarries or cement plants. It can also be contaminated by toxic substances, heavy metals, chlorinated hydrocarbons or radioactive particles. The change in soil conditions might reach an extent which will cause the dying of fine roots, leading to the degeneration of larger roots (Wieler, 1905, 1933; Ulrich *et al.*, 1979, 1983). Windfall of trees, withering of plants or changes in plant associations may be the result.

## *2.3. Changed disposition and resistance*

The ability of a plant to withstand the attack of parasites and plant diseases is strongly dependent on its vigour. Weakened trees are more successfully attacked by bark beetles and pathogenic fungi like *Armillaria mellea* (Schneider and Sierpinsky, 1968). Also trees that have been exposed to  $\text{SO}_2$  are less tolerant to frost or low temperatures (Materna, 1974).

# 3. DIFFERENT WAYS TO LOOK AT THE PROBLEM

There are various ways to look at the problem. Let us discuss three of them:

- (I) Cause-effect studies
- (II) Effect-cause studies
- (III) Ecosystem analyses.

### 3.1. Cause-effect studies

Cause-effect studies follow a line described in Table 1. They always start with a given toxicant and look for its effect on plants or biocoenoses.

#### 3.1.1. Fumigation experiments

The first simple approach used in the last century by Stöckhardt (1871), consisted in applying a certain amount of gas to a chamber in which plants were grown. Stöckhardt proved the phytotoxic quality of sulphur dioxide because the fumigated plants showed leaf necroses or died under excess  $\text{SO}_2$  concentrations. However, as great parts of the gas were absorbed by the chamber wall, the toxicity levels were very much underestimated by this method.

Correct fumigation experiments therefore require the continuous

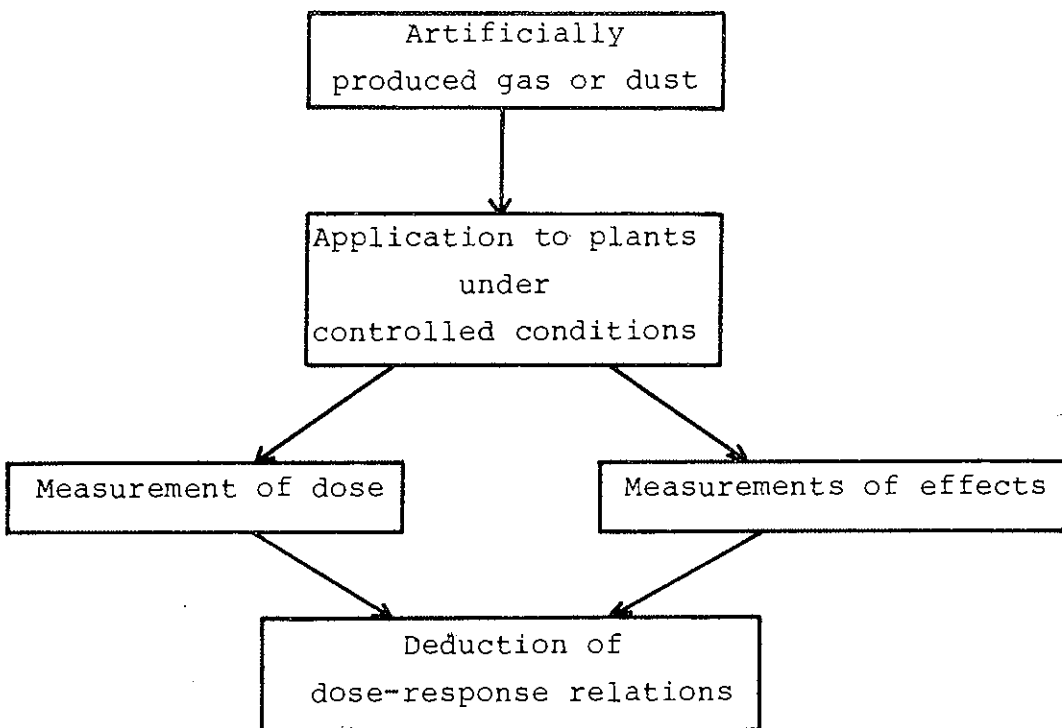


TABLE 1 - Cause-effect studies in the laboratory or greenhouse.

measurements of the toxicant within the chamber close to the plant and a steady flow of air and gas which have to be mixed properly.

Such studies were carried out by Thomas and Hill (1937).

However, critical concentrations were still underestimated because a greenhouse deprives plants of wind, dew, rain and natural climate. So open-top chambers, invented in the U.S. and used by Heagle *et al.* (1973), were a real improvement. They allowed a much more realistic view of the situation. Such laboratory experiments are the only way to get experimentally correct information on various questions such as, whether two components act additively, synergistically or antagonistically. Long-term effects and those which include the soil pathway are nevertheless hard to perform. Neither can large trees be investigated in such a way.

#### *Example 1 (unpublished data):*

Vegetative and generative progenies of two mother trees were fumigated in greenhouses with  $4 \mu\text{g} \cdot \text{m}^{-3}$  HF at three different times of the year in order to find out how much the seasonal variation of weather and plant development will affect the tolerance of Norway spruce. Another concentration of HF, either higher or lower, and a control without fumigation completed the experiment. One treatment at one period always contained 4 graftings and 8 seedlings of each mother tree. The fumigation method itself was developed by Guderian *et al.* (1969).

Parts of the results are shown in figure 2. The mean percentage of injured shoots per plant ( $\bar{y}$ ) is related to the time of exposure ( $x$ ). It is obvious that all progenies reacted much more sensitively in spring after flushing than in summer. Visible reaction in late fall was still less pronounced (not shown in figure 2). Typical symptoms of acute injury in early June can be seen in plate 5.

#### *Conclusion*

Air quality standards have to take into account the seasonal fluctuation of tolerance. The level below which no effect will be seen on Norway spruce under field conditions is, however, much lower than that found in this fumigation experiment. The observed differences between graftings and seedlings and between both progenies (see Fig. 2) require greater numbers of replication for verification and interpretation because environmental stress and genetic disposition have to be separated from each other.

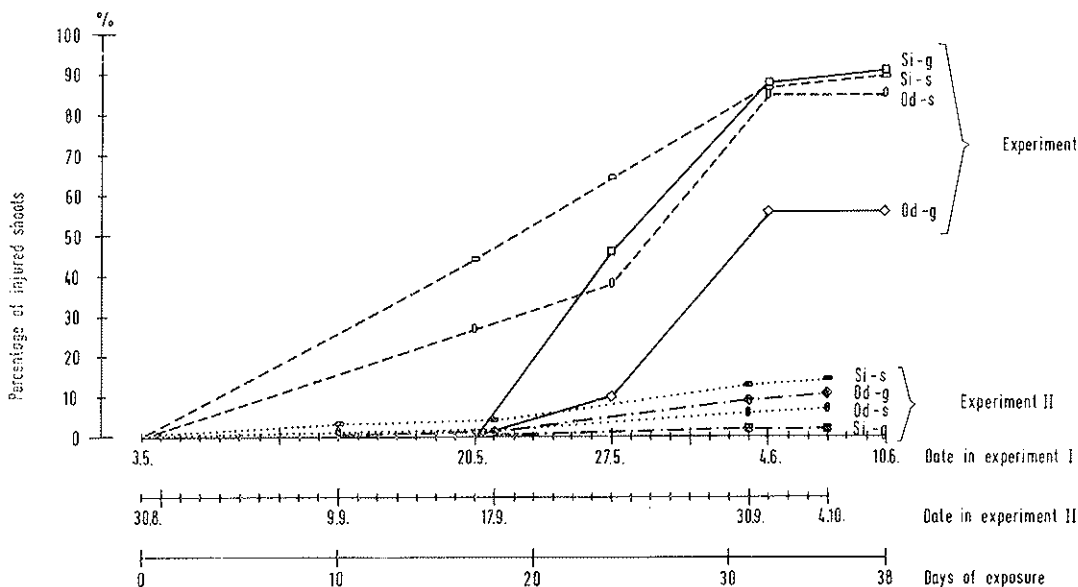


FIG. 2. Percentage of injured shoots of Norway spruce (*Picea abies* Karst) after fumigation with  $4 \mu\text{g HF} \cdot \text{m}^{-3}$  in May/June versus September. Means of 4 graftings and 8 seedlings, respectively. Fumigation from October to early December without hardly any difference to the control (not shown in figure 2).

Si-g: Graftings of clone Sieber  
 Si-s: Seedlings of mother tree Sieber  
 Od-g: Graftings of clone Oderhaus  
 Od-s: Seedlings of mother tree Oderhaus

### 3.1.2. Cause-effect studies in field experiments

Field experiments include all the variations of weather and ambient concentration of pollutants. Constant fumigation can be achieved neither by small artificial sources nor by exposing plant populations close to an industrial source. Hence the simultaneous measurements of air pollution and its effects on the exposed plants are a must.

#### *Example 2 (according to Guderian and Stratmann, 1968)*

The authors had exposed grains, vegetables, brushes, and tree seedlings in pots to the fumes of an iron smelter at Biersdorf, Germany, at increasing distance from the source which is shown in plate 1.

Station I was located close to the smelter,

Station VI, which served as a control, was situated in a neighbouring valley.

Plate 6 gives an impression of growing damage with decreasing distance from the source. The red currant bushes (*Ribes sanguineum*) at station III looked better than those at station II but they were still more affected than those at the control site VI. The authors carefully measured growth rates of all exposed plants and ambient  $\text{SO}_2$  concentrations.

### *Conclusion*

Buck (1970) concluded from the Biersdorf experiment that Norway spruce, Scotch pine, English oak, and European beech show growth depression at a mean concentration of  $0,08 \text{ mg SO}_2 \cdot \text{m}^{-3}$  if 2,5% of the measured values exceeds  $0,98 \text{ mg SO}_2 \cdot \text{m}^{-3}$  whereas no effect was found at a mean of  $0,07 \text{ mg SO}_2 \cdot \text{m}^{-3}$  and a 2,5 percentile of  $0,59 \text{ mg SO}_2 \cdot \text{m}^{-3}$ . The importance of the ratio of mean to peak concentrations in risk studies has been discussed by Buck (1970) and Knabe (1971).

The maximum immission values for  $\text{SO}_2$  as suggested by the German Association of Engineers (VDI) were strongly influenced by such experiments (Table 2). The even lower and stricter "air quality standards to protect forests" proposed by the International Union of Forest Research Organization (IUFRO) relate, on the contrary, to dose-response studies in injured forests, also including unfavourable site conditions (Table 3).

### *3.2. Effect-cause studies*

#### *3.2.1. General considerations*

Experts are asked to explain why certain plants are suffering or dying away and what toxic air pollutant or what source may be responsible for this. The general procedure of an expert can be taken from table 4. The expert should not restrict his job to just looking at the reported plant damage. Instead, he should include other plant species, the distribution of injured plants, and their relations to industrial or other sources. He should also collect plant samples to find out whether certain elements have accumulated in excess or are below the physiologically necessary minimum content which requires strict observation of certain prescrip-

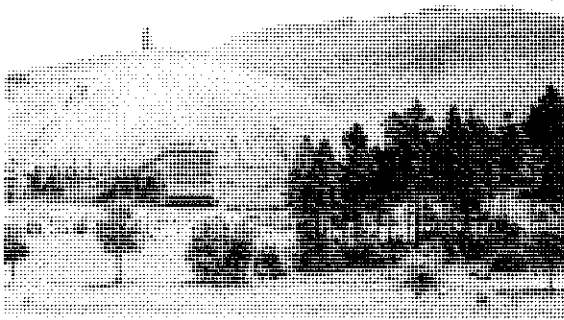


Plate 1. Denuded zone around a small iron smelter without cleaning of stack gases as a result of high ambient concentrations of  $\text{SO}_2$ . Heavy soil erosion after loss of protective vegetation could not be prevented by terraces. Typical for careless industry in the Fifties. Biersdorf, W. Germany, 1959 (Photograph by courtesy of H. van Haut).



Plate 2. Denuded hills around a copper smelter. Trees, shrubs and herbs were killed. Gully erosion can also be seen. Water courses may be blocked by eroded materials. Ogden, Utah U.S.A., 1969.

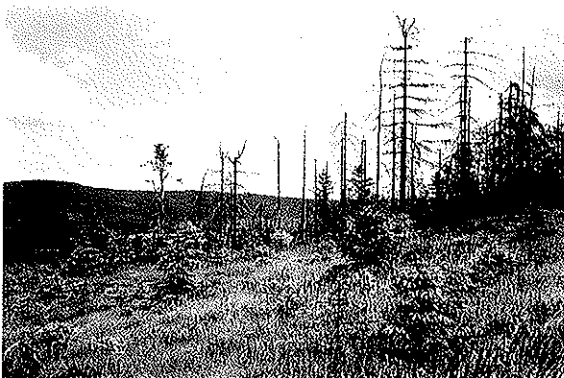


Plate 3. Forest destruction on the top of mountains in the Erzgebirge, Krusny hory, situated between the German Democratic Republic and Czechoslovakia caused by  $\text{SO}_2$ -emissions from lignite fired power plants 25 km away. Old trees, meanwhile cut, died first, medium aged trees followed. Young plants which should replace dead stand, have no future. North Bohemia, June 1970.



Plate 4. Large scale destruction of land in the Copper Valley, Tennessee. Attempts of revegetation after reduction of  $\text{SO}_2$  emissions showed little success because of soil degradation. New Coppertown, Tennessee, U.S.A., 1975.



Plate 5. Typical symptoms of injury caused by hydrogen fluoride during the most sensitive period of Norway spruce (*Picea abies* Karst). Single needles or parts of shoots appear burned. Duisburg, W. Germany, June 1976.

TABLE 2 - Proposed maximum concentrations of SO<sub>2</sub> (MIK-Werte) for the protection of plants in Germany. Values in mg SO<sub>2</sub> · m<sup>-3</sup> (according to VDI, 1976 \* and 1978 \*\*).

|   | Year | Mean concentration |                                |      |
|---|------|--------------------|--------------------------------|------|
|   |      | Growth<br>Season   | 30 min. not<br>exceeding . . . |      |
|   |      |                    | 2.5%<br>percent of time        | 5.0% |
|   | *    | **                 | **                             | *    |
| 1. MOST SENSITIVE PLANTS:   |      |                    |                                |      |
| <i>Species of the genera</i>  |      |                    |                                |      |
| Abies, Picea, Juglans, Ribes,<br>Trifolium, Medicago  | 0.06 | 0.05               | 0.25                           | 0.22 |
| 2. SENSITIVE PLANTS:  |      |                    |                                |      |
| <i>Species of the genera</i>  |      |                    |                                |      |
| Picea, Pinus, Larix, Tilia, Fagus,<br>Malus, Hordeum, Avena, Secale,<br>Triticum  | 0.09 | 0.08               | 0.40                           | 0.35 |
| 3. LESS SENSITIVE PLANTS:   |      |                    |                                |      |
| <i>Species of the genera</i>  |      |                    |                                |      |
| Acer, Alnus, Populus, Quercus,<br>Prunus, Rosa, Solanum, Zea,<br>Vitis, Beta, Brassica, and species<br>of the family of the Liliaceae | 0.13 | 0.12               | 0.60                           | 0.53 |

tions (Knabe, 1982). The expert also needs the knowledge or assistance of entomologists and phytopathologists to clearly distinguish between the effects of insects, diseases, and abiotic factors, including pollutants.

Several pictorial presentations may be of great value to the identification of the classic air pollutant symptoms, but they do not help very much to find the causes of the so-called "new" types of injury to trees. The following publications can be recommended: Lacasse and Moroz (1969), van Haut and Stratmann (1970), Jacobson and Hill (1970), Malhorta and Blauel (1980), and Farbbildheft der Allgemeinen Forstzeitschrift zum Erkennen von Immissionsschäden an Waldbäumen (1983).

### 3.2.2. Practical procedure for an expertise

At first, the expert has to check the order for the expertise and to



TABLE 3 - International Union of Forestry Research Organizations, Subject Group Air Pollution: Maximal concentrations of air pollutants for the protection of forests (in  $\mu\text{g}/\text{m}^3$  air).

| Kind of Protection   | Component                    | Annual mean                 | Mean of 24 hours                                | 97.5 percentile of the 30' values |
|--|------------------------------|-----------------------------|---|-----------------------------------|
| 1. For the protection of full productivity on most sites   | $\text{SO}_2$<br>$\text{HF}$ | 50<br>0,3                   | not more than 12 times per year exceeded<br>100 | 150<br>0,9                        |
| 2. Also for the maintenance of protective and social functions of forests on critical or extreme sites | $\text{SO}_2$<br>$\text{HF}$ | 25<br>still to be clarified | 50  | 75                                |

Ljubljana, September 27<sup>th</sup> 1978 (IUFRO 1979).

clarify his own expert status. Then the work begins, always remembering the general considerations listed above by first looking at all parts of the affected plants.

### *Crown and leaves*

Are there any changes in colour of leaves or needles? Can there be seen signs of necrosis? If so, are they irregularly distributed, which often is considered as typical for ozone injury, for example, in tobacco or pinto beans (Plate 7 and 8)? Or are they concentrated on leaf margins and tips, which often is observed after the slow accumulation of chloride (Halbwachs, 1963) or fluoride (Guderian *et al.*, 1969)? Plate 9 shows typical marginal necrosis of an elm leaf, plate 10 tip necrosis of tulip leaves, whereas the flowers themselves are not injured. Acute injury by  $\text{SO}_2$  often appears as interveinal chlorosis followed by necrosis which can be seen at an elm leaf in plate 11. On the contrary, ozone injury mostly consists of small chlorotic or necrotic spots. Pine needles (plate 12) and

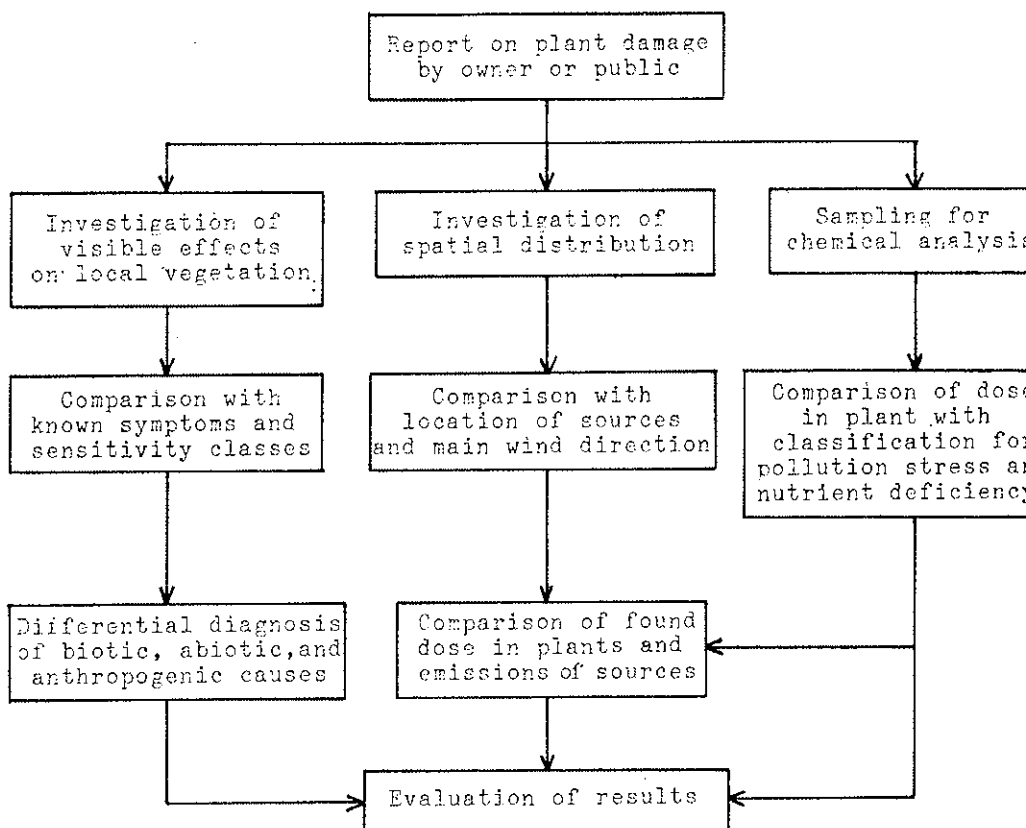


TABLE 4 - Effect-cause study. Search for causes or sources of observed plant damage.

tobacco leaves (plate 7) may serve as an example for this mottling syndrome. Bleaching of upper needles which are exposed to sunshine and dew (plate 15) may be the result of photochemical reactions within the plant cells.

#### *Premature senescence and abscission*

Are the leaf retention and colour as usually developed in other years or do the crowns appear unnaturally thin? A special sign of pollutant impact on leaves is premature senescence due either to the induction of ethylene biosynthesis by stress (Ziegler and Berndt, 1983) or just to



Plate 6. Effects of  $\text{SO}_2$  on red current brushes (*Ribes rubrum* L.) in the second year of exposure to fumes of an iron smelter. Sparse foliage, small leaf size, premature leaf abscission, and little or no fruit could be seen at a distance of 600 m from the source (left). The damaging effects were less expressed at a distance of 750 m. Healthy looking brushes could be observed at the control site situated 6000 m from the source. Biersdorf, W. Germany, 1960 (right). Photograph by courtesy of H. van Haut.



Plate 7. Sensitive tobacco plants (*Nicotina tabacum* L., strain Bel W 3) with necrotic spots on leaves caused by ambient ozone, light brown spots having been induced by ozone injury 24 to 48 hrs ago. After longer time of exposure, dead tissue will be bleached. Phytotoxic concentrations of ozone in W. Germany have been demonstrated for the first time by the use of tobacco as indicator plant (Knabe et al., 1973). Kettwig, W. Germany, 1967.



Plate 8. Necrotic leaf tissue of young bean plants (*Phaseolus vulgaris* L.) reveals the impact of oxidants, mainly of ozone. This plants is used as bioindicator in the U. S. to control oxidant air pollution. Cincinnati, Ohio, U.S.A., 1967.

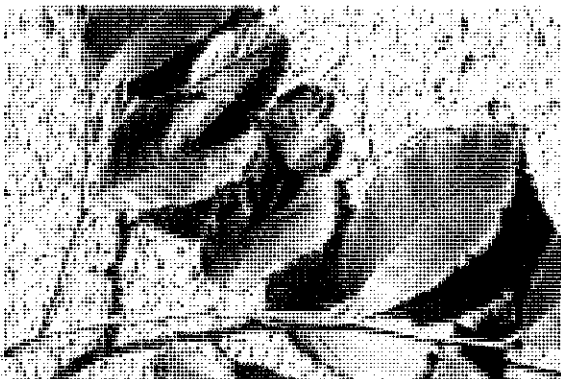


Plate 9. Marginal yellow leaf chlorosis and brown necrosis as a result of the accumulation of fluoride in leaf margins of elm

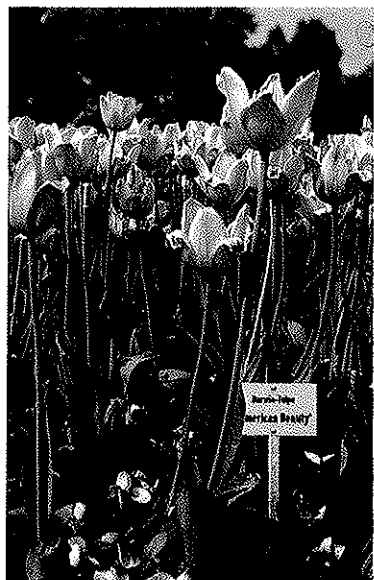


Plate 10. Spoiled «American Beauty». Leaf tips of this beautiful tulip strain (*Tulipa gesneriana* L.) burnt by accumulation of air born fluoride. Cologne, W. Germany, April 20, 1971.

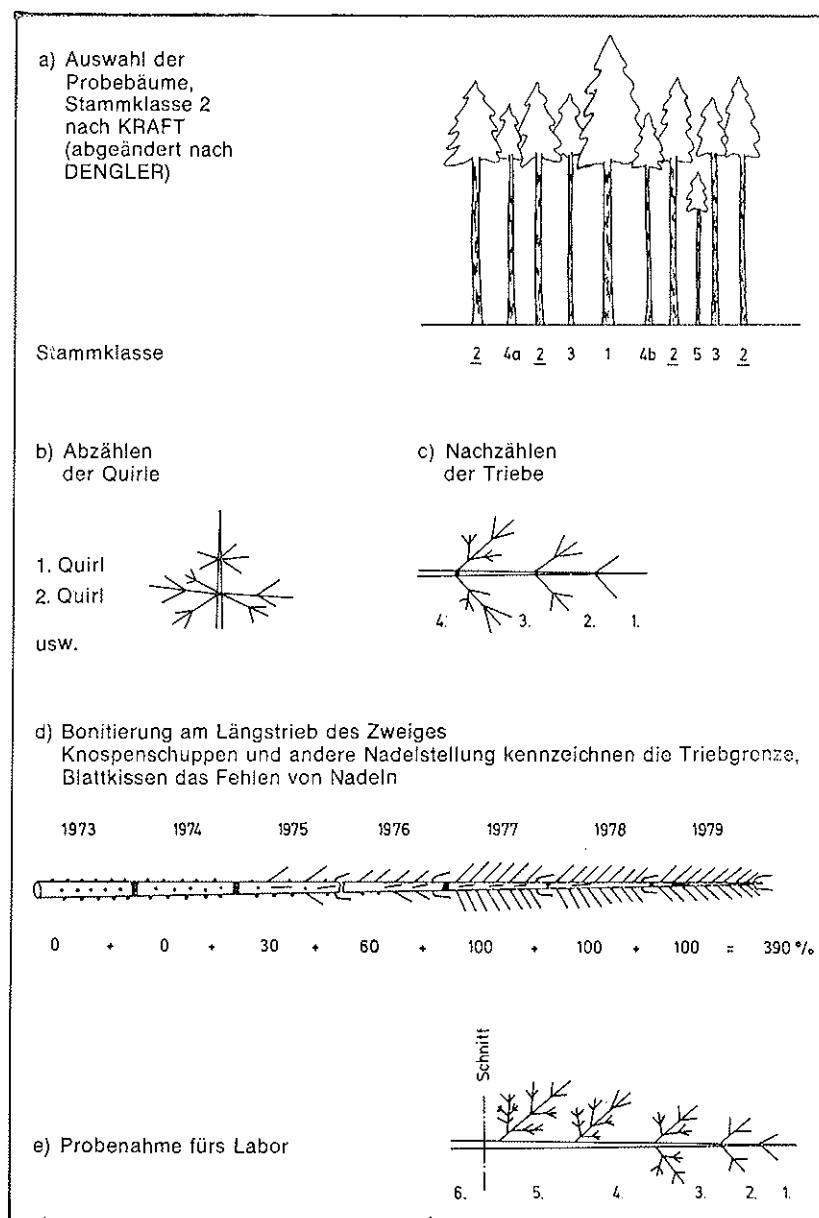


FIG. 3. Survey in spruce forest. a) Selection of sample trees class 2 (dominant); b) Counting of whorls from top to seventh whorl; c) Re-counting of annual shoots from top to seventh shoot; d) Assessment of needle retention at main lateral shoot; e) Sampling for later chemical analysis.

the accumulation of pollutants. The physiological aberration results in leaf drop in August or in the reduction of living needle years from 6 or 7 (plate 13) to 4, 3 or even less (plate 14). A strong correlation of needle loss with the accumulation of F, Cl and S in needles of Norway spruce was demonstrated by Knabe (1983). The correlation coefficient ( $r$ ) ranged from 0.7 to 0.8.

### *Twigs and stem bark*

Are twigs and the bark all right? For example, are there dead secondary branches on living main branches? A unique symptom is green leaves or needles and branches of Norway spruce lying on the ground apparently fallen down from their original position (plate 16). The cause is not known. Bark wounds without any mechanical impact are also to be looked for. Their position on the lower side of horizontal branches hints at poisonous droplets hanging there after light rainfall (plate 17). Necrotic bark spots along the stem can also be observed. They may be dry (plate 18), resinified (plate 17) or wet with stem sap oak. At present, it cannot be decided whether the fungus *Pezicula cinnamomea* acts as primary pathogen in the bark disease of red oak (Butin, 1983) or occasionally invades the plant as secondary pest after the impact of acid stem flow or acidification of the soil.

### *Roots*

Are the roots healthy and well distributed?

The distribution of fine roots in the various soil horizons can be used as a good indicator of root health. Root development is considered as very poor in soil layers containing 1 to 2 fine roots per  $\text{dm}^2$ . 5 to 10 fine roots per  $\text{dm}^2$  or 10 to 20 fine roots per  $\text{dm}^2$  are regarded as a mean or strong root development respectively. Dying root tips, for example at the border between humus layer and mineral soil hint at toxic soil conditions in the lower horizon (see Fig. 4).

### *Soil*

And what could have happened to the soil?

Ulrich *et al.*, (1984 a) have given a series of criteria for interpreting the results of soil analyses.

Soil investigations start with digging a hole with three clean sides

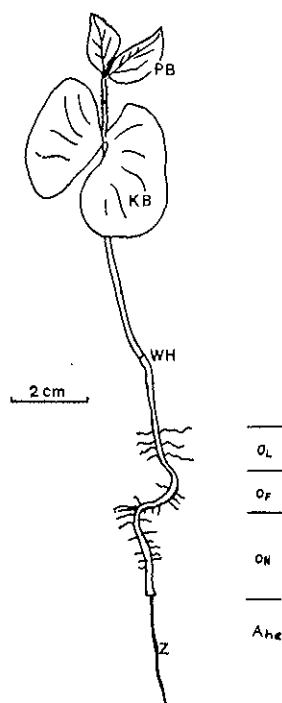


FIG. 4. Distribution of fine roots of European beech seedlings in various soil horizons (according to Becker 1982).

- $O_L$  — Litter layer
- $O_F$  — Fermentation layer
- $O_N$  — Humus layer
- $A_{he}$  — Humus containing mineral layer (eluvial horizon)

and with then describing the humus conditions and soil horizons. In the mountains of Northrhine-Westphalia, the beginning of podsolization with high contents of free or exchangeable iron and aluminium can often be observed.  $Fe^{3+}$  can easily be determined by the use of a 10% solution of KSCN by forming the red complex of  $Fe(SCN)_3$  which is then made more visible in butanole (Knabe and Bartels, in prep.).

### Example 3 (unpublished data)

A plantation of sycamore (*Acer pseudoplatanus*) on sandy soil to the north of Recklinghausen in the Ruhr district showed extended marginal

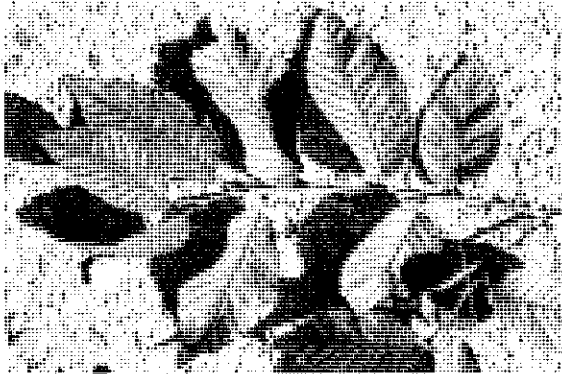


Plate 11. Intervetinal chlorosis of elm (*Ulmus pumila* L.) which is regarded as typical symptom of acute impact of  $\text{SO}_2$ . Compare difference to plate 9. Ogden, Utah, U.S.A., 1969.

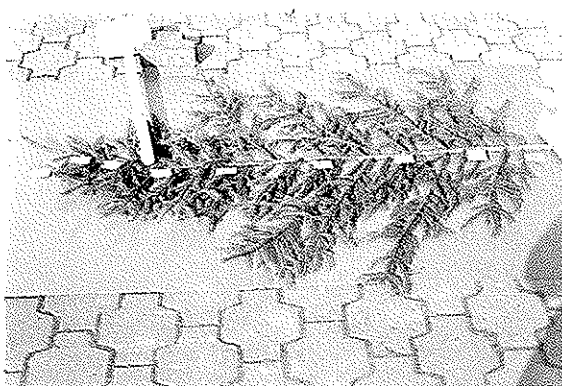


Plate 13. Six to seven living needle years on branch of Norway spruce (*Picea abies* Karst) are only to be found in areas with clean air. This example of low land spruce in Lower Saxony, W. Germany, even shows some needles from 1964. Cloppenburg, W. Germany, March 1973.



Plate 14. Only one living needle year on twig of young Norway spruce (*Picea abies* Karst) reveals high chronic air pollution on top of mountains in North Bohemia. The photograph was taken close to plant shown on plate 3. This tree cannot survive because young shoots are missing supply from older needles. North Bohemia, June 1970.



Plate 12. Mottling of one year old needles of Eastern white pine (*Pinus strobus* L.). Place unknown. Photograph courtesy of Arthur Costonis, July 8, 1966.

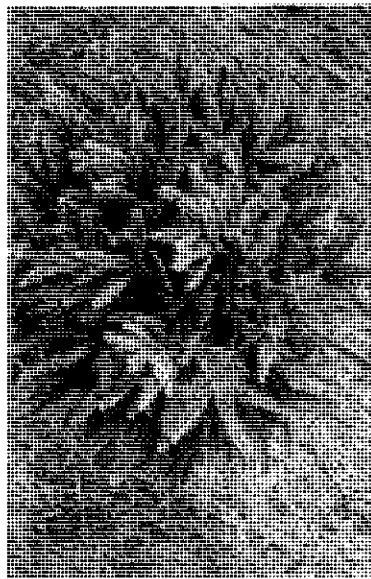


Plate 15. Chlorotic plants of Norway spruce (*Picea abies* Karst) in polluted area. Lower branches are still green. Cause may be due to photochemical reactions within the needles or on the needle surface. Kliny, North Bohemia, April 1983.

leaf necroses (see plate 19). The symptoms on leaves were similar to those observed after fluoride fumigation. However, analyses of leaves did not show an increase in fluoride, chloride or sulphur when healthy looking plant leaves were compared with sick ones (table 5). The sick looking plant leaves contained even less F as well as Ca and Mg so that nutrient deficiency seemed possible. Slightly higher contents of Cu and Si as well as a 2.5% higher content of Mn were determined. Excavated plants showed the almost complete absence of fine roots in the upper soil horizon below the humus layer. No roots had found their way from the planting hole to the neighbouring soil stratum (plate 20).

When tested with KSCN as described above, the rootless horizons showed high concentrations of free  $\text{Fe}^{3+}$  despite the poor sandy soil. (Table 6).

TABLE 5 - Element content in leaves of sycamore (*Acer pseudoplatanus* L.). Arithmetic mean and standard deviation of 8 sick and 8 healthy looking plants. All values in  $\mu\text{g} \cdot \text{g}^{-1}$  dry material (= ppm).

| Component  | sick     |            | healthy  |            | t-value<br>( $n_1=n_2=8$ ) |
|--|----------|------------|----------|------------|----------------------------|
|  | mean     | stand dev. | mean     | stand dev. |                            |
| a) No significant difference between sick and healthy leaves |          |            |          |            |                            |
| Pb   | 6.88     | 2.47       | 5.88     | 1.55       | 0.97                       |
| Zn   | 79.25    | 19.26      | 91.63    | 42.84      | 0.75                       |
| K  | 11400.00 | 2038.91    | 10887.50 | 1399.42    | 0.59                       |
| Cl   | 2312.50  | 830.55     | 2550.00  | 845.15     | 0.57                       |
| S  | 3812.50  | 622.06     | 3462.50  | 821.04     | 0.96                       |
| P  | 1312.50  | 180.77     | 1237.50  | 184.68     | 0.82                       |
| b) Contents in sick leaves lower than in healthy ones        |          |            |          |            |                            |
| Ca   | 3950.00  | 772.75     | 8537.50  | 1572.02    | 7.41**                     |
| Mg   | 887.50   | 195.94     | 2457.00  | 328.42     | 11.74**                    |
| F  | 19.22    | 5.46       | 40.57    | 10.28      | 5.19**                     |
| c) Contents in sick leaves higher than in healthy ones       |          |            |          |            |                            |
| Cu   | 9.75     | 1.39       | 6.00     | 1.51       | 5.18**                     |
| Mn   | 1345.00  | 297.75     | 512.50   | 164.56     | 6.92**                     |
| Si   | 14412.50 | 2687.23    | 10375.00 | 2489.42    | 3.12***                    |

\*\* significant at the 1% level,

\*\*\* significant at the 0.1% level.



TABLE 6 - Soil profile beside a sycamore tree (*Acer pseudoplatanus* L.) in the Haard forest, north of Recklinghausen, Germany.

| Depth<br>[cm] | Horizon        | Test on<br>FeIII | Remarks  |
|---------------|----------------|------------------|--|
| + 3 to 0      | H              | 3                | Humus layer at the stem foot of <i>Pteridium aquilinum</i> |
| - 1 to - 5    | A <sub>e</sub> | 2                | Lower stolon region of <i>Pteridium aquilinum</i>          |
| - 11 to - 16  | A <sub>e</sub> | 4                | Almost rootless  |
| - 16 to - 20  | B              | 5                | Rootless or dead roots                                     |
| - 22 to - 25  | B              | 5                | Rootless, only very few sycamore roots                     |
| - 35 to - 40  | C              | 1                | Nearly rootless, yellow sand                               |
| - 60          | C              | 1                | Living roots, light yellow sand                            |
| - 90          | C              | 1                | Light yellow sand  |

Evidence for the toxic acidification of soil by the use of the test on soluble iron (according to Knabe and Bartels, in prep.).

Range 1: no FeIII detectable, range 5: 100 µg FeIII/0.2 g soil, approx.

Mineral soil: Rootless within 0-15 cm, approx.

Border line between humus layer and mineral soil = 0 cm.

### Conclusion

The withering of sycamore plants on sandy soil seems to be more likely the result of soil acidification and nutrient deficiency than that of direct impact of air pollutants. Final confirmation of this hypothesis will only be provided by more detailed soil and root investigations as well as by fertilizing experiments.

### 3.3. Ecosystem analysis

Ecosystem analysis has become a major scientific approach which was very much enforced by the International Biological Program (IBP) the aim of which being the evaluation of biomass production in different climates and vegetation types and the quantitative determination of the flow of energy, water, and chemical components in order to lead to a better understanding of food chains, natural successions, and interactions of biota with abiotic environment.

Originally, air pollution was not part of the concept. The request for also doing immission measurements in those places where intensive

biological research is carried out — as had been suggested by Knabe (1971), at the IUFRO Congress in Gainesville, Florida — was not realized by the research groups at that time. But as soon as experimental results of deposition measurements revealed an astonishing and unexpected input of air pollutants into forest ecosystems, the interest grew rapidly. Now every book on air pollution contains chapters dealing with the ecosystem approach (Craig *et al.*, 1980; Smith, 1981; Moriarty, 1983 and Treshow, 1984) and handbooks of ecology can no longer neglect the problems of air pollution. Ulrich in Germany as well as Likens and Borman in the United States belong to the group of those scientists who promoted very much such studies of environmental interactions.

*Example 4 (adapted from Ulrich et al., 1984 and VDI, 1983)*

Ulrich and co-workers determined the precipitation ( $r$ ) and element input ( $e$ ) above a meadow ( $F_{1r}$  and  $F_{1e}$ ) and below a tree stand ( $F_{2r}$  and  $F_{2e}$ ) of both Norway spruce and European beech, as well as the element output by drainage and percolation below the root horizon ( $F_{3r}$  and  $F_{3e}$ ) in the Solling mountains, Germany (Fig. 5a). With the exception of heavy fog days,  $F_{1r}$  is always greater than  $F_{2r}$  because some water does not reach the ground. The difference in rainfall ( $F_{1r} - F_{2r}$ ) has been called "interception" which is the sum of evaporation and transpiration.

$F_{1e}$  is mostly smaller than  $F_{2e}$  because dust, certain gases, and dissolved elements of fog droplets are filtered out from the atmosphere by the forest canopy. The difference in element flow ( $F_{2e} - F_{1e}$ ) can therefore be regarded as a first but rough quantitative assessment of the atmospheric input to the canopy ( $F_{7e}$ ) (Knabe, 1977). The difference  $F_{2r} - F_{3r}$  gives the total water consumption of the forest stand, the difference  $F_{2e} - F_{3e}$  the amount of element accumulation in the soil or element loss, if negative, within a given period.

It appears as  $F_{10e}$  in Fig. 5b.

A more detailed model is shown in this Fig. 5b. The throughfall  $F_2$  of Fig. 5a is replaced by the partial fluxes stem flow ( $F_{11}$ ) and canopy drip ( $F_{12}$ ). There are also included additional fluxes as litter fall  $F_{4e}$ , dry deposition to soil  $F_{5e}$  and internal fluxes of the system as uptake by roots and flow to the crown  $F_{6e}$ , leaching of leaves  $F_{8e}$  and flow from roots to soil  $F_{9e}$ .

In this respect, the VDI (1983) gives quite an understandable calculation (pp. 179-185).

According to the results of Ulrich, there is to be considered an input

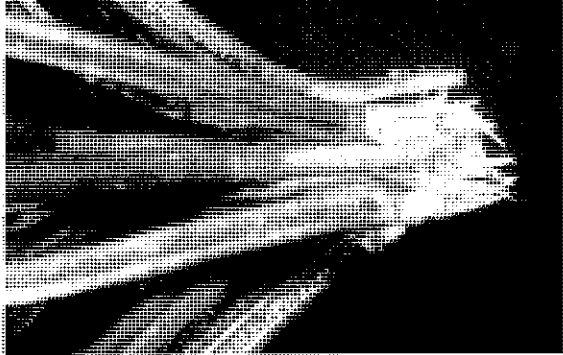


Plate 16. End of shoot of Norway spruce (*Picea abies* Karst) found on the forest floor. Shoot was torn off probably after its consistence had been weakened by environmental stress or lack of nutrients. Witten, W. Germany, March 1983. Photograph courtesy of Ms. Ebel.



Plate 17. Bark wounds from Norway spruce (*Picea abies* Karst) partly covered by raisin on lower side of branch photograph taken from below and on upper stem, here in original position. Hardeggen, Solling, W. Germany, 1982.



Plate 18. Bark disease of Northern red oak (*Quercus rubra*) in area with high air pollution. This disease is not found in areas with clean air and good soil conditions. The fungus *Pezicula cinnamomea* may be involved. Haard Forest, North to Recklinghausen, W. Germany, 1977.



Plate 20. Soil profile with roots of injured sycamore maple tree (*Acer pseudoplatanus* L.) from plate 19. Roots could not leave the plant hole but only rooted into deeper soil parts which are not as acidified as the upper soil horizons. Haard Forest, North to Recklinghausen, W. Germany, 1982.



Plate 19. Heavy injury on leaves of sycamore (*Acer pseudoplatanus* L.) maple showing marginal necroses which are not due to fluoride pollution because of low fluoride contents in leaves. Lack of magnesium as a result of soil acidification by acid rain may be the reason. Haard Forest, North to Recklinghausen, W. Germany, 1982.

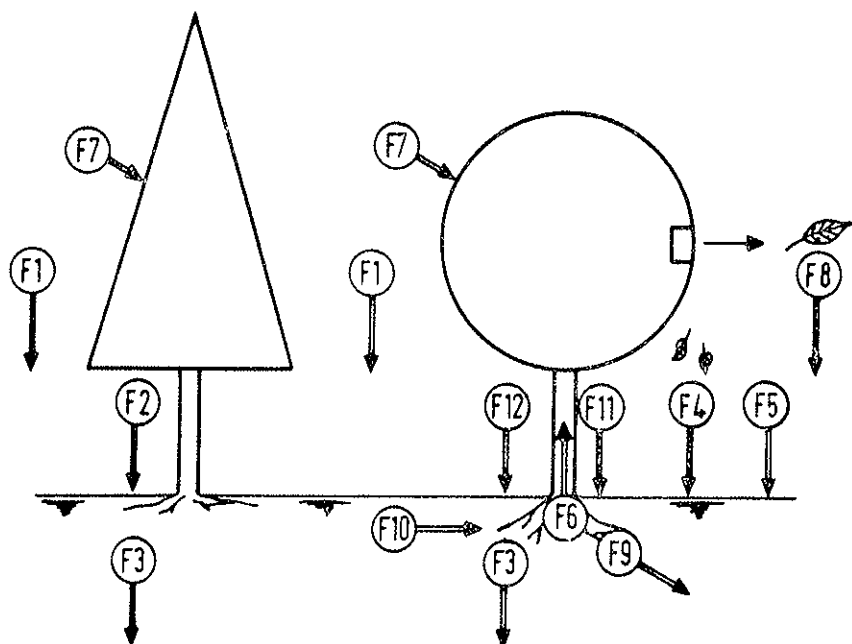


FIG. 5. Element fluxes in a forest ecosystem (Changed from VDI 1983).

Fig. 5a. "Black box"-model of main fluxes.

Fig. 5a. "Black box"-model of main fluxes.

F 2 Throughfall below forest stand

F 3 Percolation to ground water

F 7 Interception deposition to canopy

Fig. 5b. More detailed model of fluxes.

F 1, F 3, F 7 see Fig. 5a.

F 2 replaced by F 11 and F 12

F 4 litter fall

F 5 dry deposition to soil

F 6 uptake by roots and flow to crowns

F 8 leaching of leaves

F 9 flow from roots to soil

F 10 flow into soil storage

F 11 stem flow

F 12 canopy drip

of acids into the Solling from 1966 to 1973 as follows (values given in  $\text{kmol H}^+ \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ ):

wet deposition = 0.80

interception beech = 0.84

interception spruce = 2.61

production in soil = 2.50

Thus, deposition of air pollutants may be the minor or major source

of man-made soil acidification.  $1 \text{ kmol H}^+ \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$  is equivalent to the annual lime requirements of  $100 \text{ kg CaCO}_3$  per ha.

Because natural weathering of minerals in the upper soil horizons is not sufficient to neutralize that amount of acid, a gradual acidification takes place so that even calcareous soils can be affected, especially at the stem base of beech and red oak, both possessing high stem flow rates. In silicate soils, clay minerals can be destroyed, releasing  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , by replacing  $\text{mol Ca}^{2+}$

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the exchange sites of minerals. If the ratio  $\frac{\text{mol Al}^{3+}}{\text{mol Ca}^{2+}}$  is lower than 0.1 in an extract of  $2 \text{ ml H}_2\text{O} \cdot \text{g}^{-1}$  soil, aluminium is regarded as being toxic for the roots of trees and other soil plants (Ulrich *et al.*, 1984). Roots of Norway spruce may already suffer at values below 0.1. Besides that, the authors still recommend other criteria.

### Conclusion

Acid rain, or in more scientific terms, acidic deposition, has to be regarded as a real menace to wide areas in the Northern Hemisphere. There are plenty of sites, for instance in Northrhine-Westphalia, where roots remain in the humus layer and do not grow into the upper mineral soil horizon. The acids remove cations which are indispensable for plant nutrition and dissolve aluminium and heavy metals, both of geogenic and atmospheric, that is, anthropogenic origin. This results not only in root damage as mentioned above, but also in disturbed mycorrhiza and a reduced number of soil animals, as shown in fig. 6. The depletion of nutrients by leaching and the reduced circulation within the ecosystem is affecting the nutrition, resistance and growth of plants. The loss of sensitive plants and soil animals will further reduce the richness in species of a forest or lead to a final tree die-back, eventually to non forest successions which cannot fulfill all welfare functions of woods. A simplified model of these indirect effects of acid deposition is shown in fig. 6.

### 3.4. Climatic risk factors

Climatic observations can help to understand plant damage caused by air pollution better than just being focused to its concentration, because combined effects may play an important role. Climatic maps have to be read therefore from another point of view than before. Three examples are mentioned.

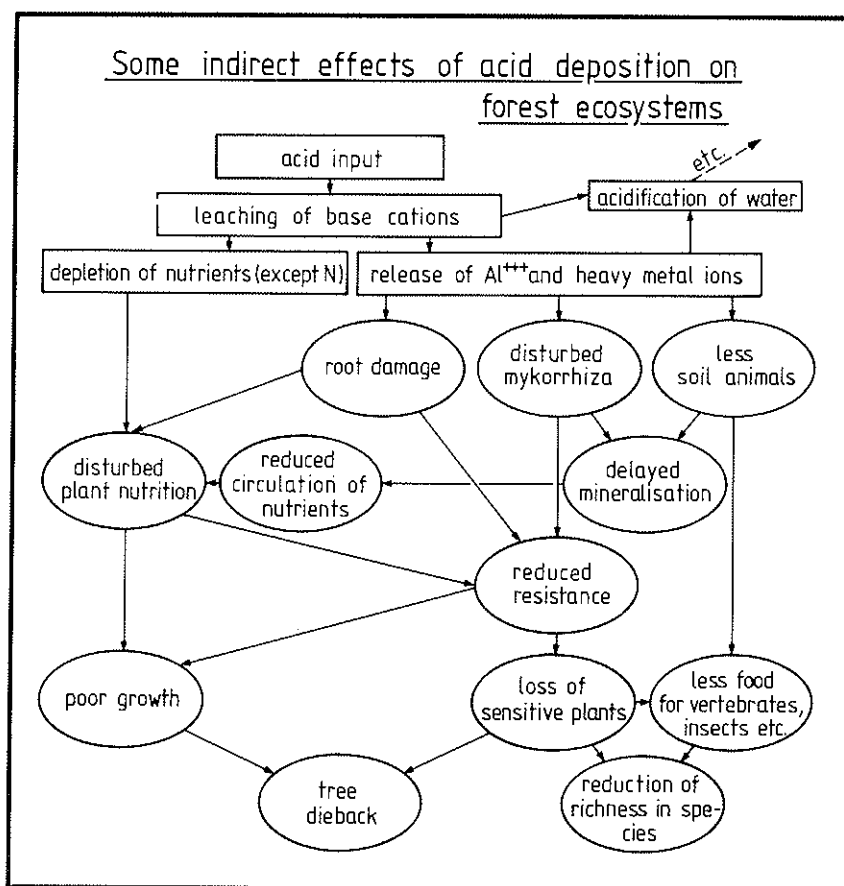


FIG. 6. Results of acid deposition and soil acidification.

*Example 1: Height of precipitation*

The amount of acidic deposition depends very much on the amount of precipitation. Hence, the risk from acidic deposition is usually increasing with rainfall.

This development is changing the importance of rainfall to forests from a very positive factor to an eventually negative factor for plant growth.

Fig. 7 shows a map of Northrhine-Westphalia describing this risk under the supposition of equal concentration and soil susceptibility. This map will have to be modified by completing it with concentration values and the results of soil investigations. The present "pilot project" of the State Institute of Ecology of Northrhine-Westphalia will fill up this gap (Block and Bartels, 1983). It should be mentioned that "high risk" in Northrhine-Westphalia may be regarded as medium risk in countries with rainfall of up to 2000 mm.

*Example 2: Combination of frost and pollution*

The map of mean temperatures in January of Northrhine-Westphalia (Fig. 8) shows those areas below a mean of 0°C where a combination of frost and SO<sub>2</sub> can lead to plant damage. Norway spruce, e.g., can tolerate winter temperatures of about -40°C in healthy conditions, but -10°C might be too much for a plant weakened by preceding or corresponding pollution impact. Forests close to the national borders of distribution are obviously especially endangered.

The combination of ammonia (NH<sub>3</sub>) and frost has also detrimental effects on coniferous trees. The needles of young fir plants (*Abies nordmanniana* Spach) in the surrounding of a chicken farm near Hamburg turned brown after cold winters, whereas they remained green after mild winters as observed by the author in the sixties.

Climatic maps of greater periods are better for risk analysis, actual maps of the climatic situation in individual years would be better for the interpretation after the damage had occurred.

*Example 3: Poisonous fog*

Fog is usually regarded as a positive factor for a forest stand because trees are filtering out additional moisture. Some forest societies in the subtropic or tropic mountains depend very much on this kind of precipitation as on the island of Tenerife or on Mount Kenya. Strongly acidified

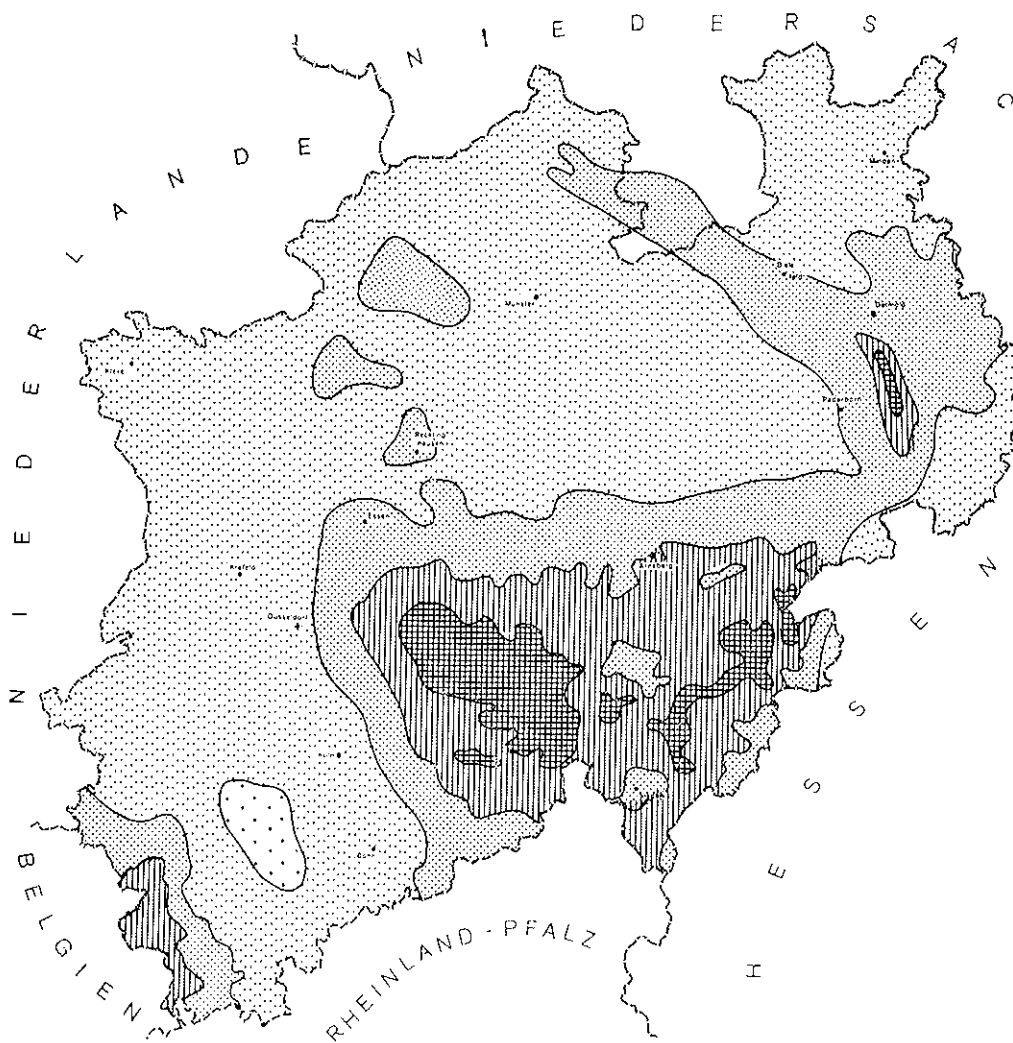


FIG. 7. Mean annual precipitation in mm per year in Northrhine-Westphalia as indication for potential total input of acids by wet deposition. Data from Deutschen Wetterdienst Offenbach for the period from 1931 to 1960. Scale 1:2,000,000.



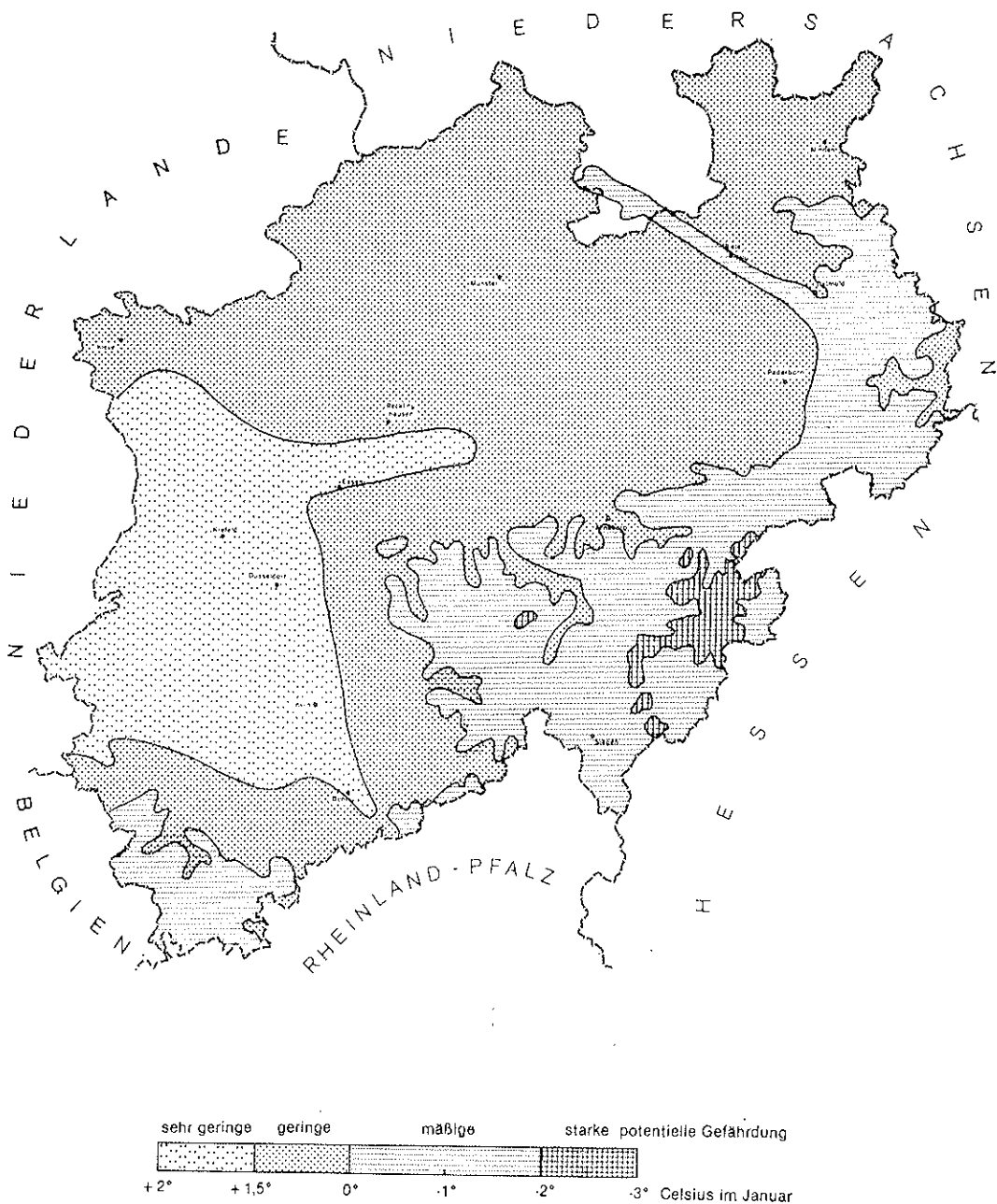


FIG. 8. Mean air temperature in January in °C in Northrhine-Westphalia as indication for potential detrimental combination of frost and air pollution. Data from Deutschen Wetterdienst Offenbach for the period from 1931 to 1960. Scale 1:2,000,000.

or oxidizing fog, containing aggressive radicals, however, which is usually called "smog" is everything else than good for a stand (cf. VDI, 1983). So foggy climate must be regarded as an additional hazard in areas with polluted air.

Fig. 9 shows a map of Northrhine-Westphalia with the number of fog days, differing between valley fog (Talnebel) and low altitude cloud-fog (Wolkenoder Hochnebel). It is obvious that 100 fog days represent a greater hazard than less than 50 days because the prospects of having some fog days with corresponding high pollution levels will be doubled.

#### 4. HIGH STACKS - MAN'S TRICK HOW TO AVOID LIABILITY

High smoke stacks have changed the situation very much. When the effects of sulphur dioxide emissions in the surroundings of metal smelters or coal burning power stations became too deleterious to the biotic environment, man invented the "high stack". At first sight, this solution seemed to be convincing in the assumption that he could produce as much as he wanted without getting complaints from his neighbours. So dilution was considered as being the solution of the pollution problem. The average stack height of power stations in the U.S. built in 1960 was 73 m, but in 1969 already 183 m (TVA, 1970, cited by Munn and Bolin, 1971). Nowadays, stacks of 300 m are not uncommon.

##### *Example 5*

The technical prescriptions for the construction and operation of industrial plants in the Federal Republic of Germany (TA Luft, 1974) still allowed almost unlimited emissions in as much as the impact on the near neighbourhood could be excluded by high chimneys. Thus, the coal-fired power plant of Dinslaken-Voerde could reach emissions values of about 23,500 tons of  $\text{SO}_2$  and almost 10,000 tons of  $\text{NO}_x$  since 1975, whereas the ill-famed smelters in the Sudbury region of Ontario, Canada, even emitted about 1,000.000 tons of  $\text{SO}_2$  per year (Linzon, 1958) which was more than the emission rate of the whole Ruhr district, Germany, in 1947.

##### *Conclusion*

Usually, high chimneys prevent liable operators or sources for damage in distant vegetation from being identified, their license depending on the

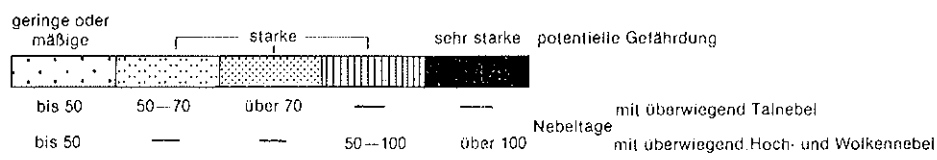
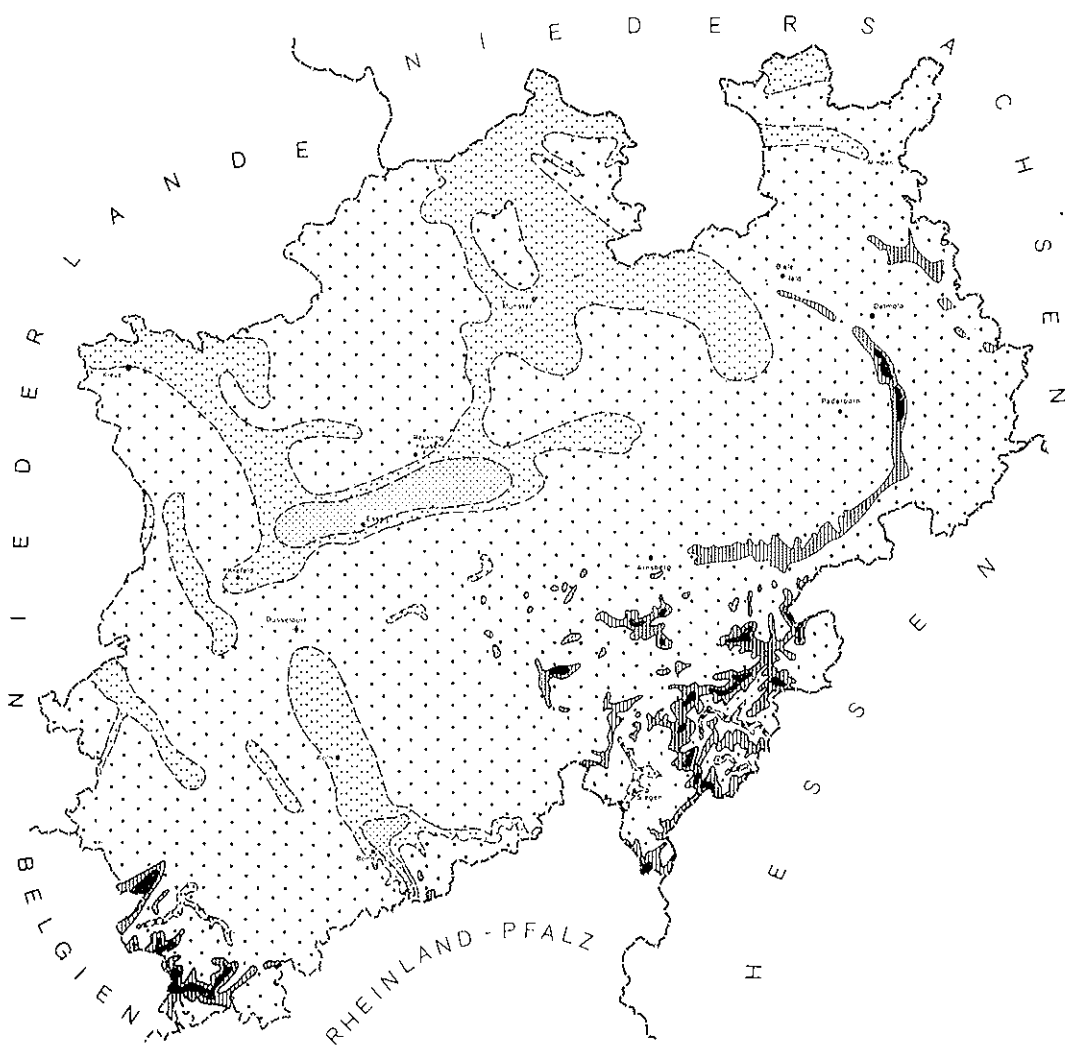


FIG. 9. Mean number of fog days in Northrhine-Westphalia as indication for hazardous acidified or oxidizing fog (smog). Upper line predominantly valley fog, lower line predominantly low altitude cloud-fog. Data from Deutscher Wetterdienst Offenbach for the period from 1931 to 1960. Scale 1:2,000,000.

maximum and average increase of concentration in  $4 \times 4$  km areas around the industrial plant. The emission being mixed with a greater air mass, the residence time of pollutants in the atmosphere is extended and the possibility of photochemical reactions increased. However, detrimental effects are by no means excluded. They usually occur in greater distance, that is, in areas where vegetation may be more sensitive because of climatic stress or poor nutrient conditions. They also occur via other pathways by soil acidification or in combination with other pollutants from different sources. Being the token of uncontrolled economic growth, high stacks have certainly contributed to the "global air pollution" as described by Munn and Bolin in 1971. From a more general point of view, high stacks have prevented a decentralized economy from being developed and adapted to its environment by favouring large installations and hiding the ill-effects.

## 5. FOREST DIE BACK - A WORLD WIDE PROBLEM

### 5.1. *From fume damage to forest decline: Affected Species*

Forests which have survived all political, economic, and social changes in the industrialized countries of the world during the last centuries are now seriously endangered.

There was a steady development from localized but very severe cases of mortality and growth loss due to oxides of sulfur or to fluoride, first to regional destruction as in the Ruhr district or the "Erzgebirge", later to a statewide and finally continental dimension of forest decline.

The first damages outside the industrial areas were observed on *Silver fir* (*Abies alba* Mill). That species had already become extinct in the Erzgebirge in the Thirties. Forty years later the decline was obvious from Poland to France, that means all over most natural stands and artificial plantations in Europe.

Today the die-back of silver fir is regarded as a real menace to the further existence of this species which reacts more sensitive to dilute concentrations of air pollution than any other tree of forest importance. Its disappearance causes great silvicultural problems because firs help to stabilize mixed forest stands in the mountains against wind fall by rooting much deeper than Norway spruce.

*Norway spruce* (*Picea alba* Karst) was the second species which showed obvious changes in health.

The localized fume damage in the "Erzgebirge" spread to regional die-

back on the top of this mountain ridge between Czechoslovakia and the German Democratic Republic from 1950 to 1980.

In 1979 latent damage could be proved for half of the spruce stands in Northrhine-Westphalia by careful counting of needle retention on felled trees still before the outbreak of clearly visible symptoms appeared in 1982 (Knabe, 1983).

Widespread damage of Norway spruce was observed also in Southern Germany after 1981 and later on in Switzerland and Eastern France while it could be seen in South East Poland also within and outside the industrial region in Upper Silesia. Extended areas were affected in South West Sweden but not as severe as in Central Europe (Scholz, 1984).

There was no clear relation between degree of damage and soil conditions but a positive correlation to wind exposure which leads to a greater flux of air contaminants. High altitudes of central highlands were affected most.

*Red spruce* (*Picea rubens* Sarg.) has shown an unexplained die-back in the coastal mountains of North East America which is supposed to be a result of regional soil acidification caused by air pollution (Tomlinson, 1983).

*Scotch pine* (*Pinus sylvestris* L.), the main forest species on sandy soils or dry sites in Europe did not escape the present decay. The reduction of needle years and needle length and sparse foliage create the impression of thin crowns and sickness. Poor sandy soils in the plains were affected most which might be due to nutrient imbalances because of high input of ammonia from increased life stock.

*Eastern White pine* (*Pinus strobus* L.) and *Ponderosa pine* (*Pinus ponderosa* Dougl.) were affected in Eastern North America and California respectively. The disease was attributed to elevated concentrations of photochemical oxidants and partially of sulfur dioxide (Hepting, 1964; Linzon, 1958).

Deciduous trees which have been regarded as more resistant to air pollution for almost a century show now also symptoms of decline. This was first observed on *European beech* in Southern Germany after 1980, later also an *English oak* in Northrhine-Westphalia which had proved as fairly resistant both to SO<sub>2</sub> and HF. A change in pollution patterns may be the reason, eventually the combination with photochemical oxidants or with ammonia.

*Sugar maple* (*Acer saccharum* Marsh.) has been affected in Ontario, Canada. The reason of this die-back is also not clearly known.

### 5.2. *Present estimation of affected area*

Scholz (1984) has reported on the present extent of forest damage due to air pollution in Europe and North-America for the UN Economic Commission for Europe (ECE). This report is based on official sources of the affected countries. This official estimate of damaged area is listed in table 7.

Most states appear with less than 3 per cent of the forested area damaged. A greater percentage has been reported by the government of Norway and Sweden (5%), Austria (6%), Poland (7%), Federal Republic of Germany (8%), Czechoslovakia (10%), and German Democratic Republic (12%).

These estimations do not reflect the actual situation however. They are much too low for what can be proved by more recent surveys, e.g., in the Federal Republic of Germany.

Table 8 brings a comparison of the surveys from 1982, 1983 and 1984 which shows a dramatic increase of damaged area. The difference between 1982 und 1983 can partly be explained by methodical difficulties in assessing slight damage by untrained personnel in 1982. The surveys of 1983 and 1984 however were made by trained foresters using the same method so that the total increase of 16 per cent of the total forest area in one year must be seen as fact and a very alarming signal.

### 5.3. *Causes for forest decline*

The wide-spread forest decline in Europe and North-America is regarded from scientists of different schools as caused predominantly by the impact of air pollution. "Without anthropogenic air pollution there would not be forest damages to the present extent" (Scholz, 1984).

As outlined in the first chapters air pollution acts in various ways. High concentrations of a single component can lead to the same degree of damage as the combination of two or more pollutants at lower concentrations or as the enforcement of natural stress which would not kill or harm a plant as severely in clean air.

Direct effects of either SO<sub>2</sub>, ozone, HF and HCl have been proved in the history of fume damages research. The steady increase in knowledge is well documented in various reviews. Scurfield (1960), Keller (1964)

TABLE 7 - Statistical data on forest damages in ECE countries (Adapted from "Länderberichte der EFC/FAO, ausgewertet vom Bundesamt für Ernährung und Forstwirtschaft, 1983", Federal Republic of Germany) - Scholz, 1984.

| Country                         | Total forested area          |                 | Area of forest damages |                          | Forest damages   |                                       |
|---------------------------------|------------------------------|-----------------|------------------------|--------------------------|--|---------------------------------------|
|                                 | Land area<br>1979<br>1000 ha | 1979<br>1000 ha | % of<br>land<br>area   | % of<br>forested<br>area | Regional centres   | Main tree species                     |
| <i>Northern Europe</i>          |                              |                 |                        |                          |  |                                       |
| Denmark                         | 4,237                        | 493             | 11.6                   | <3                       | North-western Jutland  | Pine                                  |
| Finland                         | 30,545                       | 23,321          | 76.3                   | <3                       | Local sources  | Pine                                  |
| Norway                          | 30,787                       | 8,330           | 27.1                   | <5                       | South-eastern Norway   | Spruce, pine                          |
| Sweden                          | 41,162                       | 26,424          | 64.2                   | <5                       | South-western Sweden   | Spruce                                |
| <i>Western Europe</i>           |                              |                 |                        |                          |  |                                       |
| France                          | 54,567                       | 14,543          | 26.7                   | <3                       | Lower Seine valley, Lorraine,<br>Rhône valley  | Pine, spruce,<br>beech, oak           |
| Ireland                         | 6,889                        | 317             | 4.6                    | <3                       | Local sources  | —                                     |
| United Kingdom                  | 22,820                       | 2,018           | 8.8                    | <3                       | Local sources  | —                                     |
| <i>Southern Europe</i>          |                              |                 |                        |                          |  |                                       |
| Spain                           | 49,954                       | 15,260          | 30.5                   | <3                       | Local sources  | Pine                                  |
| <i>Central Europe</i>           |                              |                 |                        |                          |  |                                       |
| Austria                         | 8,273                        | 3,282           | 39.7                   | 6                        | Upper Austria, Styria, Tirol   | Fir, spruce                           |
| Czechoslovakia                  | 12,551                       | 4,535           | 36.1                   | 10                       | Ridges of Ore mountains, Iser<br>mountains and Beskydy<br>mountains                    | Fir, spruce, pine                     |
| German Democratic<br>Republic   | 10,610                       | 2,951           | 27.8                   | 12                       | Districts of Cottbus, Halle,<br>Leipzig  | Spruce, pine                          |
| Germany, Federal<br>Republic of | 24,440                       | 7,318           | 29.9                   | 8                        | Agglomeration areas, ridges of<br>central highlands, impact areas<br>of western slopes | Fir, spruce, pine,<br>beech, oak      |
| Hungary                         | 9,234                        | 1,594           | 17.3                   | <3                       | Local sources  | Black pine                            |
| Netherlands                     | 3,395                        | 291             | 8.6                    | <3                       | Local sources  | Spruce, fir                           |
| Poland                          | 30,456                       | 8,677           | 28.5                   | 7                        | Industrial region of Upper<br>Silesia  | Coniferous forest,<br>especially pine |
| Switzerland                     | 3,977                        | 1,052           | 26.5                   | <3                       | Northern cantons, Valais   | Fir, spruce, beech,<br>pine           |
| <i>Non-European countries</i>   |                              |                 |                        |                          |  |                                       |
| United States                   | 912,680                      | 290,760         | 31.9                   | <3                       | North-eastern USA, Los Angeles<br>basin  | Pine, yellow pine,<br>Jeffrey pine    |
| Israel                          | 2,033                        | 116             | 5.7                    | <3                       | Local sources, traffic roads   | Aleppo-pine, pine<br>species          |

TABLE 8 - Increase of forest damage in the Federal Republic of Germany from 1982 to 1984 (Adapted from Bundesminister für Ernährung, Landwirtschaft und Forsten, 1984).

| Tree species | Area of tree species |                         | Damaged area (damage classes* 1+2+3) |                               |      |
|--------------|----------------------|-------------------------|--------------------------------------|-------------------------------|------|
|              | Millions ha          | per cent of all species | 1982                                 | per cent of tree species 1983 | 1984 |
| Spruce       | 2.950                | 40                      | 9                                    | 41                            | 51   |
| Pine         | 1.464                | 20                      | 5                                    | 44                            | 59   |
| Fir          | 0.179                | 2                       | 60                                   | 75                            | 87   |
| Beech        | 1.262                | 17                      | 4                                    | 26                            | 50   |
| Oak          | 0.613                | 8                       | 4                                    | 15                            | 43   |
| Others       | 0.940                | 13                      | 4                                    | 17                            | 31   |
| All species  | 7.408                | 100                     | 8                                    | 34                            | 50   |

\* class 1 = slightly damaged

class 2 = damaged

class 3 = severely damaged

describe the state of knowledge at that time. Knabe (1966, 1972) adds proposals for future forest research which does Robinson (1970) for the long-term effects of air pollution in general.

The textbooks of Garber (1967), Guderian (1977), Dässler (1981) and Halbwachs (1984) summarize the so-called classical pollution effects quite well.

Prinz *et al.* (1982) see ozone as main cause for the forest decline in Germany, however they admit the need for further clarification.

Acidification of soil combined with lack of nutrients and release of aluminium ions which act toxic to plant roots was the other line of explanation. Wieler (1905, 1933), Ulrich *et al.* (1979, 1983 a, b) and Drablos and Tolan (1980) can be used to support this theory, while it is more critically discussed in VDI (1983).

Chlorinated hydrocarbons, radioactive pollutants and other kinds of radiation (like radar), which are also mentioned as possible causes for the present die-back, need still clarification by experimental work.

The chemical industry has declared 35,000 chemicals as being produced before establishing toxicity examination for "new" chemicals. What do we know about the risks of them?



Schütt (1984) gives quite an interesting list of arguments for and against all these hypotheses while Smith (1981) points at the complexity of interactions between air pollution and forest ecosystems which should always be kept in mind.

A tree has only limited ways of response. Any damage of the root system will have an effect to the leaf mass and any reduction of photosynthesis by direct impact of air pollutants to leaves will reversely reduce the number of feeder roots and start a negative feed-back (Bossel *et al.*, 1984).

Natural causes for the far-spread die-back can be ruled out as main force (Waldschäden ... 1983; Schütt, 1984), because the damage occurs on different soils, in the plains as well as in the mountains, but with forest edges and exposed sites suffering more. Sick trees are found in natural mixed forests as well as in even aged monocultures with pronounced injury in older stands. Various tree species are affected which is unlikely for any biotic parasite as fungi, insects or viruses.

From the author's point of view there is no single cause for the present decline except you take the overall input of various chemicals into the system which is by far higher than the buffer capacity of soil and forest. As stated in the "Bundestag" at an expert hearing in October 1983, the present crisis is caused by a varying combination of pollutants with varying weight depending on site, species and climate.

#### 5.4. *Consequences of forest decline*

The consequences of forest decline are numerous and can hardly be fully understood at present. A socioeconomic evaluation has been tried in Acid rain (1984).

We know that the economic role of forests would fade out. Forestry in Europe was based on a balance between annual growth and annual cuttings. This balance is disturbed first; later annual growth will become less and less while cost will increase because a single tree management costs more than clear cuts or periodic thinning and weeds impede re-planting. Hence forest land owners will not get any return, while wood consumers will not get the steady supply which they need. So many jobs will be lost.

We also know that several welfare functions of forests will be affected. Wood covered land has a leveling effect on climate, snow smelt and run off. Bare land shows much greater peaks of wind velocity, run off and in

consequence greater erosion, while dry periods are not balanced any more by retained ground water in mountainous land. Soil erosion can lead to permanent losses in fertility. The eroded soil then will be deposited somewhere, will fill lakes and reservoirs and block water courses. Leached aluminium and heavy metals spoil water quality and endanger human health.

In Alpine areas, where forests had been an indispensable protection against avalanches, villages will have to be evacuated, roads to be closed in winter time which surely will reduce or prevent winter sport.

The recreational value of forests will be affected also, slightly at the beginning, strongly if everybody can see what happens. Such a place does not promise as good a climate as assured in the prospects. This reduction in recreational value will also be felt in and around urbanized areas.

The genetic drain will be enormous. Trees sensitive to air pollution might contain genes with great importance for the population in relation to its ability to cope with other stress factors. The loss of whole species cannot be excluded as can be seen in the increasing extinction of Silver fir in various forest areas. The loss of flowers, birds, insects and other living beings takes away what has been here before man appeared.

This brings us to think about further consequences. Does not mankind just represent one single species? Why should this species escape the bad fortune it has brought to others? Biotic systems of such high stability as forests need really a heavy chemical attack to be killed. The same chemicals enter our lungs, nutrients and water and will cause long-term changes in our body or genes which we do not notice in time. The increasing numbers of cancer in various organs all over the world speak their own language.

Or if we look from another direction. Was not all this nature delivered to man by the Lord to be cared for and well treated? Its rude exploitation, its reckless destruction was not told to man. So Christians should be especially aware of what is going on and do their best to come out of this situation.

## CONCLUSION - WHAT CAN BE DONE?

The present forest decline cannot be explained by natural factors but has to be seen as the result of increasing chemical impact. These chemicals are produced by burning fossil fuels, intentionally brought into the environment as pest control e.g., released as by-product, or left as waste somewhere.

So what can be done?

This is not the place to give detailed answers. Only some fundamental thoughts will be pointed out.

(1) Everybody who reads this paper should recognize his own responsibility. So do not read it or do something! Our actions will depend on our position in life.

(2) Everybody is a consumer, so change in consuming habits from "wastemakers" to thoughtful housekeepers who re-use goods or take care for their duration will reduce the use of energy and the release of chemicals to the environment. He can insulate his home, buy renewable goods, eat less meat and reduce driving cars or stay within speed limits.

(3) Almost everybody is a citizen with rights and duties. So he can influence the politicians of his district, political parties, authorities and press in his region or even at higher levels. We should use this power in favour of nature conservation.

(4) Some are teachers, priests, nurses or other educating people. Many of us have children who are observing our behaviour. Setting standards with our own life can influence them. A tender care for flowers, animals or the green in our surrounding will certainly have an effect on our own life and on theirs too. Informing them on the interrelations between man and nature, between chemical input and biologic response is the second way of changing the situation. Only people aware of the situation can act. So one has to learn more and more.

(5) Some of us are engineers, technicians, chemists or inventors. Many of us work in a factory, a bank or an administration. There are innumerable occasions to do something for the environment in our jobs, much more than we have thought before understanding the problem ourselves. It is time to make use of these possibilities.

(6) Only a small minority does belong to the leading circles in administration, government, church, industry, army, banks, media etc. At present they are asked to use their influence towards a better understanding of natural cycles, aiming at a survival programme for our forests as well as for ourselves.

(7) We should be well aware that the present arms race is the greatest waste of raw materials, energy, labour and intelligence we can think of, as was outlined by Pope John Paul in November 1983 analogously. This intelligence would be urgently needed to solve the real problems: hunger, social development and environmental protection.

## SUMMARY

Effects of air pollutants on vegetation, especially forests.

Air pollutants are affecting terrestrial vegetation in various ways. Direct effect of gaseous pollutants as  $\text{SO}_2$  are well known since the middle of the last century. Other phytotoxic gases as HF, HCl were detected later, photochemical oxidants not before the middle of this century. Recent findings revealed synergism between different gases as  $\text{SO}_2$  and  $\text{NO}_2$  or ozone which causes much greater effects than originally expected.

Acid mist and dew is another cause for damage to vegetation. Research has been intensified over the last years to a great degree.

The mechanism of dry deposition of acid gases on plant surfaces and their results on plants are hard to simulate and are not fully understood.

Indirect effects of air pollution on vegetation result either from a general weakening or preconditioning of plants which make them a better host for pathogenes or parasites or reduce their resistance against frost und drought. Examples are reported.

Or they are the result of changes in soil chemistry and texture.

Acids may leach nutrients and make aluminium and iron or other heavy metals soluble, so that roots find poorer growth conditions or die.

The present decay of forests in parts of North America and in whole middle Europe which is extending to France, Eastern Europe and South Sweden is regarded as a very alarming signal to mankind to change its living conditions in a way which will not cause such detrimental effects.

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## DISCUSSION

MARINI-BETTÒLO

Thank you very much, Dr. Knabe. It is very interesting and this is quite clear evidence of the impact of the chemical events in the atmosphere on the biosphere. I would like to ask Dr. Knabe if he has seen a recent report in *Environmental Science and Technology* saying that it is not always possible to correlate air pollution in general with forest decay.

KNABE

I have not seen that special publication but there are similar publications or similar arguments. The problem is not so easy. First you have to take into account the accumulation of air pollutants within the forest ecosystem. This accumulation occurs either in the soil by a steady increase of acidity and heavy metals or within living beings themselves. Increase of acidity means the loss of other nutrients, of basic cations like calcium, magnesium, potassium. Accumulation of acidity can also occur in the form of aluminum ions attached to the buffering soil colloids as a result of the disintegration of clay minerals, if the soil pH in water falls below 4.2. Below pH 3.8 also iron becomes soluble and is then adsorbed by the surface of clay minerals and other soil colloids, too. That is one topic.

Another topic: heavy metals are accumulating also within trees, within roots, within needles and other parts of the stem; so you have a constant weakening of the tree. You cannot relate this content to the present ambient concentration of the pollutant in the air, because it has been accumulated in the past. However ambient concentrations of ozone and SO<sub>2</sub> and NO<sub>2</sub> may also affect the tree and make the effect even worse. Let us take an example: plants have the ability to detoxify certain agents, like SO<sub>2</sub>; they can reduce it and metabolize it within the cell, and they can also deal with oxidants, like ozone. Well, ozone is breaking off double bonds within certain enzymes and other cell constituents, but it can be metabolized afterwards. For doing this, however, energy is necessary, and if energy production — that means photosynthesis — is reduced and the tree is missing the energy to do it, then this double impact may be too much for it. So if a scientist wants to correlate ambient concentrations to decay of forests, he should precisely distinguish

between very different cases. We can prove — I still have some slides which could be used as an example — that upper soil layers have reached a level of acidity at which any root growth is prevented, so that no root grows into that special layer. We can prove that the leaves are hurt at certain concentrations of sulphur dioxide or hydrogen fluoride, so that photosynthesis will be impossible or the leaves are dropped or burnt. And we can prove that there is a concentration of soluble heavy metals in the soil at which those metals will penetrate into the roots and cause damage there. We cannot explain, however, the sudden outbreak, the sudden widespread forest damage at present — that we cannot fully explain.

#### LIBERTI

I only wish to express appreciation for the fine presentation of the changes in vegetation that you have been able to show us. However, I want to make a couple of comments on your lecture, according to the following lines. The first one is that you described two procedures for the approach of this system: one starting from effects and going back to the causes, and the other one talking about causes and going to the effects. In your lecture you practically followed the first line, to show the effects and to describe the causes which might be responsible for them. Now my criticism is the following: I am wondering if you made any effort to make any correlation between ground concentration of various pollutants and the damages that you have been able to find in the plants. This is quite an important point, because in the presentation of your lecture you were talking about the effect of doses. When we are taking a plant, also if the plant is exposed to a serious pollutant because it stays always in the same position, it will get a certain dose. This is important because we are able to correlate the effect on doses. And I am insisting on this point because from a biological standpoint public administrators and technical people are trying to establish some A quality standard in terms of various pollutants. For instance, these days we are having a standard for  $\text{SO}_2$ , a standard for particulate matter, a standard for nitrous oxide, etc. Now if we can correlate doses and effect, we might be in a certain position to say that the data which have been established by public health people are valid as far as air is concerned, but not for the environment, because plants are more sensitive to this effect. I really would be very much pleased to have your comments on this point.

Another question I would like to ask you is the following. You show us some of your results in terms of concentration of various pollutants on the

plants, and you show us the difference between vegetable species which have not been exposed. Now these days we are very much worried as to whether most of the damage is coming through a reaction which takes place in the cells of the various species or is something affecting the adsorption of these species. For instance, in one of your pictures you showed the effect of fluoride. Now, being a chemist myself, I am always very much worried about the fluoride business, because we may have fluoride in the gaseous phase as hydrogen fluoride, which we believe is toxic. However, we may have fluoride as inorganic particles, which practically will belong to particulate matter, and according to our knowledge we believe these are practically harmless. So I believe that these days we have to go more deeply into this effect just because we have to be able as scientists to supply some information to technical people. And I do not think there is too much sense in talking about fluoride as such because we have gases, particles or fluorides in aerosolic species. I certainly will appreciate your comment on my questions.

KNABE

Thank you very much, Professor Liberti, for the questions. First, there are measurements between the ambient concentration of pollutants and the growth of vegetation. I have not made those studies myself, but there are such studies. There are comparisons between several locations in the northern hemisphere, where they have measured the concentration of air pollution and the growth of vegetation, and they found that the production and the growth rates decline with an increase of sulphur dioxide and an increase of hydrogen fluoride. Those figures could be obtained from the report made by the state institute for air pollution control at Essen. There was also found a correlation between the content of heavy metals in the atmospheric suspended matter and the content of heavy metals in the plants which have originally been precipitated on the surface. Well it is different — you can wash it off the surface partly, but you cannot wash it off totally. Cadmium shows a greater mobility, it is also penetrating the cuticula, going into the leaf, whereas lead is staying more or less on the surface.

LIBERTI

Sorry if I interrupt you, your answer is quite satisfactory. However, can it be expressed in numerical terms, because at the beginning you were talking about doses. Now it would be terrifically interesting to know this data because

the great effort which is made on an experimental basis is trying to establish what are the limits for different pollutants. In other words as a general attitude we do not like to stop industrial activities and we do not wish, in the defense of the environment, to make a limitation in various countries in any activities.

The aim that we wish to achieve is a certain regulation of production so that man's activities, and also living conditions of the society, can go forward in a very healthy way. Now in order to do this, we have to try to get figures which may be considered standard emission rates. It means the amount of toxic material which may be emitted into the atmosphere. Owing to the average turbulence situation we may have viable conditions so that the plant life can go ahead quite well. What worries me is the fact that with the benefit of the World Health Organization in Geneva certain standard values have been established so that we believe, for instance, that a certain concentration of  $\text{SO}_2$  in a certain range is said not to affect human life. My question is the following — I do not know if you are able to answer it, it is certainly a big wish of people engaged in this problem — is it possible to establish a certain limit for concentration of pollutants compatible with human health without causing damages to forests and the environment? In order to do this, we have to be able, to a certain extent, to establish a minimum dose on which a certain plant can flourish and can go ahead. I therefore would like to have your comment on the possibility of achieving this aim.

KNABE

I can give you two sets of figures. One was set up by the Association of German Engineers (VDI) — their committees have worked on these standards — and the other was established by IUFRO, International Union of Forest Research Organizations. Let us begin with hydrogen fluoride as you mentioned, and which has to be distinguished from other fluorides. In my paper I gave only the fluoride content of leaves or needles and so I could not say if it had been hydrogen fluoride (HF) originally, so I could just measure the content in the needles.

But if you come to ambient concentrations, we have a set of 0.3 microgram per cubic meter ( $\mu\text{g}/\text{m}^3$ ) HF as annual mean for very sensitive plants, 0.5  $\mu\text{g}/\text{m}^3$  HF for sensitive plants, and 1.4  $\mu\text{g}/\text{m}^3$  HF for less sensitive plants. For sulphur dioxide the three groups would require annual means of 60  $\mu\text{g}/\text{m}^3$ , 90  $\mu\text{g}/\text{m}^3$  and 130  $\mu\text{g}/\text{m}^3$   $\text{SO}_2$  and for hydrogen chloride 100  $\mu\text{g}/\text{m}^3$  HCl for very sensitive plants and 150  $\mu\text{g}/\text{m}^3$  HCl for sensitive plants. We are still missing a value for less sensitive plants. For nitrogen dioxide there was only

the annual mean for sensitive plants,  $350 \mu\text{g}/\text{m}^3$   $\text{NO}_2$ . The last figure might be outdated because people in the Netherlands (Jan Mooi) and also somewhere in America found a very strong synergism between  $\text{NO}_2$  and  $\text{SO}_2$ , and  $\text{NO}_2$  and ozone. So the value for  $\text{NO}_2$  might be much too high. The VDI has also established limitations to peak concentrations which are not listed here. The IUFRO standards for the protection of forests concern the following values as sufficient:  $3 \mu\text{g}/\text{m}^3$  hydrogen fluoride as annual mean, and  $0.9 \mu\text{g}/\text{m}^3$  as 97.5 percentile of all measurement values usually means over 30 minutes. A 97.5 percentile means that only 2.5% of the individual values should exceed this limit. The corresponding values for sulphur dioxide would be the annual average of  $50 \mu\text{g}/\text{m}^3$   $\text{SO}_2$  for normal conditions, and  $25 \mu\text{g}/\text{m}^3$   $\text{SO}_2$  for conditions with very poor sites or high mountains where climatic stresses are included, so very low values, and they are derived from the results we have found in Austria and the mountains in Czechoslovakia.

LIBERTI

Are the figures that you give us accepted by the German Government, or have they been only the results of your experience? There is a strong need for values which may be internationally agreed, which might be a guide for people anywhere. And this is quite an important point, because the evolution of living conditions is sometimes a critical political standpoint in specific attitudes by various governments. Now it would be necessary to point out the necessity of having emission standards which may be accepted and which might be useful for anybody by taking into account not only air conditions but also living conditions. I am just asking your cooperation, also to define if these figures have been issued on a local basis or government basis or an experimental basis.

KNABF

Well, I could only offer you to fix all the figures here at this round table. We could include some proposals for the outcome of the meeting or we could sit together and make some detailed proposals. I think the discussion is not the place of very detailed figures to solve this problem. However, IUFRO-values ought to be respected, because IUFRO represents all forest research organizations of the world which work on the problem of air pollution and its effects on forests.

LIBERTI

I agree with your proposal.

LAG

May I ask do your analytical figures, for instance of heavy metals, refer to a dry matter basis?

KNABE

They all refer to a dry matter basis.

BROSSET

I have a small remark on what Professor Liberti has said. I share totally his opinion, but the example he gave, I think, was a little unfortunate because if we have sodium fluorides in aerosols they may not be quite harmless, because the hydrofluoric acid has a pH of 3, and if we have a solution, for instance, of pH 4, 10% of the water-soluble fluorides will be in the form of hydrofluoric acid, so that will be still a harm risk.

LIBERTI

I was pointing out the difficulty of defining what is the fluoride in the air, because we have gaseous fluoride, liquid fluoride and particles fluoride; therefore usually we are always hearing about fluoride concentration, which in my opinion does not mean too much because the gaseous is definitely a more important fact than are the particles. So I agree fully with what you say, but my statement was just in the desire to learn more about a problem which is of the greatest importance.

WIESENFELD

The very first speaker at this Study Week, Professor Phillips, mentioned the goal of a government-sponsored study in the U.K., explicitly leaving out — saying these goals were specifically left out — some of the more interesting (to chemists and physicists) aspects of the problem; and those include those phenomena which can be referred to as the source-receptive relationship in acid precipitation, acid deposition. Specifically I think it is important to

remember that one, in assessing the problem, needs extraordinarily accurate emissions inventory data. For example, if one looks at the power generation in the United States over the last 20 years and attempts to draw conclusions from that, I think that one would be led down the wrong path, for while that power utilization has gone up as a result of presumably increased population, the actual amount of emissions has gone down because of legislation. Similar observations, I think, would also be true concerning nitrogen oxide emission. I think we have to look very carefully not only at temporal data but also at spatially resolved data, and that increasingly is becoming available although the collection of that data is an extraordinarily complex and expensive proposition.

Secondly I think one has to look very carefully at transport phenomena. Several speakers in this Study Week have referred to the effect of the introduction of tall stacks which permit an increased dilution of emissions from power plants. The inclusion of a tall stack at a power plant does not cut the deposition in the vicinity of that stack — and you can use the term vicinity in any way you like — to zero and the deposition at a distance of 500 kilometers to 100%. A very substantial fraction of the deposition associated with emission from a particular source, even with the tall stack, occurs relatively near to that source; and again, the question of how near is one, that is extremely difficult to get solid answers for — one simply does not have that kind of information. If you want to take an applied mathematician and send him into shock, you ask him to model the flow from a tall smoke-stack over a distance of about ten or twenty kilometers — that is just something that is not done. The overall transport phenomenon in acid rain is an extraordinarily complex multi-scale phenomenon. So far as the chemistry is concerned, I think that, too, varies dramatically with the climate, with the season, with the presence of oxidants of various types in the atmosphere, and I fear that there can be no single generalization concerning acid rain and the mitigation of acid deposition worldwide. This is something that has to be handled on a scale which in fact I think will be much smaller.

#### CRUTZEN

What I have missed so far in the discussion, is the absolute lack of discussion of meteorological phenomena, and Dr. Wiesenfeld's insertion here was very well placed. After all, the last two years in Germany, which have caused a definite decline in forest resources, were also combined with some very exceptional two years of summer weather. The spring was far too wet and

the summers were far too hot and far too dry, and I think the meteorological aspects of forest death should definitely not be neglected. It is not only a problem of chemical constituents in the leaves which we should consider but the whole physiology of the forest. I think even people, when they do not drink, are in big trouble very quickly, and so why should forests not be? Now, on top of that, the whole pattern of deposition of dangerous or haphazardous chemicals will be changed from wet deposition to dry deposition, and the whole chemistry and the intermediates in the oxidation schemes in the atmosphere will be totally changed under these different climatic conditions. I think this is a very important issue to pursue in the future and one should look at what compounds are really being deposited on the forest.

#### KNABE

I should like to answer this by showing part of what we have done. We tried to determine the amount of the potential hazards to forests in Northrhine-Westphalia by a combination of certain factors. One of these combinations would be total acidic deposition as a result of acid concentration and the amount of rainfall. The mountaineous areas usually get higher rainfall than the plains.

Here the potential input of acid may be greater than in the industrial areas in the plains. We have already proved this hypothesis by measurements from 1973 to 75. We have measured the acid input both in the industrial areas of the Ruhr and in two rural districts. We found differences. We found that the titrated acidity, total acidity, in Mülheim-Ruhr amounted to about  $120 \text{ mgH}^+ \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ , 60 kilometers north about the same amount, and 50 km south of the Ruhr, with high rainfall,  $155 \text{ mgH}^+ \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ . But there is also a great difference between rain outside the forest and below spruce. In the fall of Norway spruce you find about 4 times or 3 times the amount of acidity deposited measured outside the forest. At the edge of the forest we have again an addition. We find a higher acid deposition at the edge of the forest than in the middle of the forest. And if you do the same for the Federal Republic of Germany, you find areas with higher rainfall and those areas are partly very heavily attacked by the present forest decay. In the southern part of the Bavarian mountains, in the Harz mountains or in the area of the Black forest, you have higher rainfall and by this a greater impact. In another region with high rainfall, in the Alpine mountains, there are calcareous soils, which can neutralize the acids, and so the effect has not been as great, but now it is also appearing.



CRUTZEN

Are these average numbers, or are these the numbers for the last two years?

KNABE

These figures are average numbers, but you can do the same work for a more recent period.

CRUTZEN

You should take the last two years and compare it with them.

KNABE

Pardon me, you can make a map of the average over many years and you can make another map with the input of rainfall maybe in 1982.

CRUTZEN

But I did not see that map. I see the averages.

KNABE

But this is actually a matter of the meteorologists and not my task as forest scientist. It is their business to handle the climatic maps. We try to make use of them. I only came to show you the possible combination between the climatic effect, and you were asking for that. The other combination is the combination between cold temperature and emissions. The mountains generally are the coldest area in winter time and the industrial zone is the warmest area. And so the potential hazard by combination of air pollution and winter cold is greatest in the mountains and is the least in the Ruhr district.

The third combination to be mentioned is that of fog and air pollution. These areas with high frequency of fog again lie in those mountains where we have the strongest forest decay. So climate has to be taken into account, and I agree with you also that special climatic events in the last years may have affected the trees. But this research requires more time and man-power, I can only show the importance of the problem and hope that some other group will start to work on it.

## LIBERTI

Dr. Knabe, I believe that the suggestion given by Professor Wiesenfeld would be just the best, because if you follow the same system which was used by Phillips the other day, it is quite useful to present your data in terms of the emission inventory, which is already quite an approximate way of presenting the data, but it is still the figures which are more reliable. If you are setting up the data which you present to us in terms of the emission inventory in terms either of  $\text{SO}_2$  emission or of nitrogen oxide emission, you may have a certain correlation, unless you have the emission data, which are difficult to be obtained. But since we know — and this is something on which most of the chemists agree — the mechanism of oxidation of most pollutants — if we have an emission inventory, we really are able to correlate in a better way the damages we have to forestry and to vegetation in general, with the effect of pollution. Unless we have these data, it is very difficult to make a sincere and correct appraisal of the damages that we are receiving.

## KNABE

I cannot agree with this proposal. There are a number of links between the source or cause and the effect, a whole range of stages as emission, transportation, immission, deposition and dose, and they are influenced by climate, site, genetic resistance, which can alter the picture. In summary, the effect is very far apart from the source. If you measure the dose within the plant, the amount of pollutants which the plant has taken up, or the state of the soil as it has changed by air pollution, then you have a much closer relation to the effect than just by an emission survey. We have now the forest decay just in those areas which are maybe 100 kilometers away from the industrial areas and not in the industrial areas themselves. So this proposal would not work. It is, however, very useful to find out the main sources and to start measures to reduce emissions in general or for certain pollutants.

## LIBERTI

If you have emission data, you are really able to calculate the doses, because the only variable that you are meeting is the meteorological conditions. So this is a rough appraisal, but it is absolutely the best way to correlate a certain damage if this damage is to be attributed to pollution.

## PHILLIPS

May I just make a comment in reply to Professor Wiesenfeld, and without wishing to act as an apologist for the Royal Society and the Swedish Academy of Sciences and the Norwegian Academy of Sciences? The justification given for the particular choice of survey to be carried out was, I think, not being cynical economic, that was restricted in terms of economics. Perhaps I can read the reasons: This program will not be concerned with the complex processes of how industrial discharges create acid rain, nor with the degree to which productions in the United Kingdom sulphur dioxide emissions would change the acidity of rainfall or have affected those areas of Norway and Sweden. These issues are already the subject of much intensive theoretical and experimental research in many countries. I think that is probably true. So the main thrust then is the effect *in situ*. A decade ago it was considered that high acidity alone occurred either at peak values or when the snows melt or in the less severe values but over a prolonged period. This gives an explanation for the disappearance of trout in certain Scandinavian waters — you see the very specific question they are addressing. Since that time, however, it has been shown that trout can be more tolerant to acidity than was earlier thought, and current explanations relate that disappearance to the effects of acid rain and leeching aluminium into surface waters. Our present understanding does not allow us to predict the precise relationship between levels of acid rain and the composition of surface water, or its acidity after interaction with minerals in the soil or the balance of mineral elements after this process, which relates very much to things we have heard today. So they really have not addressed the question of effects on forests. It is really the fishlessness which they are addressing, and it is a very small part of what I hope, like you, will be a much wider program. I mean I personally would have liked to see the first question and the fifth question on my list of Monday being addressed, but it is for economic reasons that it is not being addressed in this way.

## KNABE

Well, may I answer a little better your question? Again, it is surely useful to have a survey of emissions; it is very very useful to reduce emissions there where the greatest emission occurs. That would be very useful. But for the direct relationship between effect and emissions I have doubts.

## CHAMEIDES

Professor Knabe is sort of saying that we need to worry about the effects (bottom of the slide); Professor Liberti is saying that we need to worry about emissions (the top of the slide). It seems fairly clear that what we are to do is to talk about all the different parts of that slide and to understand not just pollution but the link between atmospheric chemistry and the biosphere. We need to understand all of those prophecies and I think we can agree that we do not understand how all those things connect up — we have some suspicion, and we certainly should be able to agree that in the future we need to try to work together to understand from the top to the bottom and from the bottom to the top.

# CHEMICAL REACTIONS IN THE ATMOSPHERE AND THEIR IMPACT ON HUMAN HEALTH AND ANIMAL LIFE

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## INTRODUCTION

A report on the impact on human health and animal life of chemical reactions in the atmosphere, i.e., mainly of the secondary pollution, is not easy because direct cause-effect correlations are very difficult to establish even for primary pollution.

Therefore I wish to report here a number of data I was able so far to collect, and submit them to you for your comments and discussions which will surely bring new views and contributions. I may recall first of all that it is quite difficult to correlate in general air pollution with effects on human health. Only in very special events (London, Donora, Meuse Valley) there was evidence of a direct correlation of concentration of chemicals in the air and rise of human casualties or diseases. In effect as a general rule the figures of the variation of the number of deaths and of persons suffering from specific respiratory illness (bronchitis, emphysema, etc.) in relation to air contamination (composition and concentration) are statistically significant only in very few cases, because of other sources of contaminants, e.g., habit of smoking, which largely contribute to health effects (Lave and Seskin, 1970; Marini-Bettòlo, 1971 and 1981).

Moreover the above observations apply to global air pollution due to the direct effect of emissions, individual or public traffic, etc., and to the fall-out of the chemical reactions in the atmosphere.

These are the reasons of the difficulty to distinguish the effects on biological systems attributed to normal pollution (primary) and those due to chemical reactions in the atmosphere (secondary pollution).

## THE FUNDAMENTAL CHEMICAL PROCESSES

At this point it is necessary to establish which are the chemical processes of the atmosphere which may have an impact on life on the earth.

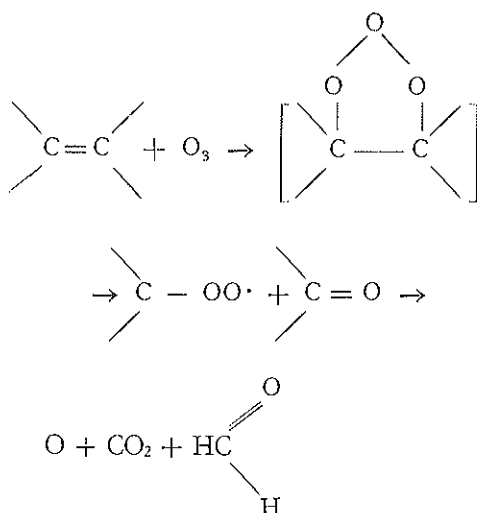
In the present approach we will deal only with the fallout of products which are detected and determined easily, not considering trace elements or other substances which may occasionally be present.

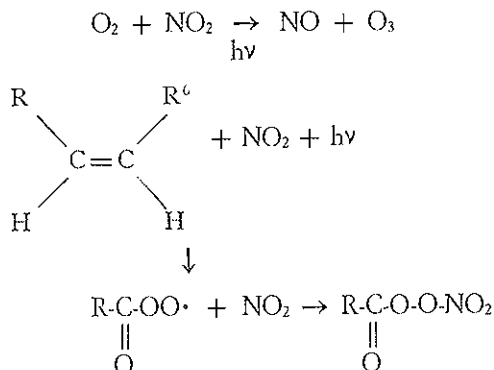
We may enumerate the most important chemical reactions occurring in the atmosphere, which have a direct effect, being then products deposited on the earth and in the lower atmosphere:

1) *Acid deposition*, e.g., acid fog, acid rain, acid snow.

The chemical composition of these products and their formation in the atmosphere are reported elsewhere in this volume (Brosset, Liberti) and thus I will only recall that the principal components are  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .

### *Ozone and Olefins*



*Peroxyacylnitrates formation*2) *Oxidants*

Oxidants formed in the atmosphere mainly by photochemical activity are  $\text{O}_3$ ,  $\text{NO}_2$  and peroxyacylnitrates.

a) *Ozone* -  $\text{O}_3$  is the main oxidant representing 90% of the oxidants present in the air, and is formed by photochemical reaction from  $\text{O}_2$  in the presence of ultraviolet radiation (see pag. 341-375).

b) *Nitrogen dioxide* -  $\text{NO}_2$  is formed, mainly from  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ . Moreover ozone can react with hydrocarbons to give other oxidants. Recent studies have cleared the mechanism of these reactions (Niki *et al.*, 1983).

c) *Peroxyacylnitrates* - Peroxyacylnitrates are compounds characterized by a peroxy group and by an adjacent  $\text{NO}_2$  which makes the substances a strong oxidant but also very reactive and unstable.

These properties may account for their biological behaviour. Peroxyacylnitrates — mainly represented by peroxyacetylnitrate, indicated as PAN — originate in the atmosphere over towns and industrial areas, through a mechanism not fully clarified, from olefins, and other hydrocarbons (car exhausts, fuel from car tank evaporation, gas formed in the refineries of crude oil) under photochemical conditions by  $\text{NO}_x$  in the presence of  $\text{O}_2$  (Stephen, 1969).

Peroxyacylnitrates constitute a part (about 10%) of the total oxidants and are formed in the city atmosphere in conditions of bright light.

The fallout, i.e.,  $O_3$ +PAN, in particular atmospheric conditions, constitutes the so called *oxidant smog* or photochemical smog.

### 3) *Radioactive fallout*

It has been of great importance in the 1950's as a consequence of nuclear explosions in the atmosphere, and mainly for the contamination of food chain by the radioisotopes  $Sr^{90}$  and  $Cs^{137}$ . At present, since the nuclear explosions in the atmosphere have been abandoned by practically all countries, radioactive fallout does not have any more importance (except in the case of a nuclear war) and thus we shall not discuss this topic.

These phenomena were studied mainly in the northern hemisphere: it is very important that similar studies may be undertaken in the southern hemisphere where in some areas particular atmospheric conditions may occur (Marini-Bettòlo, 1972).

## BIOLOGICAL EFFECTS

As mentioned, it is very difficult to establish clearly a direct correlation between global air pollution and the health of man. This because a great number of other causes may influence health, and only on a strictly statistical basis is it possible to establish some correlations.

Thus it is easily understandable that it is even more difficult, if not impossible, to establish a correlation of human health with a single aspect of the air pollution, i.e., of the secondary pollution, and with the pollutants formed by physico-chemical reactions in the atmosphere.

The same considerations apply to many animal species and even in this case it is very difficult to discriminate between the various causes.

It is statistically demonstrated that fog or smog with low pH are very dangerous for people suffering from respiratory and cardiocirculatory diseases, and that generally in areas where air pollution is present, the incidence of bronchitis and other respiratory diseases is also higher. Even in these cases it is not possible to determine a direct correlation of incidence of disease with a specific contaminant, although the greatest part of the responsibility of health troubles and even casualties has been attributed to  $SO_2$  and  $H_2SO_4$ .

Many chemicals which have become ubiquitous contaminants of the earth: PCB, chlorinated hydrocarbons, have been recognized to be res-



possible for damage to wildlife, whereas it was not possible to correlate with specific effect the products formed in the atmosphere by secondary pollution.

This is not the case of fishes and other animals which live in lakes and streams. Although in this case also there is a great amount of other pollutants in the environment there is clear evidence of the effect due to the so-called acid deposition, for its complex impact on the surface waters.

### *Health effects on man*

To establish the effects on human health of the fallout of the chemical species formed in the atmosphere, we have to distinguish between acid depositions and substances like ozone, PAN or other peroxides. In this case we have to follow a different approach, that is, we must establish, as proposed by WHO, the limits for some characteristic contaminants.

### *Effects of atmospheric acidity*

In the case of atmospheric acidity, the biological components are  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The concentration of  $\text{H}_3\text{O}^+$  is toxic, especially by inhalation. Therefore acid fogs, where pH is found also under 5, may be rather dangerous especially for persons suffering from respiratory diseases (Hilleman, 1983a). It is quite interesting that in acid fog  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  content is different in ratio from the content in rain water, because of the concentration process due to the formation of fog. Nevertheless, the assessment of the effects on health, according to a recent report on acid fog, would be extremely difficult to evaluate, except in the case of dramatic events like the London smog of 1952 and 1957. There the  $\text{SO}_2$  concentration was measured at  $680 \text{ g/m}^3$  and the pH could be calculated about 1.5-1.8.

But even in this case, the direct correlation was not possible because the other chemical species and particulates which are contemporarily present may be responsible in part for the effects on health. According to WHO panel of experts an annual average of  $125\text{-}200 \text{ g/m}^3$  (WHO, 1969, 1971)  $\text{SO}_2$  causes higher incidence of respiratory diseases in comparison with those communities where levels do not exceed  $40\text{-}60 \text{ }\mu\text{g/m}^3$ . Even in this case the global effects on health of atmospheric pollution may be misinterpreted by the pollution due to cigarette smoke. The exposure limits for protection of human health are  $100\text{-}150 \text{ }\mu\text{g/m}^3$  per 24 hours.

In acid rains and fogs there is also present  $\text{NO}_2$ . In this case a security limit was established at 190-320  $\mu\text{g}/\text{m}^3/\text{ml}$  (0.10-0.17 for one hour). The average range is 20-90  $\text{g}/\text{m}^3$  per year and the highest daily means of 130-400  $\text{g}/\text{m}^3$ .

The lowest level of  $\text{NO}_2$  at which adverse reaction can occur is 940  $\text{g}/\text{m}^3$  (0.5 ppm).

For nitrogen oxide,  $\text{NO}$ , the annual average concentration is between 4-5  $\mu\text{g}/\text{m}^3$ .

### *Effects of oxidants*

Ozone is the main component of oxidative smog. 200  $\text{g}/\text{m}^3$  (0.1 ppm) concentration for 2 hours causes disturbances in human health; thus a limit of 100-200  $\mu\text{g}/\text{m}^3$  for 1 hour is considered the limit to protect public health. And 120  $\text{g}/\text{m}^3$  (0.06 ppm) represents the average acceptable for 1 hour exposure (Muller, 1983).

### *Effects of peroxyacynitrates*

The most evident effects on human health of PAN, studied particularly in the Los Angeles area, are strong eye irritation and photophobia which causes a considerable nuisance for the population affected.

Their activity on plants is specific, so that plants can be assumed to be biological indicators for their presence in the air (Jaffe, 1969). The effect is shown by the silverying, bronzing and glazing of the lower part of tobacco leaves as well as of *Petunia* leaves, which are used for this purpose, as biological indicators.

Anyhow we must call attention to the fact that experiments have shown that the *toxic effect of air pollution on man is the result of the combined and synergic activity of all the pollutants present*.

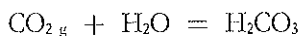
In effect the global toxicity is higher than the sum of the toxicities in the single components.

### *Effects of acid deposition on life aquatic systems*

The fallout of acid rains of surface waters has been studied for the last 15 years because of the impact on life in the lakes and rivers of Scandinavia, Scotland, and Canada as well as in the northeastern regions of the United States (Kramer and Tessier, 1982; Hilleman, 1983b).

The acidity of rains — due both to  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  — formed in the atmosphere — which may bring the pH of lakes to figures of 5-6 and even 4.5 is not the sole factor responsible for the toxicity of water for fishes, phytoplankton and zooplankton. In effect there are several chemical processes due to the interaction of acid rains and the soil, as well as the water of lakes. First of all it may occur that in the water, owing to the presence of carbonic acid system  $\text{HCO}_3^-/(\text{Na})^+(\text{CO}_3^{2-})$  may act as buffer in many lakes. This is not the case of the lakes in Scandinavia because the soil is mainly constituted by granites.

#### *Acidification Processes in Water*



$$[\text{H}^+] \sim 1.10^{-5.7} \text{ a } 25^\circ\text{C}$$

Thus the changes of the geochemical composition of lakes represents a rather composite system which gives origin to:

- 1) Lowering of pH value of surface waters.
- 2) Increase of  $\text{HCO}_3^-$  in waters.
- 3) Indirect action of the acidity on the soils.

In effect higher  $\text{H}_3\text{O}^+$  concentration in surface waters may remove from soils metal ions, mainly  $\text{Al}^{+++}$ ,  $\text{Mn}^{++}$ , which are solubilized in water. The toxicity of these ions is rather high for aquatic life and can be a cause of the destruction of the fish species and even of the disappearance of fish population! A concentration of  $\text{Al}^{+3}$   $\mu\text{g}/1,270$  is considered toxic for most fish species. Attention was drawn to this fact in 1979 by Cronan and Schoefield in the U.S.A. Successively the study of the influence of these chemical changes on fish population has been thoroughly studied by Oden and Hultberg in Sweden, by Chester (1983) in the U.K., by Likens in the U.S.A. and by Hutchison and Whitby in Canada.

An impact on wildlife of acid precipitation in forests may cause the accumulation of heavy metals like lead and cadmium in mushrooms and mosses, which constitute a part of the food chain and thus may be dangerous for both wildlife and man.

Acid precipitations may also lower the  $\text{Ca}^{++}$  content of water in lakes, thus reducing the buffering capacity of the system. In addition to

$\text{Al}^{+3}$  and  $\text{Mn}^{+2}$  also other metal ions like copper, metal, cobalt, iron are formed. Also the presence of mercury in a lake's water has been studied. There is no evidence of the mobilization of mercury by acid rain. However, for one group of lakes in Sweden there is a correlation between the concentration of Hg in fish and pH. Airborne mercury may be responsible for that (communicated by Prof. Brosset). Moreover in northern countries the snow accumulated on the soil after scavenging from the atmosphere high quantities of acids, which when melting cause a decrease of pH of the lakes.

A further damage in the acidified lakes is the development of a moss, *Sphagnum* sp which leads to eutrophication of the water body as reported by Grahn and coworkers.

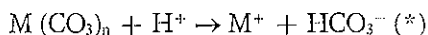
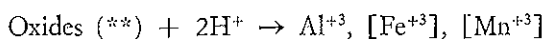
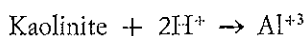
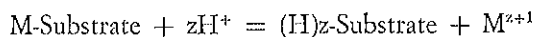
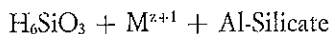
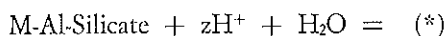
According to a recent report by Hultberg (1983), toxicity in aquatic systems is due not only to direct action of the low pH of the water and to the increase of metal ion content but also to the change of the carbon source from  $\text{HCO}_3^-$  to  $\text{CO}_2$ . This may influence the retention of phosphorous in soils by aluminium precipitation. This indicates substantial modification in the ecological equilibria in the aquatic system.

According to Hultberg (1983), in Sweden after 1978 a great number of observations have shown that in the lakes fish population has disappeared or decreased year by year, mainly perch, trout, and evach. After heavy rainfalls (1972) when the pH of Lake Bredvatten went down to 4, all the perch population died although perch is the most resistant fish species. Other populations affected by low pH are arctic char, sea trout, atlantic salmon, brown trout, and crayfish.

The same has happened in Norwegian lakes with black trout; also in West Germany some fish populations have disappeared from the lakes. The same observations were made in Canada and in U.S.A. The main toxic agent considered together with low pH is the increase of  $\text{Al}^{+3}$  concentration and the simultaneous decrease of  $\text{Ca}^{+2}$ . These events make acceptable the explanation of the toxic effect versus fishes based on the physiological stress of the fish to regulate, through the gill membrane, ion concentration which causes also difficulties in establishing the osmotic regulation. The same factors affect phytoplankton as the ecological equilibria of the lake is modified, and even the algae-invertebrate equilibria.

The increase of *Sphagnum*, as that of weeds, on the other hand is attributed to the presence of  $\text{CO}_2$  instead of  $\text{HCO}_3^-$  as the main source of carbon.

Zooplankton and zoobenthon are also modified by the chemical pheno-

*Ions Formation Processes from Soils*

mena occurring in acid lakes, e.g., the presence of *Keratella* sp., *Bosmina* sp. and *Diaptomus* sp. may be considered as biological indexes of the changes in the aquatic system. In zooplankton and in zoobenthon some species, like *Gammarus* sp. *Lepidurus* sp. *Astacus astacus*, are highly affected.

Moreover, lake acidity favours the development of aquatic insect like *Coleoptera*, *Hemoptera*, and *Megaloptera*, as well as some species of *Diptera*.

Amphibians, e.g. *Rana temporaria* and *Bufo bufo* suffer from lake acidification because of the ecological change and development of new species of algae.

Birds living near lakes are also affected because the content of metals, mainly Al, increases in fishes and plankton. Another important aspect of the effect of acid deposition is on soil microorganisms, especially in poorly buffered soils, as reported by R.J. Buck both affecting bacteria and fungi and their relative equilibria.

Even microorganisms affecting plants may find, as reported by W.H. Smith for foliar stem disease in trees, a stimulating agent in the increase of acidity and a modification in their behaviour toward plants.

## CONCLUSIONS

The present data, which with the available literature on this subject, give us an overall idea of the present state of knowledge and indicate a

(\*) M = Na, K, Ca, Mg

(\*\*) Fe<sup>+3</sup>, Mn<sup>+3</sup>, Al<sup>+3</sup>

number of gaps in the effects on life of acid precipitations, which represent so far the most important aspect of the fallout of chemicals formed in the atmosphere.

This means that more research is required. Although important progress has been made (e.g., a special program is devoted to crop diseases and insects and to vulnerable life steps) in the acid precipitation assessment programs planned in U.S., not sufficient space has been given to research on the effects on animal life and human health (E.B. Cowlings, 1982).

We believe that these correlations should be better studied and cleared because only from an exact diagnosis can it be possible to better protect the life of man and animals and all the ecological equilibria in the biosphere.

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## DISCUSSION

RANZI

The effects of acid rain on living beings, both animals and plants, are considerable. These effects are more evident in the north of Europe, where the soil is more acid than in the south, where it is more alkaline. Cases are known in which acid precipitation has caused great harm to persons, as well as to things. Deaths which have occurred in London, in the Mosa Valley, at Donora (U.S.A.) seem to be related to  $\text{SO}_2$  perhaps in combination with other toxic substances. An example usually given is that of Ducktown (Tenn.), where the discharge of  $\text{SO}_2$  from copper foundries completely destroyed the vegetation in the area and damaged the soil to such an extent that even today, a half century later, the vegetation has not managed to grow again.

Acid rain acts in a very complex way. Experiments, in which plants are sprayed with strongly diluted solutions of  $\text{H}_2\text{SO}_4$ , seem to show that the acidity of these solutions helps the base of the stem to grow. However, after a short time, the growth of plants treated in this way slows down. It appears that the acid acts on the soil by mobilizing a part of the available nitrogen. Forests are certainly affected to a great extent by the action of acid rain, and very serious damage can be seen in the industrialized areas of Germany, France, Poland and North America. Besides forestry production, which is affected the most, damage is also done to agricultural production. Interest in acid rain first arose to consider its repercussions in the agronomical field. As regards plants in general, and woods in particular, air pollutants penetrate into the leaves through the stomata and damage the plants' foliar parenchyma. The leaves exposed to  $\text{SO}_2$  become covered in spots and dry up, until only the venation remains.

Soil acidification causes the mobilization of cations, such as calcium, magnesium, potassium and aluminium, followed by lixiviation of metals: cadmium, copper, zinc and lead.

These alterations in soil composition lead to considerable changes in the related flora and fauna. Bacteria decrease and fungus flora increases. The chemical transformations occurring in the soil, due to the microorganisms contained in it, undergo change. The reduction in nitrifying bacteria brings about a slowing down in mineralization of nitrogen and in its fixation, while the decomposition of organic matter is altered.



Therefore the effect of soil lixiviation is to cause a reduction in the amount of nutrient elements.

A certain amount of aluminium is mobilized through the effect of acid precipitation and ends up in streams which carry it to lakes, where all life, both plant and animal, is harmed, to the extent, in many cases, of all the fish dying out. The increase of aluminium in the water causes intense production of mucus on the surface of fish gills, the result of which is to reduce gas exchanges through the gills, leading to death by asphyxia.

Besides aluminium, the amount of lead, manganese, cadmium, copper and cobalt is also rising in fresh water. In some cases analyses show an increase in methylmercury.

The increased concentration of such elements provokes mortality among algae, above all chlorophyceae, leading to a decrease in biomass and productivity of lakes. However, in some cases, if the acidity of the water succeeds in mobilizing phosphates, perhaps by solubilizing apatite or other phosphorus compounds, eutrophization of the water is aided.

The effect is more evident when the catchment basin lies in rock rich in silica (granite, quartziferous porphyry, etc.) with a thin covering of humus.

An effect of acid rain in streams is to increase the amount of filamentous algae. It is doubtful, however, that it is a case of direct action resulting from the composition of the water, rather than being due to a decrease in herbivorous animals. As acidification increases, the number of animal species in the water decreases. There is a sharp reduction in herbivorous insects, while in the case of carnivorous insects no such dramatic result can be seen.

In some cases the effects of acid rain can be partly offset by the hardness of water. One can take as an example the harmful effect of acid rain on mollusks' tests, less evident in lakes containing harder water.

The crustacean *Gammarus lacustris* can be regarded as a valid indicator of changes in the pH of a lake environment. It can, in fact, survive in water with a pH below 6.0. The bottom limit for *Asellus aquaticus*, on the other hand, is 5.0.

Fresh-water fish have disappeared from many lakes and fish-ponds in Scandinavia and Canada, causing serious economic loss. The first to disappear, due to their greater susceptibility, are the salmonids. So, for example, in the south of Norway where there is high acid precipitation whereas the neutralizing action of the soil is poor, about half of the lakes have lost their trout population. In an area of 13,000 km<sup>2</sup> almost all the lakes have lost their fish. In another further area of 20,000 km<sup>2</sup> the number of fish has been drastically reduced and they will soon disappear altogether. Between Telemark and Lista there are 14

streams where several years ago 10,000 kg of salmon used to be caught per year. Today this fish is practically non-existent, with at most 100 kg being caught per year. This is a tragic situation and will not improve until a stop is put to acid rain (\*).

MARINI-BETTÒLO

Professor Ranzi has mentioned some points that I had missed and I thank him very much for this. I think it is most important to have more information on these things because the impact is not only the theoretical aspect, there is also an economic aspect and I think it should be looked into with great care.

PHILLIPS

I have just a comment rather than a question. At the beginning of his talk Professor Marini-Bettòlo gave a list of emitted species which could cause direct harm to man, and missing from that list was lead. I think you could exclude it from the list on the grounds that there really is no interest in chemistry of the atmosphere; the chemistry really taking place in the internal combustion engine, or on the ground, is a local problem. In effect as it is emitted from internal combustion engines it does not travel very far, and this is a subject for action by individual governments rather than for a global approach, although there are studies around now which show that there may well be harmful effects of the direct ingestion of airborne lead.

MARINI-BETTÒLO

I thank you for this observation. It is quite important that the various governments take steps for the control of airborne substances. The phenomenon for the moment is limited or better known in the Northern Hemisphere, but we should be aware of the possibility of transport of substances which can cause damages to other countries.

(\*) A large part of the data referred to is taken from O. Ravera: *Un inquinamento recente: Le deposizioni acide e i loro effetti ecologici*, Cultura e Scuola, in press, and from bibliography in the article quoted.

See also K.W. Jensen: *Freshwater fish - a resource: Basis of accounts for Norway's natural resources* (J. Lag. ed.), Norwegian Acad. of Science and Letters, 1982, 107.

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# THE WATER CYCLE IN TROPICAL FORESTS, WITH SPECIAL REFERENCE TO THE AMAZON

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## SUMMARY

Tropical ecosystems were comparatively little disturbed during the colonization period, which started in the XVI Century. The difficulties encountered in establishing economically feasible production systems hampered the setting up of agricultural activities in the humid tropics. This difficulty still exists and even with present agronomic technology, many of the large scale attempts to use the humid tropics have failed. Therefore, as far as flora and soil quality are concerned, the humid tropic regions have only suffered major changes during the last 30 years, and in the Amazon region pressure has been exerted only during the last 10 years.

Until recently very little research work had been carried out to determine the relationship between plant cover in the area and the regional or global characteristics of the atmosphere. Our work has been developed in the Amazon region and we have tried to establish the relationship between the present climate equilibrium and the dense forest cover which extends over an area of more than 5 million km<sup>2</sup>. The research was carried out in successive stages, involving analysis of surface meteorological data, radiosonde data, satellite photographs, and analysis of chemical and isotope composition of rain water.

The general conclusion obtained through the different approaches was that the present dynamic equilibrium of precipitation and water regime

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depends on plant cover. The possible changes are analysed as a function of the available information.

## INTRODUCTION

The depletion of tropical rain forest is a comparatively recent phenomenon, with deforestation taking place at an ever increasing rate during the last 30 years. The tropical forests were comparatively little disturbed during the early colonization period, starting in the 16th Century. There were many reasons for this: the forest was a natural barrier and transport was difficult, hostile indigenous peoples made isolated settlements vulnerable, disease was (and still is) a major problem, and, maybe above all, it was quite difficult to establish large scale agricultural systems.

For example, all these factors have operated in Amazon. Even during the rubber boom of the late 19th Century colonization was primarily confined to locations on the riverbank which could be reached by boat. It was calculated that completion in 1912 of the Madeira-Mamoré railway line of 364 km cost one life for every sleeper laid (de Oliveira, 1983). We now know much more about tropical diseases, but the problems are far from being solved (da Costa Linhares, 1983). Failure in exploitation may be due to unexpected reasons. The well-funded rubber plantation of the Ford Motor Co. (Fordlândia) established near Santarem in the 30's failed by 1944 primarily because of fungus disease and an insect parasite. This was not a problem with the isolated trees of natural rubber in the jungle, but under plantation conditions the trees were close enough together for the infection to pass from one to another. At that time no effective pesticide treatment was available.

The frequently poor soils have led to much difficulty in establishing large scale cropping or pasture systems. The forest is virtually a closed system as regards nutrients, and except for nitrogen and phosphorus which are primarily in the soil, most of the nutrients are in the trees and litter (Klinge, 1976). When the forest is cleared by burning, the nutrients are in the ash and are readily lost by rain; at most they provide nutrients for two crops. This is the basis of the shifting cultivation of the indigenous people: when the land is exhausted they move to a new area. Permanent agriculture requires soil management to prevent erosion and fertilization to maintain fertility, and this has been lacking. This information is slowly being acquired (Sanchez *et al.*, 1982), but even in the last few years the

simple failure to apply phosphate fertilizer to pastures established on cleared forest at Paragominas near Belem has resulted in over 500,000 hectares of land being degraded, with severe erosion (Serrão *et al.*, 1979).

Despite these problems better knowledge of how to develop tropical forest areas, plus population pressure and financial incentives have resulted in the loss of half of the World's tropical forests, during the last 30 years. It is estimated that at the current rate over two-thirds of the remaining rain forest will have been lost by the year 2000 (Salati and Vose, 1983a). Estimates are that, as a minimum, 6 million hectares of primary forest are converted to secondary forest annually through selective logging, and a further 3 million ha converted to pasture and cropping. In Amazon alone the latest figures (Anon, 1982) suggest that a minimum of 2.3 million hectares of forest are being cleared annually.

Such extensive deforestation may possibly have profound effects on atmospheric chemistry, rainfall, and other climatic factors. Therefore, almost implicit in any consideration of the water cycle in tropical forests is the question: what effect does deforestation have? That is the theme of this presentation.

## TROPICAL FORESTS AND HYDROLOGY

On the whole hydrologists have been inclined to discount the possibility of land use changes affecting rainfall (Pereira, 1973). Moreover there has in the past been a tendency to minimize the role of recycling (UNESCO, 1971). Indeed, Linsley (1951) suggested that the concept of evaporation from the land is not important for continental precipitation, and therefore deforestation and improved drainage will have little effect on regional precipitation regimes. However, this view is changing and a recent report (WMO, 1983) notes, "it is possible that changes in land-use/land-cover may produce changes in the meteorology and certainly produce significant changes in the hydrology of the areas affected".

Why in the past has the potential rôle of precipitation recycling by tropical forest been minimized? There seem to be six or seven reasons for this: it is in the last 20 years that the rate of tropical deforestation has increased so greatly, previously the areas converted were small in relation to the whole; changes in land use have often taken place before definitive hydrological or local meteorological studies, so there is no good "before" and "after" data; there has been a tendency to regard regional

and sub-regional vegetation habitats as being defined mainly by soil type and temperature rather than rainfall regime; there has been an inclination to consider that evaporation is about the same for different vegetation types and is only reduced when rainfall itself is the limiting factor; the increased precipitation run-off resulting from deforestation, with consequent loss of water from the system, has not been adequately taken into account; in many areas of the world the probability of a major advective oceanic water contribution to precipitation e.g. in the tropical forest areas of S.E. Asia and Oceania, has masked the contribution from recycling.

Probably we have been fortunate in studying the water relations of tropical forests in the Amazon Basin because we have a clearly defined region, located on the Equator with a uni-directional source of oceanic water. Thus the horseshoe shaped Basin is characterized by a large plain bounded on the West by the Andes which are approximately 4000 m high, while in the North the Basin is limited by the Guiana Plateau having altitudes as high as 1000 m. To the South the Basin is bounded by the Central Plateau of Brazil with an altitude of about 700 m. The prevailing Trade winds blow almost continuously from the East and penetrate the whole region, bringing in oceanic water from the Atlantic. The result is a hot and humid climate which, over millennia, has led to the development of the tropical forest of central Amazon. Considered theoretically, if the forest were to be totally removed, there seems little doubt that, *if left undisturbed and similar global conditions existed*, a forest would again develop.

The timescale for this renewal is unknown, although palaeoclimatic evidence suggests it would be at least a thousand years, as can be seen from Table 1, due to Prance (1978) who used palynology data from Van der Hammen (1972, 1974) and comparable Mexican chronology. More recent pollen studies combined with 14-carbon dating suggest that there has been little grassland in the Manaus area since 4,000 B.P. (Absy, 1979; Irion, 1982). Charcoal has been  $^{14}\text{C}$  dated to 3,000-6,000 B.P., implying a drier climate that made forest fires possible (Soubies, 1980). In reality of course the land now being cleared in Amazon will not remain undisturbed, as the present rapid changes in land use now taking place i.e. roads, pasture, crops, mining, industry, etc. will result in semi-permanent modification.

Cochrane and Jones (1981) have argued convincingly that the savannas of tropical South America occupy a well defined habitat delimited by the climatic potential for growth. This has been defined primarily

TABLE 1 - *Climate and vegetation change in Amazon* (due to Prance, 1978).

| Date before present<br>(Millennia) | Climate                           | Duration<br>(years) | Vegetation                           |
|------------------------------------|-----------------------------------|---------------------|--------------------------------------|
| Last glacial period                |                                   |                     |                                      |
| 12,000                             | wet and cold                      | 1,000               | forest returning                     |
| 11,000                             | dry and hot                       | 1,000               | savanna                              |
| 10, - 9,000                        | wet and cold                      | 2,000               | forest                               |
| 9, - 2,000                         | dry and hot                       | 7,000               | savanna with large<br>forest refuges |
| 2,000                              | slightly wet and<br>slightly cold | 1,000               | forest                               |

by the wet season potential evapotranspiration regime, which was found to be about 900 mm for savanna having a 6 months wet season. Tropical forest can be similarly characterized, and it is interesting to compare the savanna figure with the Amazon forest, where evapotranspiration is of the order of 1200-1600 mm yr<sup>-1</sup>. Even more significant is the comparison of precipitation and evapotranspiration for oceans, continents and Amazon shown in Table 2. It is clear that the high Amazon evapotranspiration rate is much more characteristic of oceans than it is of average continental evapotranspiration.

TABLE 2 - *Comparison of precipitation and evapotranspiration in Amazon with averages for oceans and continents.*

|            | Precipitation<br>mm yr <sup>-1</sup> | Evapotranspiration<br>mm yr <sup>-1</sup> |
|------------|--------------------------------------|---|
| Amazon     | 2300                                 | 1200 - 1600                               |
| Continents | 710                                  | 470                                       |
| Oceans     | 1100                                 | 1200                                      |

The close connection between the forest and precipitations is clearly indicated by the preferential development of local cloud over the forested areas of Amazon and, viewed from the air, great "pillars" of cumulus sometimes appear to arise from the very top of the forest. For example Friedman (1977) noted that the western half of Marajó Island, which is heavily forested, received daily rain throughout the year. While thunderstorms built up over the forested half, none appeared over the treeless savanna eastern half.

As the Penman equation (Penman, 1963; De Bruin, 1983) for estimating evapotranspiration can be applied to different vegetation types including, with some modification, forest, there has been a tendency to believe that combined evaporation and evapotranspiration should recycle water to the atmosphere to the same extent whatever the type of vegetation e.g. whether forest, pasture or annual crops. Data from the Zaire Basin (Penman, 1963; quoted by Edwards and Blackie, 1981) have been supportive of this view, but what is overlooked is that a large part of the Zaire Basin is swampland, and that the conclusions are based on simple measurements of relatively undisturbed vegetation. Moreover, considerations based simply on evapotranspiration do not take into account the fact that deforestation tends to increase surface run-off, with reduced water recharge of the soil systems. Thus although there may be still high evapotranspiration following deforestation, it is likely to be drawing from a decreased soil water store.

Recent thinking has suggested that water consumption from bare soils and partial vegetation cover is between 400 and 500 mm yr<sup>-1</sup> whereas the corresponding figure for mature forests is 700-900 mm yr<sup>-1</sup> (Baumgartner, 1979). Similarly Molion and Bettancurt (1981) have demonstrated that evaporation differences among cover types, assuming water is not limiting, can be quantitatively explained purely in terms of energy considerations, and that forests evaporate more water than any other cover type, as much as twice that from bare soil. Practical reasons support this: tree roots exploit a large volume of soil to greater depths than most annual crops or replacement vegetation and water recharge of forest soils is good.

Simple logic dictates that if forest is cleared then the resulting decrease in evapotranspiration must lead to increased run-off, if precipitation remains the same in the short term. The problem can also be approached from the opposite point of view: what effect has deforestation on run-off? It should be noted that the forest canopy protects the forest floor from the direct impact of rain, while surface litter and organic matter helps to



ensure good water absorption. The vegetation maintains a good soil structure and thereby maintains percolation and good water recharge of the system.

Reduced infiltration rates on newly cleared tropical forest soils is found to be normal (Sanchez, 1976), and especially in Surinam (Van der Weert, 1974) and in Peruvian Amazon (Seubert, 1975) has been especially associated with compaction effects from bulldozer clearance. Schubart (1977) reported for cleared primary forest near Manaus that infiltration rates of 5 year old pasture were less than a tenth of the rates for forest. Charreau (1972) found in West Africa that run-off was 20 or more times greater from cultivated and bare soils than from forest.

Deforestation does not always result in increased run-off: Bonell *et al.* (1983) found in tropical rainforest of Queensland, Australia, that the prevailing rainfall intensities ( $4239 \text{ mm yr}^{-1}$ ) frequently exceed the saturated hydraulic conductivity of the profile. There is therefore rapid saturation of the top layer and the generation of surface flow; thus no change in run-off hydrology occurred following deforestation although clearing increased soil erosion rates tenfold. In general, deforestation seems initially to increase peak run-off of river flows, which later stabilize at lower levels. In Malaysia, conversion of natural forest to rubber or oil palm doubled peak storm flows and halved low flows with greatly increased erosion. In one catchment low flows were reduced to one-quarter (Daniel and Kulasingam, 1974). In Guatemala the once major Montagua River is more than 50 per cent reduced in volume, following the loss of 65% of natural forests during the last years (Troughton, 1980).

## FATE OF PRECIPITATION FALLING ON THE FOREST

### *Interception, Throughfall and Evapotranspiration*

The impact of forest on the hydrology and climatology of a region must in effect be the sum of events taking place on individual forested areas, such as watersheds and basins. The interception of precipitation and evapotranspiration by the forest are major events which can be determined over a defined area. In Brazil, measurements of interception in sub-tropical forest were carried out by Freise (1934, 1936) almost fifty years ago. He found that 34% of precipitation became throughfall, 28%

represented stem flow, 20% was evaporated from the crown of the trees with 18% assigned to general evaporation and losses in the bark.

More recent work has not confirmed the large proportion of stem flow. Work by Franken *et al.* (1982), carried out in typical Amazon high forest near Manaus, used a system of rain gauges in cleared areas and in the forest canopy, with an extensive series of stem flow collectors. They found that 77.7% of average precipitation reached the soil surface as throughfall, 22% of the rain was intercepted by the canopy, while stem flow only represented 0.3% of the total.

Clearly, local conditions, such as tree species, the number of trees per unit area and the average intensity of the precipitation will affect the proportions. Thus in the Amazon forest in the region of San Carlos, Venezuela, Jordan and Heuveldop (1981) found 87% throughfall and 8% stem flow, while only 5% of precipitation was intercepted.

In Malaysian tropical forest Sim (1972) found that interception varied between 25 and 80% as a function of precipitation class. Near Manaus, interception of rainfall, Table 3, was as great as 84.6% for the rainfall class of > 5 mm, with a throughfall of only 15.4%, while for the rainfall class 60-70 mm interception was reduced to 25.5% and throughfall increased to 74.1%. Stem flow was negligible regardless of rainfall class (Franken *et al.*, 1982).

A further estimate of evapotranspiration was made (Leopoldo *et al.*, 1982b) for high forest on a model basin of 23.5 km<sup>2</sup>, 60 km north of Manaus, which is drained by a large stream. This area has an average rainfall of 2000 mm. Measurements were made of precipitation, inter-

TABLE 3 - *Forest throughfall related to rainfall intensity* (Franken *et al.*, 1982).

| Rain<br>Distribution | < 5.00 mm | 5-10 mm<br>per cent | 10-20 mm | 60-70 mm |
|----------------------|-----------|---------------------|----------|----------|
| Interception         | 84.6      | 41.2                | 28.7     | 25.5     |
| Stem flow            | 0.0       | 0.0                 | 0.2      | 0.4      |
| Throughfall          | 15.4      | 58.8                | 71.0     | 74.1     |

ception and drainage, making it possible to calculate evapotranspiration. The combined results of the two studies (Franken *et al.*, 1982 and Leopoldo *et al.*, 1982b) showed that on average 25.6% and 18.7% of rain was intercepted by the forest and evaporated to the atmosphere, while 48.5% and 62.0% was transpired by the forest, while run-off accounted for 25.9% and 19.3% respectively at each location. This means that evaporation and transpiration combined represented as much as 74.1% and 80.7% at the two sites (Figure 1).

#### *Water transit time in forest soil*

It has been found that certain heavy rainstorms have enhanced concentration of the heavy isotope  $^{18}\text{O}$ . The difference in  $^{18}\text{O}$  concentration between the storm rain and the existing soil water has made it possible to trace the passage of the naturally labelled rain down the soil profile as in Table 4 (Leopoldo *et al.*, 1982a). It can be seen that although a rainstorm very quickly penetrates a depth of 15-25 cm and reaches 50 cm depth in 2 weeks, it can take almost two months to be detectable at 120 cm depth.

Further studies followed the annual variation in  $^{18}\text{O}$  and Deuterium content of precipitation and of stream water. It was found that the isotopic composition of the rainwater varied with season of the year, but this was not reflected by changes in the drainage water, suggesting a mixing of waters and a high soil water storage.

TABLE 4 - *Transit time of rainwater in Amazon forest soil determined by  $\delta^{18}\text{O}$  (Leopoldo *et al.*, 1982a).*

| <i>Depth</i> | <i>Time</i> |
|--------------|-------------|
| 15-25 cm     | 1 week      |
| 50 cm        | 2 weeks     |
| 80 cm        | 3-4 weeks   |
| 120 cm       | 5-8 weeks   |

TOTAL WATER RECYCLED BY  
THE FOREST = 74.1%

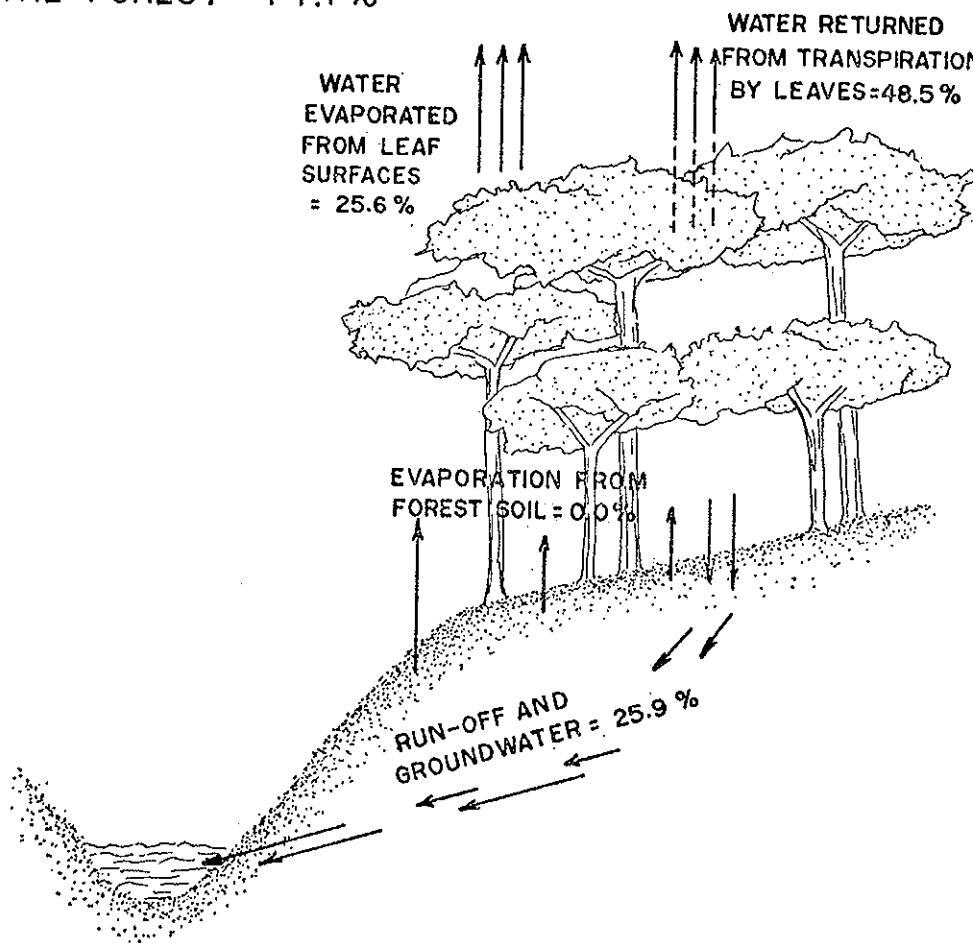


FIG. 1. Fate of precipitation falling on Amazon high forest.

Gonçalves (1979) studied the residence time of superficial waters in some hydrographic basins in Amazon and found values varying from 1.1-2.3 months. Salati and Ribeiro (1979) noted that deforestation in the Amazon Basin is likely to reduce the water residence time.

## WATER BALANCE AND RECYCLING OF PRECIPITATION

The estimates of evapotranspiration of high forest given in the previous section, clearly relate to a local situation. Average evapotranspiration, and related recycling of precipitation must clearly be less, because not all of the Basin is covered with forest. Water balance and recycling estimates are possible because of the measurements of the Amazon River flow made by Oltmann (1967). Water balance can be estimated by meteorological data or radiosonde data and recycling confirmed by stable isotope technique.

### *Evidence for water recycling using climatological methods*

Molion (1975) employed climatological data (average charts of wind and specific humidity seasonal values) and the method of Penman (1963) to estimate that about 52% of the rain falling on the region was lost through the river. Similarly Villa Nova *et al.* (1976) applied Penman's method adapted to forested regions by Shiau and Davar (1973) and calculated that evaporation represented 54%, and 46% of rainfall was lost to the river.

Allowing for the scale of the system and the inherent inaccuracies these estimates are very close.

### *Evidence for precipitation recycling using aerological methods*

Marques *et al.* (1977) obtained data for water vapour fluxes and computed precipitable water from the analysis of 658 daily meteorological upper air observations by radiosonde at stations in Manaus and Belem. The study showed that the Atlantic Ocean water vapour contributed 52% to regional precipitation, and that the water vapour was predominantly supplied to the region by the flux in the east-west direction. It was noted that a significant role is played by local evapotranspiration in the generation

of rain in the area. Evapotranspiration apparently contributed to 48% of the rains in the region studied.

Taking the studies together it can be concluded that the Amazon Basin receives  $11.87 \times 10^{12}$  m<sup>3</sup>/year of rain water, losing  $6.43 \times 10^{12}$  m<sup>3</sup> through evapotranspiration and  $5.45 \times 10^{12}$  m<sup>3</sup>/yr through river discharge (Fig. 2). Marques *et al.* (1980) observed that the amount of water vapour coming from the ocean is of the same magnitude as that lost through the evapotranspiration. It should be noted that the calculation of water vapour from the ocean is by methods and data quite independent of the calculation of evapotranspiration.

### *Isotopic estimation of water recycling*

Another independent method has been used to prove and estimate the recycling of water vapour in Amazon, using <sup>18</sup>O and D (deuterium) concentrations in rain and river waters (Salati *et al.*, 1979). The isotopic method is simple in principle and gives a deeper insight into the hydrological cycle, such as an estimate of the water vapour that enters and leaves the region.

Water has various molecular species depending on the hydrogen and oxygen isotopes of which it is composed. The stable hydrogen isotopes are <sup>1</sup>H and <sup>2</sup>H or D. The stable oxygen isotopes are <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O. Different species of water molecules are formed by the combination of these various isotopes, e.g. HH<sup>16</sup>O, HH<sup>18</sup>O, HH<sup>17</sup>O, HD<sup>16</sup>O, etc. Of these molecules the most important, due to their concentration and interest for our application, are HH<sup>16</sup>O and HH<sup>18</sup>O.

In the process of evaporation of water in the ocean, molecules of the type HH<sup>16</sup>O, which have a molecular mass equal to 18, are evaporated before molecules of the type HH<sup>18</sup>O which have a molecular mass of 20. During evaporation there is, therefore, an isotopic fractionation and the vapour from sea water has an <sup>18</sup>O concentration about 8% less than the ocean concentration. As this water vapour enters the continent it will condense and probably precipitate to become soil and river water. Since the heavier molecules condense first, the process of cloud formation and precipitation leads to isotopic depletion of residual water vapour. This should mean that, with a prevailing easterly wind, the water vapour of the westerly regions should have a lower concentration of <sup>18</sup>O.

Systematic measurements of the isotopic composition of the Amazon region rain were made, and it was noted that the decrease in <sup>18</sup>O concentra-

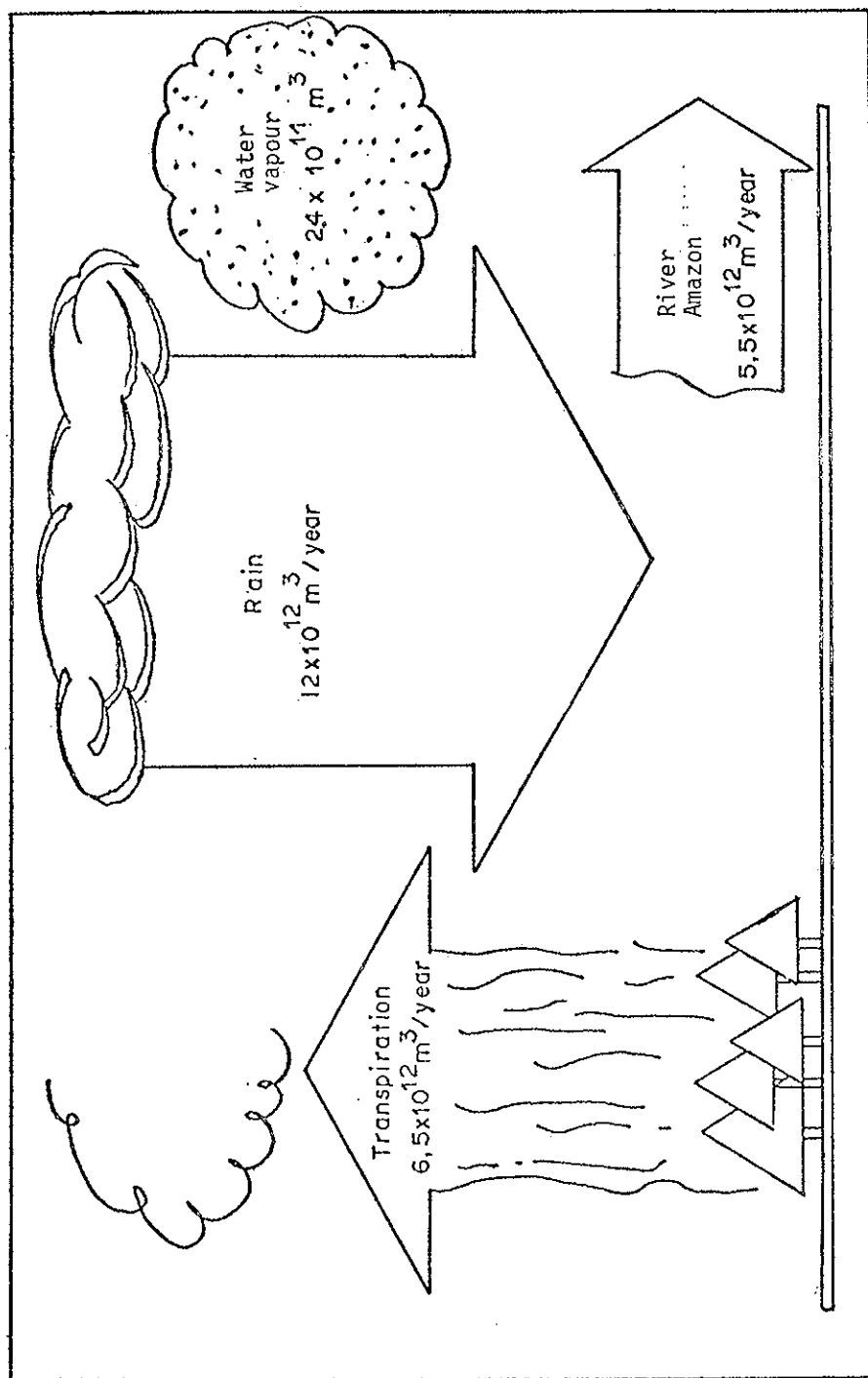


FIG. 2. Gross water balance in the Amazon Basin (Marques *et al.*, 1979).

tion was less than that expected in a process of continuous removal of water vapour through precipitation. This situation might be explained if we suppose that the water vapour produced by evapotranspiration mixes with the oceanic vapour and that rain in a certain place is formed by a mixture of these two vapours.

Measurements of  $^{18}\text{O}$  and D in rain and river waters have indeed made it possible to confirm (Dall'Olio *et al.*, 1979; Salati *et al.*, 1979) the importance of re-evaporated water for the water balance throughout the Basin, and in particular to establish a model indicating the relationship with the new oceanic water. There is a predominant zonal flow from east to west (Newell *et al.*, 1972) and vapour influx from the Atlantic Ocean was estimated from the wind and humidity measurements by radiosonde at Belem. The central east to west region of the Basin between  $0^\circ$  and  $5^\circ$  of the latitude was considered to be subdivided into eight  $3^\circ$  segments between Belem ( $48^\circ 30'$ ) and just west of Benjamin Constant ( $72^\circ 30'$ ).

Overall the small inland gradient of the isotopic composition of the precipitation confirmed the importance of the re-evaporated moisture in the water balance of the area. A model was then developed as in Figure 3, which suggests that in any one segment the rainfall comprises about half derived from evapotranspiration within the segment area, while the other half comes from water vapour derived from the neighbouring eastern segment, conveyed by prevailing winds.

## INTERACTION OF LOCAL AND CONTINENTAL FACTORS IN AMAZON

As we have noted, there is good agreement between evidence for water recycling in the Amazon obtained with different methods, such as the more conventional climatological ones and the more recent aerial and isotopic methods. However, in an overall consideration of precipitation patterns in Amazon it is necessary to distinguish between the locally derived cumulus clouds, mainly involved in the recycling process, and which are initiated by latent and sensible heat, and the high tropospheric clouds of the South American Continent. There is still little information as to the manner and extent to which local recycling interacts and is influenced by continental factors.

In the Amazon Basin there are two different rainfall regimes — in the central part and a portion of the western area of the Basin there is a definite dry period, but in the eastern and western end of the Basin there



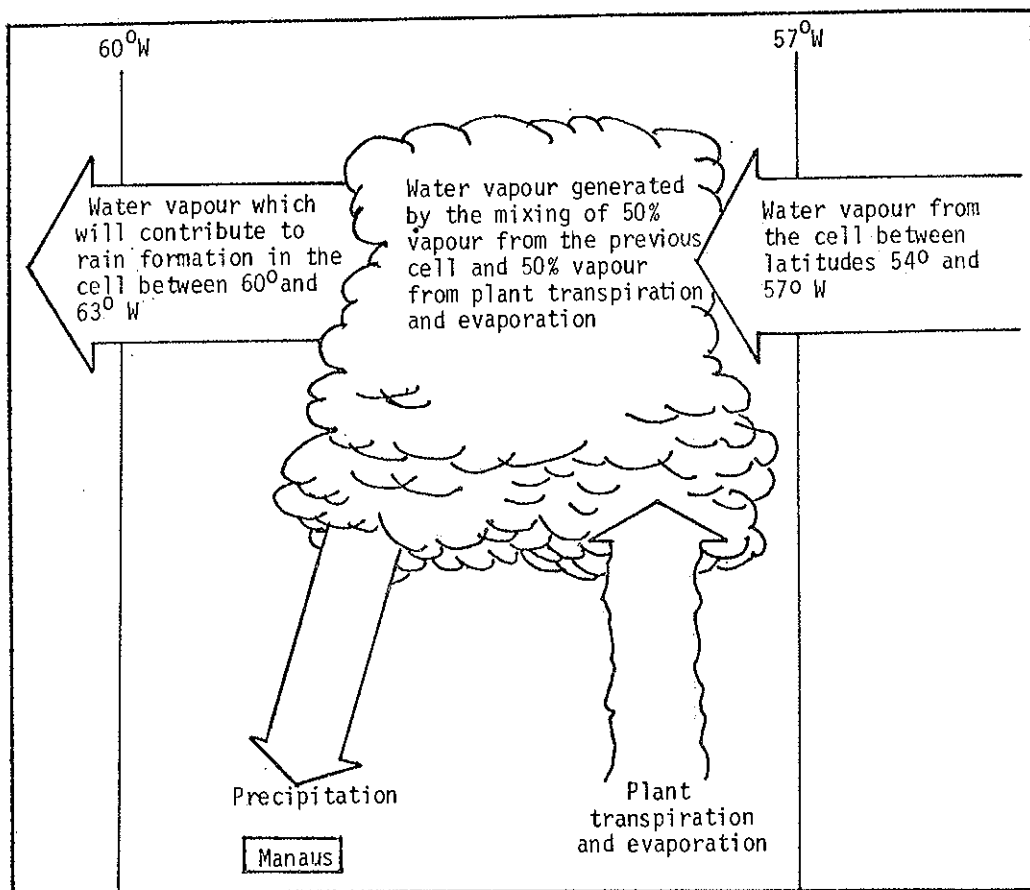


FIG. 3. General scheme to explain rain formation in Amazon from two sources of vapour: the Atlantic Ocean and the forest. The region was divided into  $3^\circ$  longitude strips. The above scheme indicates the city of Manaus (Dall'Olio *et al.*, 1979 and Salati *et al.*, 1979).

are frequent rains the entire year. The Amazon climate is characterized by mainly easterly winds and the main influx of advective atmosphere water into the Basin comes from the Northern Hemisphere Trade winds.

Classically, it has been considered that the different rainfall regimes are determined by interception of the Intertropical Convergence Zone (ITCZ) and the Equatorial Atlantic air mass in the case of the eastern region and the presence of the Equatorial Continental air mass in the western-most regions. Satellite imagery from LANDSAT has suggested (Salati *et al.*, 1979) some revision of this classical description. They did

not find indications of north-south movement of water vapour within the Basin as would be expected from the entrance of an air mass from the North Atlantic.

Kousky and Molion (1983) have more recently described the tropospheric circulation pattern and its relation to rainfall in the Amazon Basin. They noted that in summer the general pattern of precipitation is closely linked to the position of an upper tropospheric high pressure system whose centre generally forms over Bolivia and which dominates the circulation over South America. This system weakens and tends to move northwards during fall and winter, corresponding to the dry season in the southern regions of the Basin. These studies suggest that variability in the rainfall pattern may be due partially to persistent convergence zones, originating from or associated with Southern Hemisphere frontal systems. Additionally, there appear to be lines of instability associated with maritime winds. On occasion these lines propagate inland and can apparently remain active for up to 48 hours during which time they cross the entire Basin, as far as the Andes.

These large scale circulation effects are not inconsistent with the data of Salati *et al.* (1979) who noted a distinct seasonal and regional pattern of stable isotope composition, thus indicating the Basin to be inhomogenous from the hydrometeorological point of view. For example, during the months of July-September there was a complete absence of an inland  $\delta^{18}\text{O}$  isotope gradient. It was concluded that there are additional sources of advected moisture in the interior of the Basin, and that the assumption of negligible latitudinal air exchange breaks down in the western part of the Basin, which is an area of convergent flow.

Although the isotope data confirmed that evapotranspiration becomes the dominant factor during the Southern Hemisphere winter months, it was observed that while large amounts of water are apparently recycled in the central and eastern part of the Basin, in the western and southern margins the role of evaporated water is less important.

Unusually low  $\delta^{18}\text{O}$  values are sometimes found throughout the Basin during April and May, and occasionally during the late summer months of December-March; and these are not due to any large inland isotope gradient. It is concluded that the low isotopic values are imposed on the Basin from the outside. During this period the ITCZ moves southwards into the latitude of the Amazon Basin and there is a marked connection between the position of the ITCZ and the isotope data, implying that the vertical mixing in the Convergence Zone and the resultant

cloudiness affects both the isotopic composition of the rain patterns. Satellite pictures showed seasonal shift in the wind pattern such that the latitudinal component of air motion is clearly mirrored by the isotope data (Salati *et al.*, 1979).

Thus, although on average about half the water vapour in the Amazon Basin is recycled, external factors, apart from the regular water vapour influx from the North Atlantic, exert from time to time a major influence on the system. The nature of these effects and further knowledge of vapour flows into and out of the Basin requires further monitoring of precipitation patterns and isotopic analysis over a wider area, coupled with radiosounding studies (Salati *et al.*, 1983a).

## THE FOREST AND ATMOSPHERIC CHEMISTRY

Away from cities the natural background level of chemical species in Amazon Basin atmosphere is extremely low. Thus, Artaxo Netto *et al.* (1982a,b) used proton induced X-ray fluorescence analysis (PIXE) to determine that the total concentration of the natural Amazon aerosol was under  $10 \mu\text{g}/\text{m}^3$ , one of the lowest natural backgrounds ever recorded. This measurement was taken about 60 km north of the busy city of Manaus, confirming incidentally the prevailing east-west direction of the wind.

C, N and O comprise the major portion of the substrate particles, amounting to 80% of the total mass of natural aerosols and 99% of aerosols from brush-fire areas. As would be expected, deforestation by burning adds substantially to the aerosol nutrient content, as shown in Table 5. From this and the work of Lawson and Winchester (1979) there seems to be general agreement that large particulate matter of natural aerosols, such as Al, Si, Ca and Fe come from the soil, while fine particulates like S and K come from vegetation.

As already mentioned, the mature Amazon high forest is almost a closed system as regards nutrients. Few nutrients are lost, and these are balanced by inputs of nutrients in precipitation, although the concentration is low. Thus preliminary data for nitrogen have been calculated for the model basin near Manaus (Salati *et al.*, 1982) and it was found that for the months of May and June 1980, total mineral N input was 0.022 and 0.020 kg N/ha<sup>-1</sup> respectively. This is clearly a very low input, even when expressed on an annual basis. Greater total-N figures were calculated from

TABLE 5 - Concentration ( $\text{ng.m}^3$ ) of elements in Amazon aerosols (derived from Artaxo Netto *et al.*, 1982a).

| Element | Natural forest aerosol<br>60 km north of Manaus | Typical aerosol from<br>forest burning area,<br>valley of Rio Madeira |
|---------|---|---|
| Al      | 43.59   | 6264  |
| Si      | 74.41   | 31812   |
| P       | 13.30   | 20172   |
| S       | 374.10  | 18254   |
| Cl      | 72.99   | 9170  |
| K       | 189.90  | 42378   |
| Ca      | 24.81   | 37345   |
| Ti      | 7.04  | 1234  |
| V       | 9.36  | 2066  |
| Cr      | 3.72  | 143   |
| Mn      | 0.82  | 2405  |
| Fe      | 37.96   | 2816  |
| Ni      | 1.95  | 0   |
| Cu      | 0.23  | 434   |
| Zn      | 9.31  | 318   |
| Br      | 1.66  | 727   |
| Pb      | 5.01  | 1482  |

regional analyses of rain water, indicating a basin-wide input of about  $4.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ .

Based on the data of Stallard and Edmond (1981) it can be calculated that "average" Amazon rainwater contains ( $\mu \text{ moles l}^{-1}$ ): 12.4 Na, 1.0 K, 1.2 Mg, 1.1 Ca, 13.7 Cl, 5.1  $\text{SO}_4$ , 2.1  $\text{NO}_3$ , 0.5  $\text{NH}_4$  and 0.0 Si. Of course there is some variability depending on location, etc. This is well seen in the case of  $\text{Cl}^-$ , the concentration of which declines from east to west and is negligible in upper Amazon precipitation; tending to confirm the insignificance of Pacific Ocean water for Amazon precipitation.

Apart from the release of inorganic chemical species by forest burning, the major effect of deforestation is to add substantial amounts of  $\text{CO}_2$  to the atmosphere (Bolin, 1977; Bolin *et al.*, 1979; Woodwell *et al.*, 1978).

As is now well known, the significance of increased atmospheric CO<sub>2</sub> concentration is that CO<sub>2</sub> is a key absorber of thermal infrared radiation in the atmosphere, and a large increase in global CO<sub>2</sub> levels could result in global temperature rise (Woodwell, 1978; Niehaus, 1979).

Estimates of standing biomass in the Amazon high forest are 500-1000 tons ha<sup>-1</sup> and it is the largest remaining tropical forest. One calculation has estimated (Troughton, 1980) that if half its carbon was released over the next 20 years, and half of that amount remained in the atmosphere, then it would increase the CO<sub>2</sub> concentration of global atmosphere by about 5%. The Amazon River carries much particulate and dissolved organic carbon to the ocean, much of which must ultimately become CO<sub>2</sub>. Similarly, major forest debris such as floating logs, have been calculated to contribute approximately  $1.6 \times 10^6$  t C yr<sup>-1</sup> to the biosphere (Kempe, 1982; Richey, 1982).

The soil organic matter of cleared tropical forest contributes substantially to atmosphere CO<sub>2</sub>. About 25% of organic carbon is lost from forest soils within 12 months of clearance (Miller *et al.*, 1982). When it is considered that a typical forest soil contains over 100 ha<sup>-1</sup> of organic matter in the first 30 cm and about the same amount from the 30-100 cm horizon (Klinge, 1976) then it is clear that the potential production of CO<sub>2</sub> is very high. Ewell *et al.* (1981) studied slash and burn technique at a Cost Rican wet forest site. They found that after burning, the forest soil evolved CO<sub>2</sub> at such a rate that after 154 days decomposition and respiration as much C would be released into the atmosphere as was released by the burn.

Globally, the net carbon loss from tropical forests into the atmosphere from tropical deforestation and changes to secondary forest, pasture and crops, has been estimated (Seiler and Crutzen, 1980; Dickinson, 1981) to be about  $1.0 \times 10^{12}$  kg carbon, or equivalent to about 17% of that due to fossil fuel burning. This amount tends to support the view that the current increase in atmospheric CO<sub>2</sub> is primarily due to increased fossil fuel combustion (Niehaus, 1979; Broecker *et al.*, 1979). Nevertheless, there is sufficient uncertainty in the basic data, e.g. the rate of deforestation and the amount of biomass, to permit wide variation in the final estimates. Thus, other estimates have suggested that the release of carbon due to tropical deforestation is  $3 \times 10^{12}$  kg carbon or even more, with overall releases from biota estimated to approach  $6 \times 10^{12}$  kg carbon (Woodwell, 1978; Woodwell *et al.*, 1978). This latter amount is more or less equivalent to that released by fossil fuels.

## POTENTIAL EFFECT OF DEFORESTATION ON THE REGIONAL WATER CYCLE

The solar energy which falls on the central Amazon region i.e. near Manaus is on average  $425 \text{ cal cm}^{-1} \text{ day}^{-1}$ , which is used principally for evaporation of water and the evapotranspiration of plants (Villa Nova *et al.*, 1976). It is estimated that 50-60% of the solar energy is used in this way.

In the case of deforestation on a large scale the energy balance will be altered. A large part of the energy which today is used by plants in the process of transpiration will be used for heating the soil and air. The water balance is inevitably related to the energy balance, as indicated in Table 6. It is clear that the Bowen ratio of sensible to latent heat will be modified by removal of forest, and this represents change in the exchange of energy between surface and atmosphere. Fraenzle (1979) has noted that quite a large change in albedo does not yield a significant change in production of sensible and latent heat. The Bowen ratio can be greatly altered by deforestation but sensible heat remains essentially the same in the short term, so what is changed is principally evapotranspiration.

Deforestation will affect the water cycle directly with a tendency towards greater surface run-off, as the replacement vegetation or bare soil

TABLE 6 - *Forest Energy and Hydrological Cycles are Linked.*

|         |   |   |
|---------|---|---|
| Albedo  | = | Reflected Solar Energy  |
|         |   | Incident Solar Energy   |
|         | = | 0.13 Tropical Forest<br>0.16 Savannah<br>(0.1 - 0.5, Soil)                        |
| Bowen * | = | Sensible Heat (H)   |
|         |   | Latent Heat (Evaporation)   |
| Ratio   | = | 0.25 (Forest)<br>0.50 (Bare Soil)<br>2.00 (Extreme Suggestion for Cleared Amazon) |

\* Changes primarily due to E.

will retain much less water. Even with techniques such as contour ploughing and terracing, the water loss from surface run-off will be greater, and the soil less permeable than the forest soil with its mass of roots. Thus there will be an increase in the amount of water drained off by streams and rivers, especially during heavier rains, and a corresponding decrease in the amount of water available for evaporation and transpiration.

With less water available for evapotranspiration there will be a decrease in relative air-humidity, which will alter the energy balance. The incident solar energy instead of being used for water evaporation will be used for heating the air. This phenomenon was noted by Ribeiro and Santos (1975) in an area of "campina" near Manaus, where air temperatures were found to be much higher than in the forest. Similarly Cunningham (1963) recorded that forest clearance in Ghana resulted in maximum soil temperature at 7.5 cm depth increasing from 27 to 38 °C. The effects of deforestation on air temperature can therefore be noted even in small deforested areas.

It was noted (Salati *et al.*, 1983a) that in small clearings there is likely to be little measurable effect, because the drier air will be swamped by moist air from surrounding forest. However, the recycling of water will have been reduced by a small amount, and the effect of a great number of small clearings could in aggregate be very large. Deforestation of large areas, say greater than one kilometer and less than one hundred kilometers in diameter, should result in a significant reduction in water returned to the atmosphere, diminished local cloud cover and an increase in solar radiation. Precipitation due to local recycling is likely to be reduced.

Reduced local precipitation could have severe effects in central Amazon, where there is already a distinct dry period. If a relatively small reduction in annual rainfall resulted in an extension of the dry period there could be serious consequences. Fearnside (1982) noted that in Manaus in 1979 there was a period of 73 days without rain. If this became common, then inevitably there would be marked ecological changes. There have been a number of attempts to model the effect of Amazon deforestation on precipitation and temperature, and we have recently reviewed them (Salati and Vose, 1983b and c), and concluded that the Henderson-Sellers (1981) suggestion of a decrease in rainfall of 600 mm yr<sup>-1</sup>, and a small temperature increase is most valid of the current predictions.

Within Brazil, reduced precipitation in Amazon could mean that less water vapour was available for export to Central Brazil i.e. the cerrado area. Marques *et al.* (1979, 1980) determined from radiosonde studies

that water vapour is exported south from the Basin to Central Brazil and to the Chaco Paraguaio in almost every month of the year, but principally in March and December. Less rainfall in these areas could have consequences for cropping.

As Amazon accounts for 30% of the land area of the 20° Equatorial belt it has, together with the Congo region, a marked degree of continentality. Thus large changes of land surface cover in these areas due to deforestation could affect regional climates. In such large scale studies it is necessary to consider the influence of the variation of the quantity of water vapour which condenses in the higher parts of the atmosphere, as it is during evaporation that solar energy is transformed into latent heat and is released in the highest layers of the atmosphere where the water vapour condenses to form clouds. This energy is partly responsible for the circulation movements of the upper atmosphere, while part of the water vapour is transferred to the polar regions, where upon condensation it releases energy. This serves to transfer energy from the equatorial to polar regions. Estimating the climatic consequences of deforestation on a continental or global scale involves many problems, as recently emphasized by Wilson and Henderson-Sellers (1983).

Despite past suggestions (Newell, 1971) that Amazon deforestation might affect the atmosphere general circulation, the present general consensus seems to suggest (e.g. Dickinson, 1981) that tropical deforestation, while it might cause local changes, is not likely to cause global climate change greater than due to natural climatic fluctuations. However, the consequences of deforestation on the climate, whether micro-, meso- or macro-, is still an open question.

More data from remote sensing of general weather patterns, better and more detailed information of water vapour circulation patterns at local level, and improved modelling studies should eventually remove some of the uncertainty. In the meantime, the likelihood of at least local disruption of hydrological cycles seems sufficiently great that a conservative approach to tropical deforestation seems highly desirable.

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# EFFECTS OF CHEMICAL EVENTS ON ENVIRONMENT IN AFRICA

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## 1. ECOLOGICAL CHANGES

Africa with less than 6% of its area covered by tropical forest is one of the least forested areas in the tropical region [1]. At the same time Africa has one of the fastest growing populations [1]. There are at present over 146.1 million heads of cattle with an annual growth of 1.7 percent. At the same time the number of sheep and goats in Africa have been estimated to be 250.6 million heads with annual growth rate of 2.1 percent [1]. By the year 2000 there will be 169.8 million heads of cattle, 292.8 million heads of sheep and goats [1]. Increased livestock population will accelerate rangeland deterioration, soil erosion and desertification. The amount of soil dust arising from areas with no vegetation cover may change the sun's albedo of the region.

It is not only the increase in livestock population which has deleterious effects on Africa's environment, but the human population will also result in high pressures exerted on the existing life-supporting resources. Africa's increasing population must be fed, they must be housed, they deserve decent jobs and standards of living as a right. In order to provide for the above the African peasants have to clear more land areas occupied by virgin forests for shifting to agriculture, livestock raising and settlement. According to the study group on "The Global 2000 [1], Report to the President of the U.S.", there will be 50-70 percent population increase in the areas practicing shifting agriculture, the area of land burned and cultivated each year by shifting agriculture will also increase. The study estimates that 25 percent of the land surface primarily in the

tropical region is occupied by 300 million people who practice shifting agriculture. Thus, shifting agriculture on lands that cannot sustain continued intensive agricultural use are beginning to damage permanently the productivity of the area and to reduce its carrying capacity, according to the report.

A second compounding factor is that to cook food energy must be used. The surest alternative energy source for the peasants is firewood. The rural people depend on firewood for cooking and lighting, the increasing urban population also depends to a large extent on firewood or charcoal. The burning of forests for shifting agriculture and the burning of wood for charcoal making increase the amount of carbon dioxide and particulates in the atmosphere.

Africa is rich with variation of traditional cultures which have existed for centuries in equilibrium with their environment. Today, population growth in Africa, changing technologies, and altered life-styles have made the balancing mechanisms ineffective. Social-ecological systems which took centuries to evolve are being broken down with disastrous results for both humans and their life-supporting environment.

There is a great need for land use planning and policy in order to achieve the objectives of the African governments and satisfy the needs of the people. However, one generality which is common in Africa is the fact that qualified staff to organize and man the projects are few, money may be limited and many land use problems are of great urgency. For many countries in Africa land use planning is as much a problem of the densely settled areas as it is of the sparsely peopled regions. These seemingly contradictory survival and development endeavours pitched against conservation and nature in Africa will continue. In the words of the International Union for the Conservation of Nature and Natural Resources [2], "the dependence of rural communities on living resources is direct and immediate . . . unhappily people on the margins of survival are compelled by their poverty — and their subsequent vulnerability to inflation — to destroy the few resources available to them".

The ecological changes taking place in Africa could affect the local climates in three ways.

- 1) The ratio of solar radiation reflected from and absorbed by the earth's surface could change;
- 2) the ratio of convection and evaporative heat released from the earth's surface could change; and
- 3) the hydrological cycle could be modified.

There is some evidence that these changes might be taking place already in Africa. Reference here is made to the very severe drought which occurred in the Sudano-Sahelian belt of Africa extending from the Sahara to the Equatorial forest between 1968 and 1974. In 1982/83 Eastern and Southern Africa is undergoing yet another severe drought affecting both nature, animals and human life. Although one cannot extrapolate the regional situation to translate into a global situation due to lack of scientific data, it cannot be ruled out completely that what we see in Africa will not affect other regions either directly or indirectly. The changed climatic pattern may be a result of chemical events which are taking place in Africa.

## 1.2 *Termites Shorten the Carbon Cycle*

One such event is the role played by termites in altering the ecological pattern of an area. Termites consume large quantities of wood — 90 to 98 percent of the consumed cellulose is respired as carbon dioxide [3]. Figure 1 is a diagrammatic model of the terrestrial carbon cycle. Given the present atmospheric carbon dioxide concentration of 330 ppmv, the atmosphere contains about 700 Gt (1 Gigaton =  $10^9$  metric tons) of this gas. Measurements of  $\text{CO}_2$  made at Mt. Kenya [4] show that the concentration of  $\text{CO}_2$  in Africa is not different from that measured elsewhere (328.5 ppmv *vs* 330 ppmv). Therefore, it can be assumed that despite the low number of industries and automobiles that emit  $\text{CO}_2$  in the continent, the atmospheric  $\text{CO}_2$  must have come either from the biota within Africa or drifted from other regions into the continent. Woodwell *et al.* [5] have estimated that in the 1950's the total amount of carbon held within the living biota was about 830 Gt. More than 90 percent was in the standing crop of plants in forests and woodlands. Of the total within forests and woodlands, 461 Gt or nearly 60 percent was in tropical forests. The carbon held within terrestrial humus has been estimated recently as 1000 to 3000 Gt, or one to four times the quantity in the living biota [6, 7]. The distribution of carbon in the biota is greatest in the tropical regions, while the humus is more abundant in the temperate and boreal zones where lower temperatures retard decay.

Previous estimates of biotic carbon pool losses have used forest harvesting as the measure. Bolin [8] using data from Food and Agriculture Organization (FAO) and other sources calculated the net release of  $\text{CO}_2$  from the harvest of forests globally as 1 Gt of carbon per year. The estimate is indeed on the low side. Figure 1 shows the total dead organic carbon

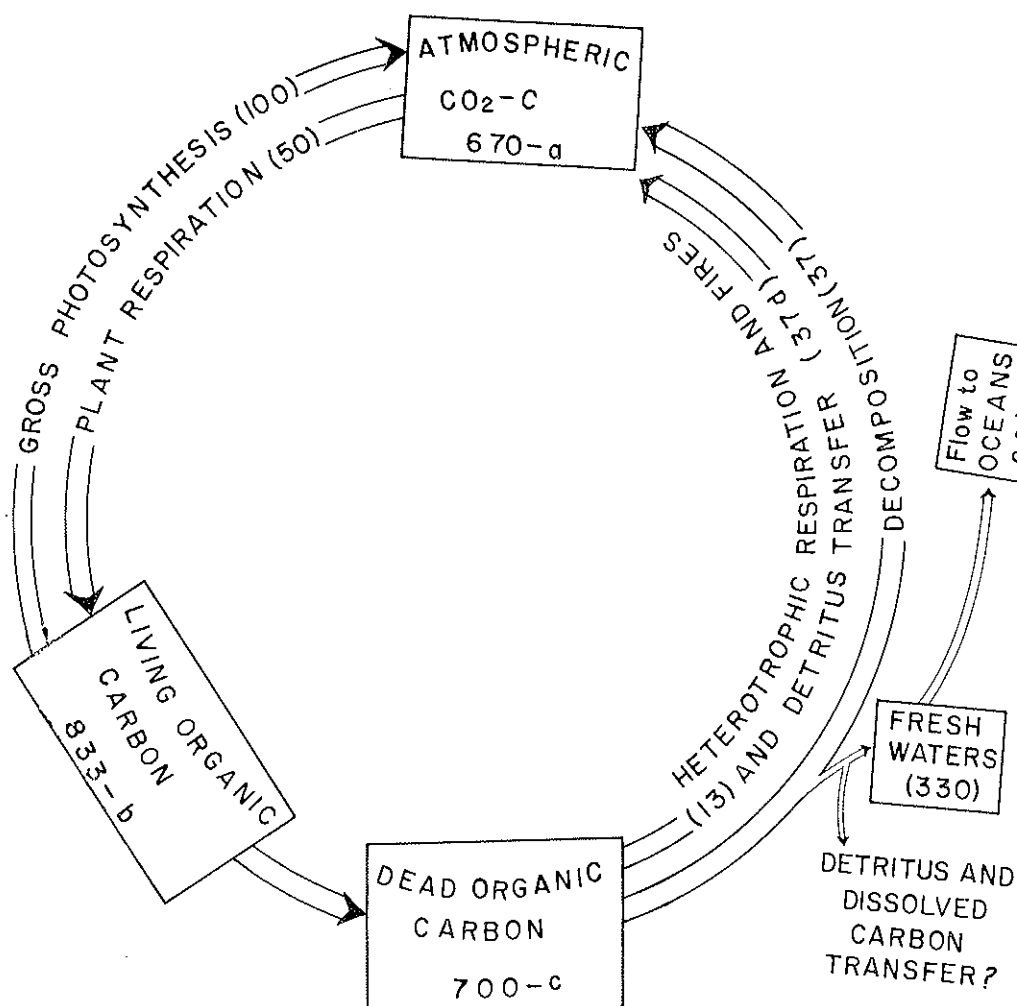


FIG. 1. Diagrammatic model of the terrestrial carbon cycle. Estimates are given in 10<sup>9</sup> tons. Question mark indicates that estimates are not available.

- a) other estimates are 683 (SCEP, Ref. 1, page 161) and 700 Gt (Bolin).
- b) Bolin estimates 450 Gt.
- c) Bolin, based on Delviche's nitrogen estimates and a carbon/nitrogen ratio of 12, an alternative estimate is 9,000 Gt.
- d) Bolin estimates 25 Gt.



as 700 Gt. Of the dead organic matter it is estimated that 76 percent is carbon with decay rate of  $< 0.001 \text{ yr}^{-1}$  and 24 percent carbon with rapid turn-over rate of a few years. Therefore, given the global deforestation rate of about 1 to 1.5 percent per year one would conclude that since 1950 only 33 to 49.5 percent of living biota carbon has been released to the atmosphere. Furthermore, given the fact that of the released carbon dioxide about 50 percent is deposited in the oceans or used for photosynthesis, and given further that the amount of fossil fuels burned in Africa during the same period is possibly less than one percent of the total burned globally, the 328.5 ppmv  $\text{CO}_2$  concentration found in Africa is too high for an isolated continent. Both the first and second alternative sources of  $\text{CO}_2$  are important and we may assume that this level of  $\text{CO}_2$  came from sources within the continent. The previous estimates of carbon release quoted above did not take into account the role played by other living organisms such as termites.

In our previous report [9] we showed that termites occupy 68 percent of the terrestrial land area where 77 percent of the terrestrial NPP is produced. We estimated the world's termite population to be  $2.4 \times 10^{17}$  and they consume materials equivalent to 28 percent of the earth's NPP and an average of 37 percent of the NPP in areas where they occur. These estimates are biased to the low side. We calculated that globally termites emit 13 Gt of  $\text{CO}_2$  carbon per year. Our recent measurements of  $\text{CO}_2$  emitted by higher termites (*Cubitermes*, *Trinervitermes* and *Macrotermes* species) show our previous estimates to be slightly high. Nevertheless, the role of termites is to shorten the carbon cycle which otherwise would have lasted a few decades to 100 decades. We have in Africa the high concentration of atmospheric carbon dioxide which has been released from the dead organic matter by termites.

A much more serious aspect of the carbon dioxide scenario is the fact that to an already high atmospheric  $\text{CO}_2$  is being added an increasing amount of  $\text{CO}_2$  released from fossil fuels burning. The number of cars with inefficient combustion engines is increasing in Africa. Similarly, the number of industries burning fossil fuels is also increasing. Given this trend, I can therefore foresee the carbon dioxide situation worsening in Africa unless corrective actions are taken.

### 1.3 *Termites Emit Methane*

Methane is an important atmospheric trace gas which affects the chemistry of the troposphere [10] and of the stratosphere [11]. It is

also a "greenhouse gas" with the potential to affect the earth's radiation balance [12]. The major sources of methane emission into the atmosphere have been reported to be rice-paddy fields, natural wetlands, enteric fermentation processes in ruminants, biomass burning, and leakages from geological gas reservoirs [13]. The estimated tropospheric reservoir of methane [13] is  $3.5 \times 10^{14}$  g to  $12.1 \times 10^{14}$  g (0.35 – 1.21 Gt). Recently, it has been suggested by Rasmussen and Khalil [14] that the methane content of the atmosphere has been increasing by 2 percent annually.

Methane has been found in the guts of various xylophagus insects, including scab beetles (*Oryctes*), wood-eating cockroaches (*Cryptocercus*), and various lower termites (*Reticulitermes*, *Cryptotermes*, *Coptotermes*) [15, 16]. Termites have the potential and do release large quantities of methane into the atmosphere. They are ubiquitous on the land surface; they process large quantities of biomass; their digestion is primarily dependent on anaerobic decomposition by symbiotic bacteria in the higher termites (family Termitidae) and by protozoans in the lower termites (all other families); and their digestion efficiency is high, usually greater than 60 percent [17]. In addition, human activities, including clearing of tropical forests and conversion of forests to grazing and agricultural land or road building, tend to initially decrease the number of termite species and increase the densities of one or two surviving species by about five fold [18]).

We have made both field and laboratory measurements of the emission of  $\text{CH}_4$  and  $\text{CO}_2$  from both higher and lower termite families (*Macrotermes*, mound building species, *Cubitermes*, soil feeders, *Trinervitermes*, *Reticulitermes*, lower termites, and *Gnathermitermes*). Similarly, we have made laboratory measurements of the emission of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{C}_2$  to  $\text{C}_{10}$  hydrocarbons, and reduced sulphur species from *Reticulitermes* and *Gnathermitermes* species. In addition, emissions from arboreal nests of an unidentified species of Nasutitermitinae were sampled in the field in Guatemala and analyzed for  $\text{CH}_4$  and  $\text{C}_2$  to  $\text{C}_{10}$  hydrocarbons [9].

Table 1 shows the mean emission rates ( $\bar{X}$ ) and standard errors ( $s/\sqrt{n}$ ) for  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{CO}$  from three *Reticulitermes* and two *Gnathermitermes* colonies [19]; n is the number of days during which samples which were analyzed during the 55-day showed little variability ( $\pm 10\%$ ). The variability between days was sometimes much higher. These emission rates are about in the middle of methane production rates reported by

TABLE 1 - Normalized emission rates per termite; R1, R2 and R3 represent three different colonies of *R. tibialis* Banks and G1 and G2 represent two different colonies of *G. perplexus* Banks.

| Colony | CH <sub>4</sub> (μg/day) |       |    | CO <sub>2</sub> (mg/day) |       |    | CO (μg/day) |       |    |
|--------|--------------------------|-------|----|--------------------------|-------|----|-------------|-------|----|
|        | X                        | S/√n  | n  | X                        | S/√n  | n  | X           | S/√n  | n  |
| R1     | 0.447                    | 0.023 | 21 | 0.091                    | 0.005 | 10 | 0.006       | 0.003 | 11 |
| R2     | 0.237                    | 0.016 | 22 | 0.107                    | 0.010 | 11 | 0.018       | 0.008 | 10 |
| R3     | 0.592                    | 0.031 | 22 | 0.137                    | 0.010 | 11 | 0.060       | 0.014 | 10 |
| G1     | 0.456                    | 0.042 | 11 | 0.410                    | 0.026 | 7  | 0.091       | 0.019 | 7  |
| G2     | 0.338                    | 0.034 | 11 | 0.210                    | 0.023 | 7  | 0.053       | 0.017 | 7  |

Breznak [16]. This agreement is good considering the differences between the techniques used in the two investigations.

Similarly, Table 2 gives the same values for the higher termites representing the fungus combs feeders (*M. subhyalini* and *M. michaelsensi*), the soil feeders (*Cubitermes* spp.) and wood feeders (*Trinervitermes* spp.) [20]. The *M. michaelsensi* nest was sampled by placing a teflon tube through a stainless steel pipe into the nest and sampling the gases coming out of the teflon tube.

We excavated the nest of a *Trinervitermes* species and *Cubitermes* species and took the nests to the laboratory for sampling using the teflon enclosure technique [19]. All the CO<sub>2</sub> measurements were done using the Matheson CO<sub>2</sub> detector tubes and Matheson pump. Table 3 gives the

TABLE 2 - Methane and Carbon Dioxide content in the interior air samples from a *M. michaelsensi* nest in ppmv.

| Sample        | [CH <sub>4</sub> ] | [CO <sub>2</sub> ] | $\frac{[\text{CH}_4]}{[\text{CO}_2]}$ |
|---------------|--------------------|--------------------|---------------------------------------|
| Ambient       | 1.678              | 330                | 0.494                                 |
| nest sample 1 | 14.59              | 26000              | 0.056                                 |
| nest sample 2 | 16.41              | 26000              | 0.063                                 |

results of the  $\text{CH}_4$  and  $\text{CO}_2$  measured for the *Trinervitermes* species and *Cubitermes* species.

We also carried out measurements of gases emitted by termites when the *Trinervitermes* species nest and the *Cubitermes* species nest were broken down and the termites without the soil nest placed into a 1 litre Mason jar. The soils of the two species nests were also placed into another Mason jar and the air above each jar determined for  $\text{CO}_2$  and  $\text{CH}_4$ . The number of *Cubitermes* termites placed into the Mason jar were as follows:

|                                     |      |
|-------------------------------------|------|
| workers with dark, soil filled guts | 2033 |
| workers with pale bodies            | 160  |
| larvae of all sizes                 | 963  |
| Soldiers                            | 3    |
| White soldiers                      | 4    |
| Last-instar nymph                   | 37   |
| next to last-instar nymph           | 16   |

The total number of *Trinervitermes* termites placed into the Mason jar were as follows:

|                       |      |
|-----------------------|------|
| major soldiers        | 343  |
| minor soldiers        | 280  |
| major worker soldiers | 17   |
| minor worker soldiers | 60   |
| major workers         | 1727 |
| minor workers         | 1363 |
| Larvae                | 290  |

The jars were sampled every five minutes for  $\text{CH}_4$  and  $\text{CO}_2$ . Sampling was stopped after one hour. The amount of  $\text{CH}_4$  concentration emitted by *Trinervitermes* termites rose from 1.793 ppmv, the ambient concentration, to 22.46 ppmv at the end of one hour. The *Ternervitermes* termites  $\text{CO}_2$  concentration rose from 400 ppmv, the ambient concentration, to 2500 ppmv at the end of the hour. The air above the soil gave  $\text{CH}_4$  and  $\text{CO}_2$  concentrations that were not significantly different from the ambient air concentrations. The *Cubitermes* termites emitted  $\text{CH}_4$  concentration which ranged from the ambient concentration of 1.749 ppmv to 27.26 ppmv at the end of the hour while the  $\text{CO}_2$  concentration ranged from 400 ppmv in ambient sample to 2500 ppmv at the end of the experiment. The soil materials had identical result to that of the *Trinervitermes* soil.



In addition to *Macrotermes*, *michaelsensi* and *subhylinus* *Trinervitermes* and *Cubitermes* species we have also sampled gases emitted by *Odontotermes badius*, *Amitermes unidentatus*, and one *Syncanthotermes* species (grass feeding termites). All the termites sampled in the field and in the laboratory emitted large quantities of methane and carbon dioxide. The methane to carbon dioxide percent ratios were close to one for the *Trinervitermes* and *Cubitermes* species and slightly higher for *Amitermes unidentatus* and *M. Subhylinus* as shown in Table 4 for the *Amitermes* species. In some cases the ratio was about 0.3 to 0.4 percent.

Therefore, our original proposal that termites do emit large quantities of methane and carbon dioxide into the atmosphere is still valid given the field experiment we have undertaken to prove our original laboratory experiments.

## 2. Climate Change

It is now generally agreed that the amount of CO<sub>2</sub> in the atmosphere has increased and continues to rise. The major concern of increased CO<sub>2</sub> is the climatic change that may arise. In the excellent report [1] on "The Global 2000" the study group has proposed three environmental consequences of the changed climate. I intend to analyse each climate scenario and point out my views on the Africa region.

*Scenario No. 1: No change.* This scenario with a probability of 0.30 assumes that there will be no change in climate by the year 2000. The

TABLE 4 - Concentrations of Methane and Carbon Dioxide in a Teflon bag enclosure air sample of an *Amitermes unidentatus* in ppmv.

| SAMPLE       | ELAPSED<br>TIME<br>(Hrs) | [CH <sub>4</sub> ] |       | [CO <sub>2</sub> ] |    | [CH <sub>4</sub> ]<br>%<br>[CO <sub>2</sub> ] |
|--------------|--------------------------|--------------------|-------|--------------------|----|---|
|              |                          | X                  | σn    | X                  | σn |   |
| Ambient      | 0                        | 1.663              | 0.007 | 400                | —  | 0.4140  |
| Bag sample 1 | 2                        | 6.704              | 0.064 | 600                | —  | 1.117   |
| Bag sample 2 | 17.5                     | 41.525             | 1.005 | 3700               | —  | 1.122   |
| Bag sample 3 | 18                       | 43.755             | 0.305 | 3900               | —  | 1.122   |
| Bag sample 4 | 21.5                     | 50.480             | 1.100 | 5000               | —  | 1.010   |

warming effect of increasing CO<sub>2</sub> will be balanced by the cooling effects of a natural cycle of falling temperatures. Because of both population and livestock growth in Africa the environmental consequences of this scenario will not be minimal for the region. There will be increased demand for energy, increased shifting agricultural practices and decreased forest areas. The continent will find it hard to support its population and malnutrition may increase.

*Scenario No. 2: Warming.* The scenario with a probability of 0.25 assumes that due to the increased CO<sub>2</sub> in the atmosphere there will be by the year 2000 an increase of 1°C in global temperatures. Most of the warming will occur on the polar regions and the higher middle latitudes. Precipitation increases are predicted for the higher middle latitudes with little change elsewhere. Pressures on forests in Africa will be the same as in scenario No. 1 due to increased population growth and concomitant needs for food, fuelwood, building materials, and other forest products.

*Scenario No. 3: Cooling.* This scenario also with a probability of 0.25 assumes that cooling might occur if the global cooling trend that began in the 1940's were to continue. This would lead to a global temperature decrease of 0.5°C with 1°C cooling in the higher and middle latitudes and smaller changes near the Equator. Precipitation amounts will generally decrease, with month to month and year to year variability increases. Storm tracks shift Equatorward, bringing precipitation to the higher latitudes of deserts but causing Equatorward expansion of these deserts. Monsoon failures will become more frequent and severe and the Sahel will experience more frequent and severe droughts. In essence this scenario is the one that will affect Africa the most. Rainfall in Africa depends to a large extent on the Monsoons. Thus food production would decrease, forested areas would also decrease due to low rainfall. Human suffering and ecological changes in the magnitude of the Sahelian region experience or more would be expected. Massive irrigation projects in areas with fresh water or desalinated water would be expected to be undertaken in order to counteract the effect. There is no alternative which favours Africa.

### 3. *Strategies and Priorities for Research*

Some of the man-made changes taking place in Africa discussed in this paper may cause further ecological and climatic alterations. At present

we do not have enough data to predict the actual changes. The scientific knowledge of atmospheric chemistry in Africa is sparse or non-existent. Furthermore, the unplanned, unmanaged development projects that have taken place in the region need re-directing and reorienting. It is clear that the supply of wood for energy occupies a major place in solving some of the ecological problems. In this respect, land use planning and policy should be embarked on by the respective governments as a priority. The planning will enable users to know areas suitable for agriculture, mining, urban and community development. It will also identify areas suitable for forestry and agroforestry.

Furthermore, greater efficiency in energy production and use should be achieved. At present there are several losses incurred in oil and gas production, electricity production and transmission. These losses worsen the pressure on natural forests as alternative replacement source. There is also a need to develop fuel-wood plantations instead of cropping natural forests. A study in ways and means of producing better kilns in the charcoal production, a process now experiencing 50-84 percent losses of the energy value, is long overdue. The wide use of such kilns will greatly help the situation.

The establishment of an Atmospheric Research Centre in Africa is long overdue. Given the commonality of research topics in this area for the region and the fact that atmosphere has no boundary, it becomes clear that the present University set up in Africa is incapable of handling all aspects of the atmospheric study. Such a centre can only be started with the help of UN bodies such as WMO, UNESCO, IOC, etc. with the co-operation of African Universities and the Organization of African States. The first goal of the centre should be to gather together a group of climate modellers, a community of scientists which must include meteorologists, oceanographers, glaciologists, biologists, geochemists, chemists, paleo-climatologists, and social scientists to draw up full scenarios of the future course of climate and its effects in each nation of the region. Such a detailed scenario should include description of the seasonal changes in temperature, precipitation, evaporation, and so forth on a regional and national scale, taking into account the rate of fossil-fuel burning and changing patterns of deforestation and reafforestation. The modellers should also anticipate the behaviour of ice-sheets, snow-covers, and sea-ice.

Complementary to the above, the scientists at the centre should develop for each state methods for assessing climate changes in human or economic terms. We in Africa need to predict the effect of a given change



of weather conditions on: (a) the yields of staple foods such as maize, wheat and vegetables; (b) the important tropical plants such as coffee, tea, sisal and others; and (c) poultry and animal husbandry. All these may be difficult to quantify, but attempts must be made to reach the best possible estimates. Further energy demand and transportation/communication patterns will depend on climate change and a fair assessment of their implications should be taken into account.

There is a need to assess on a regional scale the economic (and institutional) interactions between various specific activities or sectors. The development of the economic system of a region or country and to show its sensitivity to a given scenario of climate change is essential. Although models cannot predict the future, they help to slow the relative economic response to a given situation, such as changes in agricultural productivity, price and sources of energy, shifts of trade etc.

The way people and social institutions will react to climate change will differ from region to region, country to country. Some countries will gain, some will lose. It is not too late for the African countries to involve in their future plans the alternatives to increased carbon dioxide, reduced fossil-fuel consumption, and a higher reafforestation rate.

One salient point which has been assumed in this paper is that the present high rate of population increase will be reduced and made steady. It will be almost impossible to effect a lasting land use planning and policy if the present rate of population growth is maintained. With the dwindling arable land and the increasing drought patterns in the region an increased population growth will not be sustained.

The chemistry of the ozone layer in the tropics has not been extensively studied. We do not know the level of the ozone concentration with exactitude. We have demonstrated that termites do emit large quantities of methane in the tropics. The emitted methane is transformed into CO which can affect the ozone layer. Therefore, studies of ozone layer profile in the tropics would be an essential component towards our understanding of the atmospheric chemistry.

Lastly, with the expected industrialization of Africa, there will be more industries and automobiles emitting  $\text{NO}_x$ ,  $\text{SO}_x$ , particulates, PAN, etc. into the atmosphere. At present we do not have enough or complete background data on the concentrations of the above. The potential photochemical reactions that may take place in the tropics may be assumed. Although at present the region has relatively low level of oxides of nitrogen

and sulphur, this does not negate the importance of their study. The effects of these compounds in causing acidic rains, which may adversely alter the pH of the lakes, is well documented. In addition, the oxides of sulphur are closely linked with photochemical smog. Studies of these gases should be initiated as soon as possible.

#### ACKNOWLEDGEMENT

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analyzed chromatographically for  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  by the method described by Rasmussen and Khalil [14]; for  $\text{C}_2$  to  $\text{C}_{10}$  hydrocarbons by the method of P.R. Zimmerman [EPA 904/9-77-028, *appendix C* (Environmental Protection Agency Region IV Air and Hazardous Materials Division, Atlanta, 1979)] and for reduced sulphur compounds by the method of S.O. Farwell, *et al.* [Anal. Chem., 51, 609 (1976)].

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## DISCUSSION

HARE

I would like to comment on both the Salati and Wandiga presentations. I think one should congratulate these two speakers on bringing forward the special environmental problems of the tropical countries. They have very much illuminated those special problems. This morning, as I understand the wishes of Prof. Marini-Bettòlo, we should be looking for general conclusions; and one general conclusion that I would hope that we would come to would be that the special environmental resource and human problems of the tropical world deserve as much attention from the scientific community as they can get. These two speakers should be assured of the full support of the scientific community. The thing that strikes you at once when you go to any Third World capital is the loneliness and the isolation of the small scientific community that tries to do its work in those areas.

May I make some specific remarks? First as regards the Amazonian rain forest, I was most interested in the data that our speaker gave us. In fact, the run-off data from the Amazon which he mentioned represents something like 85% of the total discharge of the streams of the United States, and about 40% of the discharge of the streams of Canada. So this is an enormous river system. Secondly, the finding that he presented that the precipitation is largely internally generated, that it is maintained at this high level by the re-evaporation of rainfall that has already fallen, and is not simply an abstraction from an oceanic source, that too is confirmed in Africa, where a very substantial proportion of the precipitation falling from the African monsoon is actually re-evaporated water. One can demonstrate this by simple applications of the continuity theorem. In fact, the rain that falls at the eastern end of the monsoonal thrust — actually the trajectory is turned from the southwest towards the west — comes from the southwest. The trajectory turns towards the west because as it rises it enters the Equatorial easterlies. But at the limit of the trajectory, about two-thirds of the precipitation has been on the average re-evaporated at least once. And so the point that our speaker made is certainly completely confirmed from the African continent.

The second point concerns the second paper, and has a bearing on the same point. It arises from the suggestions made by Prof. Wandiga about the role of termites and the possibility of climatic change in Africa. First of all, as

far as climatic change in Africa is concerned, I recently chaired a meeting on behalf of the Economic Commission for Africa of the UN. We reviewed the status of the climatic change to which he referred. And it is true that the spatially averaged rainfall over inter-tropical Africa has been declining progressively since about 1958-59. Every year there are patches of good rainfall. Every year the size of those patches of good rainfall decreases. 1983 was probably the driest year in the history of the continent, judging from the recorded precipitation history. And so the continent has come through 22 years of desiccation. These happen to be the years of decolonization. The African republics achieved their independence just as the rainfall began its downward swing. In Mauretania in 1983 the rainfall was so low and the exotic streams, coming from the south, from the rain forest belt, were so low that a state of national emergency was declared about six months ago. Something like one-third of all the territories of Mauretania are without resources of water and food. The population of Nouakchott has increased by tenfold in the last eight years. With the abandonment of territory, the people have come to the capital city. Now is this climatic change, or is it simply an extreme fluctuation? As a statistician I would say it is an extreme fluctuation; as you look at the record you can see other similar anomalies. Hence one could say that this is within the population expectation; this is what you might expect from the climate. But increasingly I wonder about this. There are two feedbacks that are tending to reduce the rainfall. One is the albedo feedback, to which Professor Wandiga referred. As the ground is bared, as the particle loads have increased, the reflectivity of the surface has increased. Possibly the induced mechanism of accelerated subsidence is at work. Secondly, if it is indeed true that the rainfall is derived near the end of the trajectory primarily from re-evaporated water, then reduced water-holding capacity in the soil provides a positive feedback that will tend to accentuate drought. It would appear that to some extent this is true. One of the things that will tend to reduce water-holding capacity is a sharp reduction in the organic content of the soil. It is my impression in those parts of Africa that I know that there is a rapid net loss, not only in mineral fine components, but in the organic content of the soil. There is a degradation of litter, and a consumption of soil humus. Both of these tend to reduce the water-holding capacity from which re-evaporated rain is derived. So that one can see the mechanism of which he spoke as part of a second feedback process.

The rôle of termites is comparable to the rôle of many other decomposers. The earth photosynthesizes that cellulose to the tune of maybe seventy gigatonnes a year. It respire an equivalent amount if the biomass is constant, but it

looks as if in these very dry regions the net respiration, the net decomposition of organic material, is now exceeding the rate of photosynthesis. One of the processes whereby this would be done could be an acceleration of the work of the decomposers, such as the termites to which he refers.

So I have nothing optimistic to say either, Mr. Chairman; I was delighted to have these papers before us, and to express the personal view that the plight of the tropical countries and particularly Africa and Brazil (I did not say South America — I said Brazil — because of the enormous extent of desertified terrain in northeastern Brazil) absolutely need the attention of the scientific community. I hope they will get it, and that it will be among our recommendations that we support all the work that can be done.

MARINI-BETTÒLO

Thank you, Professor Hare, for giving us so much information, and for having drawn attention to the desertification.

SALATI

I only want to add a comment on the water balance. The figures presented have been obtained from independent measurements and not by difference.

The discharge of the Amazon has been made by the U.S. Geological Survey during several months. Rainfall was measured in a large number of meteorological stations, and the evapotranspiration was calculated based on meteorological data obtained at the same stations.

WANDIGA

I would agree with most of the comments that Professor Hare made, but I would like also to bring out one point which possibly I did not bring out yesterday. What I said is that we are proposing that termites may be accelerating the decomposition of the biomass in the Tropics, and we are not at this moment saying that the amount of  $\text{CO}_2$  is affecting the climate. But as soon as I say that, I must also add that in Africa we have a lot of inefficient combustion engines; in other words, the automobiles that have been used in Africa right now are either those which were made 10 or 20 years ago or those which do not have efficient combustion engines, and these are, again, adding to the amount of carbon dioxide, which is already high, plus the fact that the creation of industries (and some of these industries are not really the modern type of industries that are being set up in the industrialized countries) is again

another added aspect of the CO<sub>2</sub>. So what I was trying to suggest is that, given the high concentration of CO<sub>2</sub> already present, which must have come from the biotic cycle, we are going to see even an additional higher concentration of CO<sub>2</sub> in Africa unless we reverse the trend. And this is the first thing I think I would like to make clear.

I would also like to agree with you that the last 20 years, as shown, were the period of decolonization. During colonial times most of the colonizers passed and enforced the land conservation laws, and when we became independent we thought that these were colonial laws and therefore abolished them, and we allowed our people to cut forests, to plow maybe up to a 45° angle on the hills. The result was an acceleration of the deforestation. This fact has had an effect in almost every country, and therefore we have seen less or fewer forests remaining because of the disregard of the colonial conservation laws. Regarding other things that you said, I think I would agree with you that certainly we are seeing reduced capacity of holding water in the continent and therefore we can expect less rainfall. Although in these twenty years there were fluctuations, I do not expect better conditions unless the African governments enter into a very massive reforestation program.

LAG

I should like to ask a question about water analysis in the Amazon regions. Have you any figures and calculations about the C/N ratio in the water? Is that somewhat like what you have in the terrestrial humus? Is it possible to give an answer to that?

SALATI

Yes, there are analyses and the data are available, especially published in *Acta Amazonica* and in the Max Planck Institute of Limnologie, Plön.

KNABE

I would like to make a comment from the point of view of my time in the Inter. Bureau of Forestry at Hamburg. The difference between the forest in the tropical zones and in the temperate zones is mainly that the lowest content of organic matter in the Tropics is in the living part of the ecosystem and not in the detritus or in the humus. So if you cut the most living part of the ecosystem, you at once lose the main part of the nutrient contents, i.e., the main part of the organic matter. Secondly, the decomposition of the rest of the



organic material, as Professor Hare explained, will also be reduced, but third — that has not been mentioned — the soil under the cover of the rain forest is formed by a material able to retain water, whereas when the cover is removed, it changes its properties and is not able to hold the same amount of water as before. So it is really a great hazard to remove a shade tree cover from such soil types.

#### CRUTZEN

I wanted to support strongly what Dr. Hare said and also point to another problem. We have here two representatives from the tropical countries who are strongly interested in air chemistry and want to start up a program there. I want to emphasize how much they need our support, even moral support, because I found this out at the meeting in Africa to which Dr. Wandiga invited me in June and at which I gave a lecture on air chemistry. There was a lot of enthusiasm among the participants to get going, but immediately, after they showed a brief period of enthusiasm critical voices came up, saying is this really the major problem we have in Africa? We have such worse problems to deal with — should we really put resources into this basket? And of course one tries to defend atmospheric chemistry in that environment, but I do not really think it was up to me to do that allocation — I just wanted to indicate that these people have problems in their countries selling the issue and they need all our support to do that.

I have one specific question to Dr. Wandiga about the termite work. I was involved in that a little in the beginning, but one thing which still surprises me is the use of methane, compared to carbon dioxide: you obtained values just a little below 1%. Now if cellulosic material is decaying under totally anaerobic conditions, you would have really 50-50 would come out of it: of 100% cellulose, 50% of the carbon going into methane and 50% into CO<sub>2</sub>. Now here it is only 1%, so somewhere on the way even 99% gets lost, or a large part of this environment anyhow is aerobic and methane is used. So then the problem comes up: where should one really measure the emissions? Should one go into the termite nest or should one collect methane and CO<sub>2</sub> outside the nest or put a bag over the system? I wonder if in the research which has been going on over the last years, with which I am not so acquainted, one has been looking at these factors, with a whole bunch of these common species.

#### WANDIGA

As you know, in the digestive system of the termite, the anaerobic part of

it is only in the guts, and then from the guts it goes to the stomach, where the aerobic system does operate, and that is where most of the methane is being lost or utilized. We have looked both inside the mound and outside the mound, and the ratio of methane to  $\text{CO}_2$  is very much the same, so we think it is being utilized within the animal itself.

CRUTZEN

So the conclusion is that the termite overall metabolism is still 99% aerobic and just 1% anaerobic?

WANDIGA

Yes.

REVELLE

I want to make a comment but I want to ask a question about the methane first. Would you conclude then that the methane is being used as a nutrient by the termites? That it is actually metabolized in the energy cycle of termites?

WANDIGA

Of all the literature, entomological literature, I have seen, nobody has invoked that, but from the fact that we have seen very low levels of methane being emitted we imply that it must be utilized somewhere, or never produced.

REVELLE

I would like to make a comment on something that a Brazilian colleague said about forest plantations. It seems to me that one of the most serious problems in the tropical countries is how to reforest the areas that have been deforested and to establish a steady state of equilibrium condition. The problems that he cited are very severe: the problems of disease, of pests that attack these newly planted trees, and the problems of nutrient cycling, which in the case of many trees result in the continuous reduction of the plant nutrients in the soil. But the problem really is how to make forest plantations in which none of these things happen. And nitrogen-fixing trees are clearly a major opportunity, but we also need fast growing trees, trees that are so-called

pioneer species. And we need to find, by forest research, those that are disease — and pest-resistant. One example is the tree that has been widely talked about: *Leucaena* which seems to be quite pest — and disease-resistant. It is a very fast-growing and nitrogen-fixing tree.

But in more general terms it seems to me that one of the very important kinds of scientific research and development that are needed in the tropics is forestry research. In the past, forestry research has not attracted very good scientists or very many scientists, for the reason that the results come so slowly, because one result per generation, most scientists are not satisfied with that kind of scientific progress. In recent years, however, the new biology has made it possible to obtain results about once every six months, particularly with tissue culture of individual tree cells, which turn into little trees, and you can then do a lot with these very young individual trees.

And it may be that there are many other ways in which the new biology will be very applicable to forestry — it is certainly being pushed in the United States by the big forestry companies. In general, the scientific problems of forestry here cannot be over-estimated in terms of their human importance, because of the firewood problem which Wandiga spoke about and the general problem of substituting biomass energy for fossil fuel energy, which in the long run we will have to do anyhow, but the quicker we can do it, I think, the better off the world will be, certainly from the standpoint of the carbon dioxide problem, and from other standpoints too; I would urge that we not only think about atmospheric chemistry but of some of the implications of these chemical cycles that are so worrisome in the Tropics.

## SALATI

Usually colonizers do not take into consideration the agricultural practices, but only the utilization of the land by the number of hectares. It is difficult to establish a relationship between the chemical aspects of the atmosphere and the forms of land management. When you consider the problem in terms of millions of square kilometers, it becomes regional and then it is possible to make a connection between them. It is therefore important to note that either chemical reactions and their consequences, or the amount of water vapor transported, the amount of dust or pollen, can have their values altered when forest areas are changed to agriculture. Amazon colonization is rather difficult. The Portuguese preferred to start colonization in southern regions where climate is more appropriate, while the Spanish chose especially higher altitudes. Even now the Amazon population does not reach 10 million inhabitants in over 6

million km<sup>2</sup>. It would be important to study the rational and ecological utilization of the region.

#### CANUTO

I was telling you yesterday that there is a new financial system of the United Nations, called the United Nations Financial System for Science and Technology, which came up under the auspices of the 1979 Science and Technology Congress in Vienna. This Financial System has funds and the problem that you presented, in my understanding, fits perfectly in that program. So if that could be of any use, I think that I will be more than glad to give you more information about it.

#### HARE

I think that I should say that clearly what is being said around this table at the moment illustrates the basic principle on which this meeting is based, which is that all such studies are interdisciplinary. I have stopped calling myself a meteorologist, I call myself an atmospheric scientist because I know damn well I cannot get along without people like Crutzen and Rowland here, and I hope they feel they cannot get along without dynamicists and climatologists — none of us can get along without soil scientists and ecologists when it comes to this class of work. We will come back to that later on.

At this moment I only wanted to lay a further point before the meeting, that arises out of these two interesting papers, and that is that it is not merely that the so-called South politically, the tropical countries, have a lower living standard and are at a lower level of development, and have perhaps a more difficult physical environment than the middle latitude countries. It is that special stresses are now arising out of two circumstances, both of which were referred to by both speakers. The first is the population explosion, which is a matter for the scientist to concern himself with; and the other is that I must say that in the last two decades the tropical climate, rather climates in the plural, have behaved extraordinarily badly. The timing could not have been worse.

Now, may I bring that point home just by briefly looking back at Africa? The African drought, the Sahelian drought, even Professor Wandiga said it ran from 1968 to 1974. It did not, Professor Wandiga. It began before that and it continued. Drought has devastated the Sahel, the Sudano-Sahelian belt, every republic from the Atlantic right through to Ethiopia. Somalia, Kenya and

Tanzania have been somewhat more fortunate, especially lately, and Nigeria has been more fortunate. And this illustrates the biblical principle: "To him that hath shall be given and from him that hath not shall be taken away even that which he hath" because (for God's sake) it is the richest countries in Africa that have had the best time climatically. The most important event of the late 70's has been the extension of drought into southern Africa and even into the Union of South Africa. One began to think that only the Union of South Africa was immune from drought on the continent, but now even the Union is affected; the whole continent has undergone this extraordinary dessication. I cannot place too much emphasis on the fact that this is unprecedented and that it is imperative that the scientific community make itself heard about the matter. Discussions of economic affairs before the United Nations are almost entirely in terms of power-bloc politics, who will do what, whether the Soviet Union is intervening in that, whether the United States is intervening in that. This is all irrelevant to the problems of the continent, which are imposed and dictated by this deterioration of nature. It follows that it is in our laps, the scientists, to do and say something about this, and I never lose an opportunity, Mr. Chairman, which is why I butted in at that point.

FINAL CONSIDERATIONS  
AND  
CONCLUSIONS

## FINAL CONSIDERATIONS AND CONCLUSIONS

### INTRODUCTION

As we approach the dawn of a new century, we feel deeply anxious for the welfare of the planet Earth, and of the generations that must succeed us. Human numbers are growing explosively. Each human being must eat, keep warm and seek shelter. As we do so, in an ever-growing multitude, we place greater stress on the resources that support us. Already the signs of that stress are universal. The last terrestrial frontiers have been removed, the last solitudes penetrated.

Human technology has allowed this growth and must provide for the future. Yet that same technology threatens nature, and may even destroy the very benefits that we seek. Chemistry is at the heart of mankind's remarkable capacity to make needed things, to move mountains and to penetrate far places — even space. Wisely used, chemical technology can immensely enrich our species. Unwisely used, however, it can contaminate nature, most notably the atmosphere and hydrosphere. Technology presents us all with a Faustian bargain.

As scientists we are aware of both gains and hazards. We believe that the immense challenge of the future can be met. We recognize, however, that the global system is an entire whole, and that no one body of knowledge can allow us to use it safely. Nature does not recognize the scientific disciplines into which we have divided scholarship. It is imperative that we seek to use chemical knowledge with as full understanding of the global system as we can command. We recognize, too, that science should not and cannot dictate the manner in which humanity solves its problems. We can offer help, advice and the technical means. Objectives remain the choice of our entire society.

The Pontifical Academy of Sciences brought us together in the full knowledge of the unity and integrity of the global system. It assumed

in its planning that we should adopt a holistic stance. Nevertheless, it posed certain specific questions:

— do rising levels of carbon dioxide in the atmosphere pose a threat to future climates?

— what dangers are presented by acid deposition and by the dissemination of heavy metals or other toxics?

— do changes in the stratosphere imply reduced ozone levels, and hence threats to human health and climate? How big are the changes, and the threats they present?

— what is the role of the atmosphere, and especially its chemistry, in the burgeoning problems of the tropical world? What, specifically, can be said of changes in rainforest and arid environments?

— does nuclear war threaten climatic disturbance? What will be the aftermath of such a catastrophe?

The papers written in answer to these questions by the specialists who attended will be published in a separate volume. We present summaries in the following pages, based not only on the original papers, but on thorough and searching discussions. Certain general conclusions emerged that need immediate scrutiny.

Firstly, we noted that many of the problems of atmospheric chemistry are upon us before we notice them, and before we have any chance to study them and modify our technology. The potential for damage arises before any symptoms are noted. And the damage done may be irreversible for decades, or even centuries. This is true, for example, of the carbon dioxide build-up, and of the effect of the chlorofluoromethanes on stratospheric ozone.

Secondly, we were often struck by the inequities that seem to be built into our system. Those who gain from technology may well not be those who suffer the consequences — or, to put it in reverse, the whole world may have to absorb the consequences of actions that have benefited only the industrialized countries. And these consequences occur on a variety of time scales, so that even the future may be mortgaged: acid deposition, for example, works over years and decades, carbon dioxide over centuries. Our descendants will have to clean up the mess we leave behind.

What solutions can we offer? Having arrived at this forbidding situation, can mankind extract itself? Certainly we believed so, as we should not have come to Rome. We defined these needs:



— better factual knowledge, in itself a gigantic challenge involving further technological innovation, more sophisticated laboratories (in more places, including the tropics), the wide use of satellite systems, and above all sustained monitoring of the environmental complex;

— better synthesis of the results of research, in a more holistic and interdisciplinary framework than we have usually adopted;

— better means of communicating the urgency, validity and human implications of what our research reveals. Chemists have not been good communicators, even among themselves. They need to cultivate the art of talking intelligibly to politicians and statesmen, as well as to their fellow scientists.

Those who came to Rome became aware, in fact, that they showed a common concern — that it is our duty to preserve the habitability, beauty and integrity of the planet that has been given to us as a home. In so doing, if this generation of scientists can miraculously overcome its own defects, it will be providing for the future generations of humanity.

It is in that well-intentioned but perhaps over-optimistic spirit that we offer this summary report.

## TROPOSPHERIC CHEMISTRY

As a result of advances in our understanding of the tropospheric photochemical system during the past decade, tropospheric chemistry is now viewed as one component of the complex system of biogeochemical cycles through which nature recycles the elements necessary for life on earth. The role of tropospheric chemistry in these cycles is to transform reduced compounds emitted from the surface into the oxidized form in which they are returned to the biosphere, lithosphere, and hydrosphere. These processes influence a wide range of environmental parameters; these include the climate, by controlling the concentration of some "greenhouse gases", such as methane and ozone; the stratospheric ozone layer, by controlling the rate of injection into the stratosphere of chemicals which affect the ozone level; and the biosphere by limiting the levels of toxic gases near the surface.

Although the troposphere is a critical region of the atmosphere, our understanding of this chemical system is far from complete. Of all regions

of the atmosphere, the troposphere is spatially and chemically the most heterogeneous and complex. This complexity is derived from the wide variety of species present in the troposphere and from the temporal and spatial variability characteristic of the emissions.

While some effects of pollutants on the local scale are well documented, such as urban photochemical smog, and on the regional scale, such as acid deposition, the effects of man's activities on a global scale are less certain. In particular, the possibility exists that the release of compounds into the atmosphere as a result of anthropogenic activities may be overtaking the ability of the troposphere to oxidize these materials, causing a general perturbation in tropospheric composition. Recent observations of increasing methane concentrations in the atmosphere suggest that these perturbations may be occurring. However, until we understand tropospheric chemistry and its interactions with biospheric processes on a global scale, it will not be possible to assess man's role in this system. As a result, *it is recommended that an international scientific program be launched to study global tropospheric chemistry.* One important element of this program must be an ambitious effort to develop instrumentation to measure atmospheric compounds with high specificity, reliability and accuracy. The major areas where such a program should focus are briefly outlined below.

The key species in tropospheric chemistry is believed to be the free radical species, OH. It is this species that is hypothesized to initiate the oxidation of many of the reduced compounds emitted into the atmosphere and thus has a major role in controlling the trace gas composition of the atmosphere. While photochemical models predict OH to be present in the lower atmosphere, this prediction has yet to be confirmed by direct atmospheric measurements. A major goal of any research program in global tropospheric chemistry should be a test of photochemical theory for OH. This will require not only measurements of OH levels in the atmosphere but also simultaneous measurements of the concentrations of the species which control OH. Concurrently with the test of the OH photochemical theory, more detailed studies of tropospheric chemical transformation and reactions should be prepared.

Another important goal of a tropospheric chemistry research program should be to establish a global air sampling network to characterize the distribution of atmospheric compounds today. In order to determine if the tropospheric composition is changing, a commitment must be made to maintain this network into the 21st century. The interchange of

species at the earth's surface due to biologic and lithospheric emissions as well as wet and dry, deposition also needs to be studied, both from the point of view of understanding the flux of material being exchanged and elucidating the physics and chemistry of this interchange. The synthesis of the knowledge gained in this global tropospheric chemistry research program should facilitate the development of a coupled chemical/dynamical model of the troposphere which will facilitate the assessment of future environmental problems of anthropogenic and non-anthropogenic origin so that we may deal with them in an orderly and rational manner.

## THE OZONE LAYER

The stratosphere itself exists through the absorption of ultraviolet energy by ozone, and the concentrations of ozone are controlled by complex chemistry dominated by free radical catalytic chains involving species of  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{ClO}_x$ . The anthropogenic release of long-lived molecules at the earth's surface inevitably results in their eventual transfer to the stratosphere, decomposition by ultraviolet processes and the release of additional free radicals, for participation in these chemical chains. The increasing amounts observed in the troposphere of halogenated compounds such as  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  and of nitrous oxide and methane provide more  $\text{ClO}_x$ ,  $\text{NO}_x$  and  $\text{HO}_x$  in the stratosphere, and can be expected to affect the chemical balance throughout the stratosphere. The effect of additional chlorine is most noticeable in the upper stratosphere, and experimental measurements have confirmed a diminution over the past decade in average ozone concentrations at 40 km altitude. Lesser effects are anticipated at other altitudes and are less certain in magnitude. The atmospheric lifetimes of 50 years and more for some of these compounds will maintain an altered atmospheric composition throughout the 21st century.

There is also present in the stratosphere a particulate aerosol layer which can, at least temporarily, have an impact on the earth's radiation budget and climate. This layer is formed primarily through oxidation of sulphur-bearing precursor gases of tropospheric origin. Anthropogenic activities contribute to the upward flux of these gases.

The major chemical cycles describing catalytic ozone destruction by  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{ClO}_x$  are now reasonably well characterized. The development of sophisticated computational models has facilitated the unification of field studies with laboratory experiments. At high altitudes where the

stratosphere achieves a photostationary state, the chemistry seems well understood, while at lower altitudes, chain termination steps and associated reservoir species have by no means been so accurately characterized.

Field measurements of reservoir species in the lower stratosphere and further laboratory investigations of kinetics governing catalytic chain termination processes must be pursued in order to assess with confidence the effect of further anthropogenic emissions upon the stratosphere.

Our understanding of stratospheric aerosols is still far from being satisfactory. In particular, the gas-to-particle conversion processes involving  $\text{SO}_2$  oxidation and condensation nuclei formation are still poorly understood. Future research, therefore, should include in situ measurements of aerosols, trace gases and condensation nuclei involved in aerosol formation. Accompanying laboratory studies of relevant chemical processes are also needed.

The further refinement of direct probes and remote sensing tools based on exquisitely sensitive spectroscopic techniques will play an important role in the continued development of stratospheric chemistry and physics. In this regard, it should be noted that most field studies to date have been conducted in relatively narrow geographical regions. Observation of substantial three-dimensional structure (and fine structure) in the stratosphere calls for more extensive geographical coverage in future experiments.

## ATMOSPHERIC CARBON DIOXIDE AND CLIMATE CHANGES

### *The Present State of Understanding*

Highly accurate measurements in many parts of the world show that the concentration of carbon dioxide in the atmosphere increased by nearly 9% between 1958 and 1982, from 315 to 343 parts per million by volume. Credible estimates from the core measurements show that the atmosphere  $\text{CO}_2$  content in the middle of the 19th century was about 280 parts per million indicating a 22.5%. Probably two-thirds to three-fourths of this increase came from the burning of fossil fuel — coal, oil and natural gas — and the remainder from clearing of forests to expand agricultural land to meet the needs of rapidly growing human population. It is likely that atmospheric  $\text{CO}_2$  will rise to about 600 ppm by the latter half of the 21st century, approximately twice the mid-19th century value.

Because carbon dioxide in the atmosphere absorbs and reradiates infrared radiation, the increase of carbon dioxide will result in a rise in the temperature of the lower atmosphere and the upper layers of the oceans. Model calculations for a CO<sub>2</sub> doubling indicate that after ocean and atmospheric temperatures have approached equilibrium, the average global temperature will be between 1.5 and 4.5°C higher than in the 19th century. The temperature rise at high latitudes will probably be at least twice as large as the global average rise, while temperatures in the tropics will increase by a smaller amount.

The atmosphere content of other infrared-absorbing gases (called greenhouse gases) notably methane, chlorofluorocarbons, tropospheric ozone, and nitrous acids are also increasing. Consequently, temperature in the lower atmosphere during the next century will probably be higher than the above estimates. The world climate will be significantly warmer than at any time during the past 100,000 years. This tendency will persist for many centuries, until the excess atmospheric CO<sub>2</sub> is absorbed into the oceans.

Thermal expansions of the upper ocean waters and disintegration of glaciers will bring about a rise in sea level of at least 70 centimeters during the next century and possibly 5 to 6 meters during the following several centuries. The volume of water in areas of low rain and snow fall will probably decrease by 30 to 40%, with drastic consequences for irrigated agriculture. Rain-fed agriculture in higher latitudes will benefit from a longer growing season and warmer temperatures. Higher carbon dioxide will act as a fertilizer for crop plants, when temperatures are not too warm and sufficient moisture is available. Net photosynthetic production should increase. The effects on natural ecosystems are difficult to predict, in the present state of ecological understanding. Effects in different world regions are likely to be widely different.

### *What Kinds of Research are needed?*

1. Economic and social research on the factors which will determine future emissions of carbon dioxide. This should include the probable rise of future rates of world energy use and the future misuse of energy sources — that is, the ratio of energy from fossil fuel combustion to that from other energy sources. Also needed are better estimates of possible future changes in the areas of forests.

2. Possible changes in atmospheric carbon dioxide related to ocean

circulation and ocean biological production, and to uptake or release of carbon in the land biota and in soil organic matter and soil calcium carbonate.

3. Future changes in atmospheric concentration of other greenhouse gases (methane  $\text{N}_2\text{O}$ , chlorofluorocarbons, tropospheric ozone).

4. How can the fertilizer effect of carbon dioxide be utilized to maximum advantage in human food and fibre production?

5. What changes in river flow can be expected in different areas of the world, resulting from rising temperature and probable changes in precipitation?

6. What will be the likely rate of rise of sea level and the probable range of rates of sea level rise? What will be the effects of sea level rise in different areas?

#### *The Need for Assessment of the likely effects of $\text{CO}_2$ increase in different world regions*

The  $\text{CO}_2$  problem is global, but its net effects will be different in different regions. Though these effects will not be fully manifest for several decades, prudence requires that nations in these regions make their own assessment of the effects and initiate plans to mitigate the deleterious effects and take advantage of the beneficial ones.

#### ATMOSPHERIC ACIDITY

The atmosphere is an oxidizing medium, and as a consequence, chemical species of anthropogenic origin emitted usually in urban environments, undergo change in oxidation state which may result in increased chemical and biological activity. A specific consequence may be the conversion of material to water-soluble forms, which then can have dramatic impact upon the biosphere with which they come into contact. Such emitted species of importance in industrial nations include sulphur dioxide, oxides of nitrogen, heavy metals, photochemical oxidants and organic materials.

In the specific case of emissions of sulphur dioxide and oxides of nitrogen, the change in oxidizing nature of the atmosphere subsequent to chemical reactions in the atmosphere, and upon deposition, results in changes in the acid base and redox equilibria in the aqueous phases.

These processes are not evenly distributed, since the effects observed in any locality depend upon the emission distribution pattern and transport, the rate of oxidation in the atmosphere, and the rate of deposition, which depends upon climatic factors.

Some local effects are well known, from extensive studies in localities such as Scandinavia, but much less information is available on a global scale, and there are some indications that chemical changes are occurring in remote areas, such as the North Polar region, and effects of this have not been widely studied.

Oxidation in the atmosphere may take place homogeneously in the gas-phase, in the aqueous phase, and heterogeneously, and can lead to particulate formation. The latter is poorly understood.

It must be recognized that transfer of species from the atmosphere by dry deposition is a *continuing* process, whereas that in aqueous phase, through precipitation, is periodic, and strongly dependent upon meteorological conditions.

Dry deposition of different species in the gas-phase is dependent upon their chemical properties and the nature of the surface. When deposited, such species, for example  $\text{SO}_2$ , may react further in the soil giving substances with increased acid properties. However, the same species may have been produced in the atmospheric process, and are deposited by gravitation.

The wet deposition is of species which have either played the role of condensation nuclei ( $\text{H}_2\text{SO}_4$  — droplets) or have been washed out during the precipitation event.

A number of observed effects are now with a greater or lesser degree of confidence ascribed to the deposition of acid materials, heavy metals and other species. They include:

(i) Destruction of animal life, particularly fish during the breeding seasons in spring, where run-off of melting snow causes sudden drops in pH. The effects are not solely due to concentration of acid, but clearly involve the solubilization of other elements, notably aluminium, which in higher concentration becomes toxic.

(ii) Damage to plant life, discussed below.

(iii) Damage to buildings, particularly materials such as calcium carbonate stone, and feldspar. However, a detailed scientific understanding of these harmful effects is still lacking.

It is thus recommended that:

1) the oxidation of sulphur dioxide should be investigated in

greater detail, in the real conditions of the atmosphere where homogeneous as well as heterogeneous reactions occur simultaneously and might affect each other.

2) the causes of the decay of organic materials should be investigated thoroughly in order to evaluate the relative mechanism and the impact of their metabolites on the environment.

#### EFFECTS OF CHANGES IN CHEMICAL CLIMATE ON WATER, SOILS AND BIOTA

The atmosphere has been used to discharge waste products of human activities, such as fuel burning and industrial processes to a great extent.

The following changes in chemical climate have special importance for biota:

- the increase of photochemically reactive compounds in the atmosphere

- the increase and continuous input of acidity both by wet and dry deposition

- a wide distribution of heavy metals in biota and soils. Besides that, biota and soils are contaminated by radioactive fallout and persistent pesticides or other organic compounds or potential hazard to life.

Dealing with the effects we have to differentiate between

- acute and chronic effects by direct impact on plants, animals and human beings, especially by gaseous pollutants such as  $\text{SO}_2$ , HF, HCl and photochemical oxidants

- long-term effects by accumulation in soils and biota and inclusion into the water and nutrient cycles of ecosystems. The accumulation of acidity in mineral soils and water and the build-up of reservoirs of heavy metals, persistent chlorinated hydrocarbons, and radioactivity to the disposition of living beings are regarded as having great importance.

The following examples stress the importance of immediate counter measures.

- The present decay of many German and other European forests as a result of the impact of air pollution, especially photochemical pollutants and acidic deposition.

- The extinction of many fresh water animals including fish in various Scandinavian and Northeast-American lakes and rivers.



Thus increased research is necessary for a better understanding of the overall change of the biosphere and ecosystems, and detailed studies on the mechanism of pollution effects besides the development of waste-free technology are also required.

Even if we know about the uncertainties of source-effect relations, we strongly recommend immediate action according to the present state of knowledge, even if this is not complete. General aims should be:

- Utmost care in dealing with nature,
- Reducing the amount and number of chemicals put into the environment.
- Developing means of action which will secure life and environment for future generations.

## PROBLEMS OF THE TROPICAL WORLD

Human numbers are growing fastest in the tropical world. With this growth goes an increase in livestock, and in cultivated soil. Pressure is increasing rapidly on life-support resources, and on land. Control depends on an understanding, not only of the social questions involved, but of the demands each living being makes on essential resources.

In humid areas, the rate of world deforestation is estimated at 6 to 10 million hectares per annum, 2 to 4 millions of which are in South America. The biota being destroyed holds the greater part of the nutrients, which are lost to the ecosystem. This deforestation rate represents a tragic loss of plant and animal species. The usual techniques of soil cultivation, especially where precipitation is high — often above  $2,200 \text{ mm a}^{-1}$  — accelerate the natural loss. Special technology is needed for such humid tropical regions. Existing research on such techniques needs to be increased and intensified.

Despite the known rapidity of chemical cycling and sensitivity to human activities, we still know far too little about the over-all nutrient requirements and their relation to the global biogeochemical cycles. Very little knowledge exists, furthermore, about the sensitivity of tropical ecosystems to soil, air and water pollution. This may be expected to increase in the future due to expanded agriculture and *intensity*. It is important that the gathering of background information needed for studies of such cycling of nutrients, elements and pollutants be accelerated — together with estimates of human impact.

The dry land surfaces of the tropics are also deteriorating rapidly, because of increased human numbers. In the past twenty years drought has been severe in many areas. In some parts of Africa large areas have been abandoned. Two feedback processes may be at work:

(i) surfaces denuded of vegetation have increased reflectivity. This may decrease rainfall, by encouraging atmospheric subsidence. Large amounts of fine soil (mineral and organic) have been removed by the wind;

(ii) reduced photosynthesis (due to removal of vegetation) and increased respiration and decomposition (due to soil organisms) may be reducing stored organic material. This in turn (with the loss of fine mineral material) may reduce water storage. Much tropical rainfall comes from re-evaporated rain. Hence such losses may act to reduce rainfall further.

The dry lands of Africa, northeastern Brazil, Australia and possibly other regions have all suffered from these biophysical and biochemical changes. The new countries of Africa, particularly those of the Sahel, of East Africa and of the margins of the Kalahari, have been worst affected.

Future climatic change induced by  $\text{CO}_2$  increase may also affect the tropical environment adversely. A temperature rise of  $2^\circ\text{K}$ , unless accompanied by a rise in rainfall, will add to the difficulties of farmers and herdsmen. It will also make still more difficult the provision of adequate drinking water, the design of irrigation systems and the maintenance of good health standards.

These problems are so grave that we believe that the scientific community as a whole should give all possible aid and encouragement to those members who live and work in the tropical countries. The need for adequate equipment, funding and even physical access is desperate. So also is the need for trained scientists and for institutions capable of supporting them. Science has a major role to play in the problems of development. Its long tradition of international cooperation can serve to strengthen — even to make possible — the necessary social and political action.

\* \* \*

In this century mankind has reached, for the first time, the point where it can alter its environment in a time scale shorter than the one needed to understand and quantify the implications of such actions. The

ozone layer depletion, the global warming due to  $\text{CO}_2$  increase, the immission of acid chemicals in the ecosystem are examples of such changes of our environment.

Dramatic changes in atmospheric temperature which would severely strain the survivability of life on earth would also certainly occur in the aftermath of a nuclear explosion due to the accumulation of particulates blocking the sun's light.

In spite of the great progress made in recent years and reported at the present Study Week in the understanding of the physical and chemical phenomena occurring in our atmosphere, major gaps still remain that call for further study and research. As examples, we can cite our limited knowledge of tropospheric chemistry in tropical regions, the lack of information about the  $\text{CO}_2$  increase in the atmosphere (and the implication thereof), as well as the various stages of acidic precipitations. This lack of knowledge hinders a precise assessment of what are otherwise generally perceived as possible major alterations of our environment. For example, on the basis of the present knowledge, we cannot today fully appreciate the implications on soil, vegetation and animal life of such phenomena.

It is also felt that besides the need of more theoretical studies, more field research is needed in areas such as the tropics and high latitude regions, as well as volcanic explosions which offer the unique opportunity to study the response of the climatic system to a quantifiable perturbation.

Finally, the need was felt to promote the awareness of Governments and international Institutions as well, about the need to cooperate among themselves with the aim of solving problems that are increasingly perceived as not limited to a single nation but which involve the whole biosphere.

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