proceedings of the concawe seminar on atmospheric emissions and their effects on the environment in europe with particular reference to the role of hydrocarbons

Prepared by the CONCAWE Secretariat

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Den Haag
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Acknowledgements

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Universität Freiburg (Plates 5 - 8, page 65)

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in providing these illustrations.

CONTENTS

1. FOREWORD

In Europe, one of the major environmental issues is the phenomenon called "acid rain". Originally it concerned mainly the long-range transport of air emissions, principally sulphur oxides, as a potential cause of the acidification of lakes in Scandinavia. More recently "acid rain" is said to contribute to forest damage in Central Europe. In this case the pollution is attributed to photo-oxidants such as ozone, which, it is alleged, under certain weather and air chemistry conditions, may attack tree growth. Photo-oxidants are formed by a combination of hydrocarbons, especially the more reactive types, nitrogen oxides, trace amounts of other chemicals, and intensive sunlight.

Governments, supranational organisations and research insitutes are currently carrying out wide ranging studies into the many aspects of the "acid rain" phenomenon, and particularly forest damage. A number of computer models have been developed to similate the conditions under which damage may result.

CONCAWE, as an organisation supported by the major European oil companies, believes that it is necessary to have a better understanding of the complex inter-relationships involved, so that legislation designed to protect the environment can be soundly based and cost-effective. CONCAWE is supporting this objective by gathering facts and disseminating information to authorities, the industry and the public.

In the case of hydrocarbon emissions, CONCAWE felt there was a need for an up-to-date overall view of the progress and inter-relationship of research, computer modelling and actual field effects. To meet this objective CONCAWE organised a seminar entitled "Atmospheric emissions and their effects on the environment in Europe with particular reference to the role of hydrocarbons", which was attended by representatives of the scientific world, the EEC and the American and European oil industry.

The CONCAWE seminar showed that although there is a considerable multidisciplinary research effort contributing to a growing knowledge of the causes and effects of photo-oxidants in the European atmosphere, there are uncertainties in many areas. In particular, too little is known about the way in which photo-oxidants relate to other stress factors in causing damage to vegetation in remote rural areas such as the forests of Central Europe, and whether such effects are an episodic phenomenon or the result of a long-term build-up of pollutants. The present knowledge of the chemistry of development of photo-oxidants, and the atmospheric transport involved in the European situation, is incomplete, and consequently the optimum means of controlling the development of photo-oxidants remains unclear.

This report records the papers presented and discussions during the seminar and reflects the different points of view on the issues raised. The speakers, among the foremost experts in their fields, were selected so as to cover as many aspects of the topic as possible. The views expressed are those of the speakers and CONCAWE is convinced that the seminar represents a valuable review of this subject, and will contribute to public awareness of the complexity of the problems involved and the need for further research into the causes, mechanisms and effects of atmospheric pollution.

2. SPEAKERS

The speakers who made presentations at the CONCAWE Seminar, under the Chairmanship of Mr. E. van Veen (Shell, Internationale Petroleum Maatschappij B.V., Den Haag, Netherlands) were:

Ir. L Brader	Director, Plant Production and Protection Division, United Nations Food and Agriculture Organisation Rome, Italy
Dr. F.E. J. Briffa	Research Planning Department, Shell International Petroleum Company, London, UK
Dr. R.A. Cox	United Kingdom Atomic Energy Research Establishment, Harwell, UK
Dr. H. van Dop	Royal Dutch Meterological Institute (KNMI) Ministry of Transport and Waterways, De Bilt, Netherlands
Dr. L.J. McCabe	Researach Department, Mobil Research & Development Corporation, Paulsboro, New Jersey, USA
Dr. P. Mathy	Directorate General for Science, Research and Development, European Commission, Brussels, Belgium
Prof. Dr. H.W. Zöttl	Director, Institute for Soil Studies and Forest National Sciences, Albert Ludwig University, Freiburg, Federal Republic of Germany

In addition, in response to requests from the floor, Dr. P. Builtjes, Division for Technology in Society, Netherland Organisation for Applied Scientific Research, Apeldoorn, Netherlands, attending as a representative of the European Commission, gave a brief ad hoc presentation on the PHOXA model.

3. PARTICIPANTS

The following invited guests took part in the Seminar:

Name	Company
Mr. A. Campobasso	AGIP Petroli S.p.A., Italy
Mr. A.C. Helas	Amoco (UK) Ltd., UK
Mr. A. Ayala	Aserpetrol, Spain
Mr. F.G. Larminie	BP International Ltd., UK
Mr. J. McKay	BP International Ltd., UK
Mr. M.D. Long	BP International Ltd., UK
Mr. D.M. Whitehead	BP Research Centre, UK
Mr. J.B. Wilson	BP International Ltd., UK
Mr. E.D. Edwards	Burmah Oil Trad. Ltd., UK
Mr. J. Aboulafia	CFP/CFR, France
Mr. A.B. Atkin	Conoco Ltd., UK
Mr. C.S. Frangoulis	EKO, Greece
Mr. G. Pluche	Elf S.A., France
Mr. G. Marruzzo	ENI, Italy
Dr. R. Barnes	Esso Research Centre, UK
Dr. F.O. Foster	Esso Engineering Services Ltd., UK
Mr. J.B. Godden	Esso Europe Incorporated, UK
Mr. R. Muths	Esso, France
Mr. R. Th. Sobel	Kuwait Petroleum Company, Netherlands
Mr. J.B. Berkley	Mobil Europe Incorporated, UK
Mr. R.B. Callen	Mobil Oil Cooperation, USA
Dr. R. Hamann	Mobil Oil AG, Germany
Mrs. A. Laiho	Neste Oy, Finland
Mr. W. Bjerke	Norsk Hydro A/S Rafnes, Norway

Name	Company
Dr. I. Bruner	OMW AG, Austria
Mr. A. Cross	Phillips Imp. Petr. Ltd., UK
Mr. D.D. Handford	Phillips Imp. Petr. Ltd., UK
Mr. E.C. Cadron	Petrofina S.A., Belgium
Mr. R. van Ermbt	Labofina, Belgium
Mr. P. van der Wee	SIBP, Belgium
Mr. I. G. Brycee	Shell. Int. Petr. Maatschappij, Netherlands
Mr. N. O. Crossland	Shell Research Centre, UK
Mr. J. Felton	Shell Int. Petr. Maatschappij, Netherlands
Mr. E.O.H.M. Ruempol	Shell Int. Petr. Maatschappij, Netherlands
Dr. K. Selby	Shell International Petroleum Company, UK
Dr. R. Ott	Deutsche Shell Chemie, W. Germany
Mr. H.J. Tausk	Shell Int. Petr. Maatschappij, Netherlands
Mr. E. van Veen	Shell Int. Petr. Maatschappij, Netherlands
Mr. J. van Oudenhoven	Shell Int. Petr. Maatschappij, Netherlands
Mr. J. Waller	Shell Int. Petr. Maatschappij, Netherlands
Mr. O.R. Haugland	Statoil, Norway
Mr. G. Gunderson	Statoil, Norway
Mr. A.De Meulemeester	Texaco S.A., Belgium
Dr. G.F. Goethel	Veba Oil AG, W. Germany
Mr. K. Henrich	Union Rheinische Braunkohlen Kraftstoff AG W. Germany
Mr. P. Lieben	OECD, France
Dr. P. Builtjes	TNO, Netherlands

4. PROGRAMME

21 October 1985

08.00 - 08.45 hrs:	Registration
08.45 - 09.00 hrs:	Opening address of the Chairman
09.00 - 10.00 hrs:	"Emissions, transport and deposition process in the atmosphere"
Lecturer:	Dr. H. van Dop (KNMI, Netherlands)
10.00 - 11.00 hrs:	"Review of atmospheric photochemistry"
Lecturer:	Dr. R.A. Cox (Atomic Energy Research Establishment, Harwell, UK)
	Questions and answers arising from Dr. van Dop's and Dr. Cox's presentation
11.00 - 11.20 hrs:	COFFEE BREAK
11.20 - 12.20 hrs:	"Possible causes of forest damage in Germany"
Lecturer:	Prof. Dr. H.W. Zöttl (Albert Ludwigs Universität, Institut für Bodenkunde, Freiburg)
	Questions and answers arising from Dr. Zöttl's presentation
12.20 - 13.00 hrs:	"US experience of hydrocarbon and NO_x emissions control"
Lecturer:	Dr. L. McCabe (Mobil, USA)
	"The PHOXA model" (Ad hoc presentation) Dr. P. Builtjes
13.00 - 14.15 hrs:	LUNCH
14.15 - 15.15 hrs:	"EEC research programme on air pollution matters"
Lecturer :	Dr. P. Mathy (European Commission, Brussels)
15.15 - 16.15 hrs:	"The development of ozone in European atmosphere and its implications for the environment"
Lecturers:	Ir. L. Brader (Food and Agriculture Organisation of the United Nations) and Dr. F. Briffa (Shell International, London)
	Questions and answers arising from Ir. Brader's and Dr. Briffa's presentation
16.15 - 16.30 hrs:	TEA BREAK
16.30 - 17.30 hrs:	Panel discussion

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"EMISSIONS, TRANSPORT AND DEPOSITION PROCESS IN THE ATMOSPHERE"

Presentation by
Dr. H. van Dop
Koninklijk Nederlands Meteorologisch Instituut
Ministerie van Verkeer en Waterstaat

ABSTRACT

Forest die-back on a large scale in Europe and North America has led to renewed investigations into the role of air pollution and its ecological impact. Essential elements in the extremely complicated process, from emissions via transport, chemical transformation and deposition to supposed effect, are the dispersion and deposition of the pollutants. A large proportion of the pollutants are able to travel over a considerable distance, of the order of 1000 km. This paper indicates how dispersion over these distances can be described. A summary is given of box models, trajectory models and grid models. The latter models contain the most detailed description of the atmospheric transport and deposition process. However, they require an enormous amount of meteorological information. Also, computer time and storage requirements are excessive. Finally, the process of deposition, accompanied or not by precipitation is discussed.

1. INTRODUCTION

Recently, acid deposition has attracted attention on a large scale due to the suspected relationship with forest die-back. Dramatic pictures were shown in journals and magazines and attracted the attention of a lot of people. They pointed attention to the air pollution problem, but if you look at the estimated costs of damage due to air pollution, it is clear that damage to forest and lakes is relatively unimportant (Fig. 1). The damage to lakes, fish, and decrease in fish yield are only relatively small amounts, whereas the estimated damage to buildings due to acid rain is the most important contribution. Of course, these are estimates and the uncertainty is a matter of much discussion but, in any case, the numbers are much larger than, for instance, the costs connected with forest die-back.

In Fig. 2 a summary is given of a chain of processes leading to (acid) deposition, and indicating at which stages these processes can be influenced. The air pollution usually starts by initiating some (combustion) process which yields waste, and the waste is emitted. After the emission follows the dispersion in the atmosphere. During its transport in the atmosphere it is being transformed by all kinds of chemical processes and, in the end, almost everything that's going up comes down again: it is deposited on the earth where it may have its effect. Some of these effects can be measured and evaluated.

Several organisations are doing research in this field (Fig. 3). Let's have a brief overview of the situation in Holland. Most of the research is on a governmental level, by the Ministries of Economic Affairs, Agriculture, Environment and Transport. There is a national policy in the field of air pollution and this policy is supported by research carried out by bodies such as the Institute for Public Health in The Netherlands (RIVM). Non-governmental organisations are also active in the field of air pollution research: the Institute for Applied Scientific Research (TNO), the research company of our co-operating electricity companies (KEMA) and also oil industry companies such as Shell. Heavy industry is also involved (Hoogovens).

On the international scene we have many others. Germany and the Netherlands are the countries who are most active in the air pollution field, but the European Economic Community (EEC) is also active in the field. The OECD is interested in air pollution problems, mainly in photochemical air pollution. IIASA, the International Institute for Applied Systems Analysis in Vienna is doing some work and the World Meteorological Organisation has an environmental programme too.

The main organisation in the United States is the Environmental Protection Agency, (EPA). The National Academy of Science is developing programmes in the field of air pollution and some private companies, e.g. Systems Applied Incorporated, (SAI) and Environmental Research and Technology, (ERT) in air pollution studies. As a matter of fact, SAI is participating in a project in Europe called PHOXA (1), a study which is currently being carried out in the field of photochemical air pollution in Europe.

2. SOURCES OF AIR POLLUTION

What are the major emissions we are talking about? The major components are oxides of nitrogen which are formed in every combustion process by the oxidation of nitrogen. Hydrocarbons, perhaps better described as Volatile Organic Compounds (VOCs), sulphur dioxide and ammonia (which is maybe a particular Dutch problem) also contribute to the acidification. Also important, of course, are the natural sources such as, for instance, biological decay. Forest fires are a natural source of air pollution (SO_4, VOCs and carbon dioxide); lightning is a source of ozone. A fairly big source of air pollution are vulcanic eruptions: the El Chicon in Mexico emitted a tremendous amount of particulates, but also much sulphur dioxide.

The anthropogenic (man-made) sources are all connected with the burning of fossil fuels and that's the main source of air pollution: coal, oil and natural gas. Another source in tropical regions is biomass burning, where it is one of the major sources of air pollution. We, of course, are mainly interested in the burning of fossil fuels. Looking at the globally emitted amounts, we observe that the natural emissions level more or less (within a factor of two) with the anthropogenic emissions, but the problem is that the natural emissions are emitted evenly over the whole globe, while the anthropogenic sources are concentrated in a few industrial belts in Western Europe and in the Eastern part of the United States, and there they cause the problems.

We distinguish between point sources (elevated emissions from a power plant, or petrochemical industry) and diffuse sources, which are mainly low-level sources: domestic heating, bio-industry, small industry and traffic, which is a major source of NO_x.

3. AIR POLLUTION MODELS

After its release into the air we have lost our control over the fate of the pollutant. It is dispersed, and in fact the mechanisms in dispersion are fairly simple. We can distinguish between "horizontal" dispersion, which says that the air pollution is taken away at the mean (horizontal) wind speed, and turbulence. For horizontal dispersion the mean wind speed is the major agent. With "horizontal" we usually refer to dispersion which is parallel to the surface. The vertical mean wind speed is usually very small: a daily average can be a few centimeters per second so that the most important dispersion mechanism is turbulence. It may be noted, however, that in clouds larger vertical velocities usually occur, so they can be quite effective in the vertical transport of air pollution. Turbulence is a fluctuating air motion, and it means that pollution is gradually transported to higher altitudes. This is illustrated in Fig. 4. Here two characteristic situations are depicted: a night-time situation, when the turbulence is usually low and thus the vertical dispersion is also low. This means that a high altitude emission will not reach the surface very quickly and that ground-level emissions will stay near the ground. During day time the situation is different: the turbulence is usually large and so also is the vertical dispersion. That has two effects: emission from ground sources will be diluted sooner than during the night-time, but that holds also for emissions from high sources. Thus in this situation both high and low sources contribute to the ground level concentrations. This situation is only true close to the source, say not further than 15 km away.

In some way we have to transpose this picture into a mathematical model. Here, a somewhat more detailed picture is shown (Fig. 5) and it is becoming already more complicated. The terrain is not level any more. The little dots represent the air pollution during daytime when there is intensive mixing. Clouds are present which act as a kind of "vacuum cleaner": they suck up the air, and with it they suck up also the air pollution. In clouds all kinds of chemical processes occur, which will be discussed by Dr. Cox hereafter. Again during night-time a shallow stable layer builds up and air pollution usually remains in this layer, though in the upper layer air pollution is still present due to the vertical mixing from the previous day. We include this in a mathematical model, introducing a few layers: a cloud layer, where we model all kinds of chemical and physical processes, a mist layer and a surface layer. So, for some detail in the vertical direction at least a few layers are required. The evolution in dispersion modelling, however, started much more simply and the first type of models, the most simple models, were box models.

3.1 BOX MODELS

In a box model, for instance, an industrial area is considered and a box is put over it. Horizontal wind speed is neglected, so it is a box with closed walls. Assuming that we know all the emissions in this box, and if we know all the chemical reactions, we are able to calculate the build-up of concentrations in the box volume. This is, of course, for chemists a very attractive model since there are hardly any computer limitations. The chemistry can be made very complicated. Of course, a shortcoming in these kinds of model is that they do not resolve the locations of the sources and they don't say anything about the variability of the concentrations within the box. An example is a study by Brice and Cox (3) in the UK for the southern part of England in an area of 450 x 360 km^2 with a box height of 1300 m. They calculated ozone levels during seven subsequent days. In Fig. 6 a typical result with this kind of modelling is given. The emissions are held constant after the fourth day and what you see is the typical pattern for ozone concentrations, building up in an oscillatory way, having peak values in the late afternoon. When the emissions are cut down ozone concentrations gradually decrease. Note that not only ozone concentrations in ambient air are calculated, but also the accumulative process of deposition of ozone.

These models can hardly be called realistic because of all their simplifications.

3.2 TRAJECTORY MODELS

The next step in sophistication is the trajectory model. Here we have the possibility of the description of simple horizontal transport. There is a better resolution in space and time. Due to the complexity of the model we have to put some limitations on the complexity of the chemistry. These kinds of model are widely operational. They are used both in the United States and in Europe (4,5,6,7). A recent example is the Shell LAPSE Project, where the trajectory model was used to study the occurrence of high photochemical oxidant levels (8,9). The area of application was Europe and the height of the modelling area was variable.

How does a trajectory model work? I may indicate that by using this example: Fig. 7 is a map of a part of Europe and on this map I have drawn a few trajectories. Here, a trajectory starts at 3 o'clock in the afternoon on Day One. By knowledge of the wind field we can construct the path of an air parcel. An air parcel has a typical horizontal extension of, say, a 100 km and a height of thousand metres. When the air parcel is travelling it is taking up pollution from emissions when it passes over industrial areas. Also, on its path it is depositing material. In the parcel itself there is chemistry going on. We assume again that the pollutants are well mixed in the parcel. We are able with this kind of model to calculate the chemical content of the parcel at the receptor location. Fig. 7 gives trajectories for just one receptor point, but we are able to repeat the calculations for another desired location. In this way a picture of the "chemical mixture" present over Europe can be obtained. We note that Fig. 7 shows three trajectories. One was calculated by taking the wind field at ground level or, say, at 10 m height. The other trajectory was derived from the wind field as it was measured at a height of, say, 1500 m. Those trajectories are quite different, so the problem arises as to which emission locations the parcel really passes. Do we have to take the first or the second trajectory or something in between?

The early models always used the 850 mbar (1500 m height) trajectories. Nowadays it is more common to use a mean trajectory that is somewhere between 1500 m and ground level, and we take this trajectory as representative of the path of the air parcel. In the present case it is very uncertain which sources contribute to the air parcel, because of the large divergence in the trajectories. This only an example and there are many cases where the three trajectories are much closer together so that there is less ambiguity. We are able to calculate ambient concentrations but also to calculate the deposition. Fig. 8 is an example of the use of a trajectory model for the evaluation of dry deposition of sulphur dioxide in Europe (7). Lines of equal deposition values are constructed, and the highest values here, in central Europe and Germany, amount to 5 g per m^2 per year. Despite all their uncertainties, these models are frequently used for policy purposes.

The "transfer matrix concept" is based on these models. This is an important political concept in air pollution because by this matrix it is possible to calculate the concentration in a certain country as a result from the emission in another country. So, we can compose a matrix with the emitting countries in rows and the receiving countries in columns. The figures in this table detail the emissions of one country to any other receiving country (Fig. 9). For instance, for Belgium we observe that of the total sulphur deposition in the country, 58% is coming from abroad. If that is true, that is an important number because it tells the Belgium government that if it cuts down completely sulphur emissions originating in its own country, the sulphur dioxide deposition reduces only by 40%. In some countries it is even worse. In Austria, for instance, there would be little or no need to abate sulphur dioxide concentrations locally because the situation would not improve very much. Reliable or not, these are interesting figures, and the problem is to improve the confidence in these kinds of numbers.

The same trajectory model can be used for modelling photochemical oxidants. Up to now we have discussed the modelling of sulphur dioxide with very simple linear chemistry. You could use that kind of model also for more complicated situations and put in hydrocarbons and nitrogen oxides and make a simulation, for example, of an air mass arriving in Norway, in Langesund (10) and calculate the ozone concentration gradually rising, reaching values of 65 ppb (Fig. 10).

3.3 GRID MODELS

Finally, the most detailed but also the most complicated models are "grid models". They have a fine resolution in space and time. The considered area is divided into boxes of say 50 x 50 km, with a height of say 50 - 100 meters up to 1.5 - 4 km. So the whole areas is filled with boxes and we are able to model transport and chemistry in each box and keep track of all kinds of processes, including cloud formation and cloud dissolution in the box. We are able to give a fairly detailed description of transport and diffusion. However, the model is so extremely detailed with respect to the atmospheric dispersion process that we have to put some limitations on the atmospheric chemistry. Chemistry cannot be as detailed as some chemists would like, and research is going on in condensing chemical models to smaller models which are more easy to handle. Nevertheless, such large models can only be run on supercomputers. Most of the models are not fully operational yet. Centres where these models are designed are Systems Applied Incorporated (SAI) at San Rafael (3), which was one of the first Institutes where they developed grid models. The model is applied both in the United States and in the PHOXA project in Europe (1). At the US Environmental Protection Agency, (EPA), Rayleigh, a regional-scale oxidant model is being developed to be applied in the Eastern United States (2). Environmental Research and Technology (ERT),is also developing a model (11). This model is also being applied both in the United States and in the PHOXA project in Europe.

The US National Centre for Atmospheric Research (NCAR) at Boulder, is developing a model (12). In Europe, in a combined effort by KNMI and RIVM (De Bilt) also a simplified acid deposition and photo-oxidant grid model is being developed. It is being applied in an area in Europe (Fig. 11) containing the EEC and the major emissions from the Eastern European countries.

It will take at least three to five years of development and testing before these models can be applied on a routine basis.

4. DEPOSITION

The above models calculate concentrations in air. How do we derive from that the deposition on the soil? We distinguish between two kinds of deposition processes, dry and wet deposition. Dry deposition is the process by which material attaches to the soil or reacts with the soil or vegetation. For this process we have a very simple formula which says that the amount of dry deposition equals the ambient air concentration at the observation height multiplied by the deposition velocity. The problem is reduced to deriving deposition velocities for various combinations of compounds and surface types. Then we are able, given the ambient concentration, to calculate the amount of dry deposition.

In Fig. 12 some deposition velocities are tabulated. It should be borne in mind that, in general available data are not more than educated guesses. Note that an error of 50% in such a number means that the total dry deposition estimate is wrong by 50%.

4.1 WET DEPOSITION

The other process by which pollution reaches the surface of the earth is wet deposition. We do not yet know very much about wet deposition. In wet deposition we distinguish three processes: the rain-out process, the wash-out process and interception.

Rain-out occurs when air pollution is present in water droplets, in clouds, and when the rain process starts; then the rain together with the air pollution reaches the earth's surface. The second process, wash-out, is the process where rain is falling from a cloud through a polluted layer underneath the cloud and partially absorbs the pollution. So, relatively unpolluted rain might fall through polluted layers and might pick up pollution there and take it down to the earth's surface.

Finally, interception is a process which is connected with polluted ascending air masses. The ascending air is cooling and the water vapour in the air condenses. In the condensation process air pollution enters the water (fog) droplets. The fog is transported over the terrain, over crops, and over forests: leaves will very efficiently intercept fog droplets.

5. SUMMARY

I would like to conclude this review by indicating the major sources of uncertainty and gaps of knowledge in describing emissions, transport and deposition.

(1) Meteorological data. There are two sources of meteorological data: these are measurements and mathematical models. The situation at the moment is that in Europe we have a very dense observation network, so there is in fact no lack of meteorological data. In meteorological modelling progress is being made, but we can still do better.

(2) Emissions. There is generally an enormous lack of knowledge about emissions. Over the whole of Europe the knowledge of total emissions of hydrocarbons and of nitrogen oxides and even of sulphur dioxide is still a matter of research and discussion. The situation in the Eastern European countries, which also contribute to the air pollution problem in Western Europe, is even worse.

(3) The chemical composition of the troposphere. The chemical composition of the troposphere is, in fact, hardly known. We can get some knowledge of it by atmospheric flights, or by balloon measurements. Of course, at the earth's surface there are data on what kind of compounds are present in the atmosphere, but at higher altitudes the data are very poor.

(4) The chemistry and removal processes. The next speaker, Dr. Cox, will certainly address the problem of the uncertainties in chemistry. With respect to dry deposition, more reliable data will gradually become available. Wet deposition, though, is still a poorly understood process. Much more research and experimental data are required for a satisfactory description of this process.

6. REFERENCES

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Fig. 1 Estimated costs of damage due to acid deposition.

FORESTS		
	GERMANY	0,2
	EEC	0,1
LAKES		
	SCANDINAVIA	0,03
	SCOTLAND	0,0005
BUILDINGS		
	UK	4,3
	EEC	14
	MAINTENANCE	0,54-2,7

Fig. 2 Schematic chain, indicating the steps leading from (combustion) process to effect on the environment. The thick arrows indicate at which stages "the chain" may be affected by abatement policy.

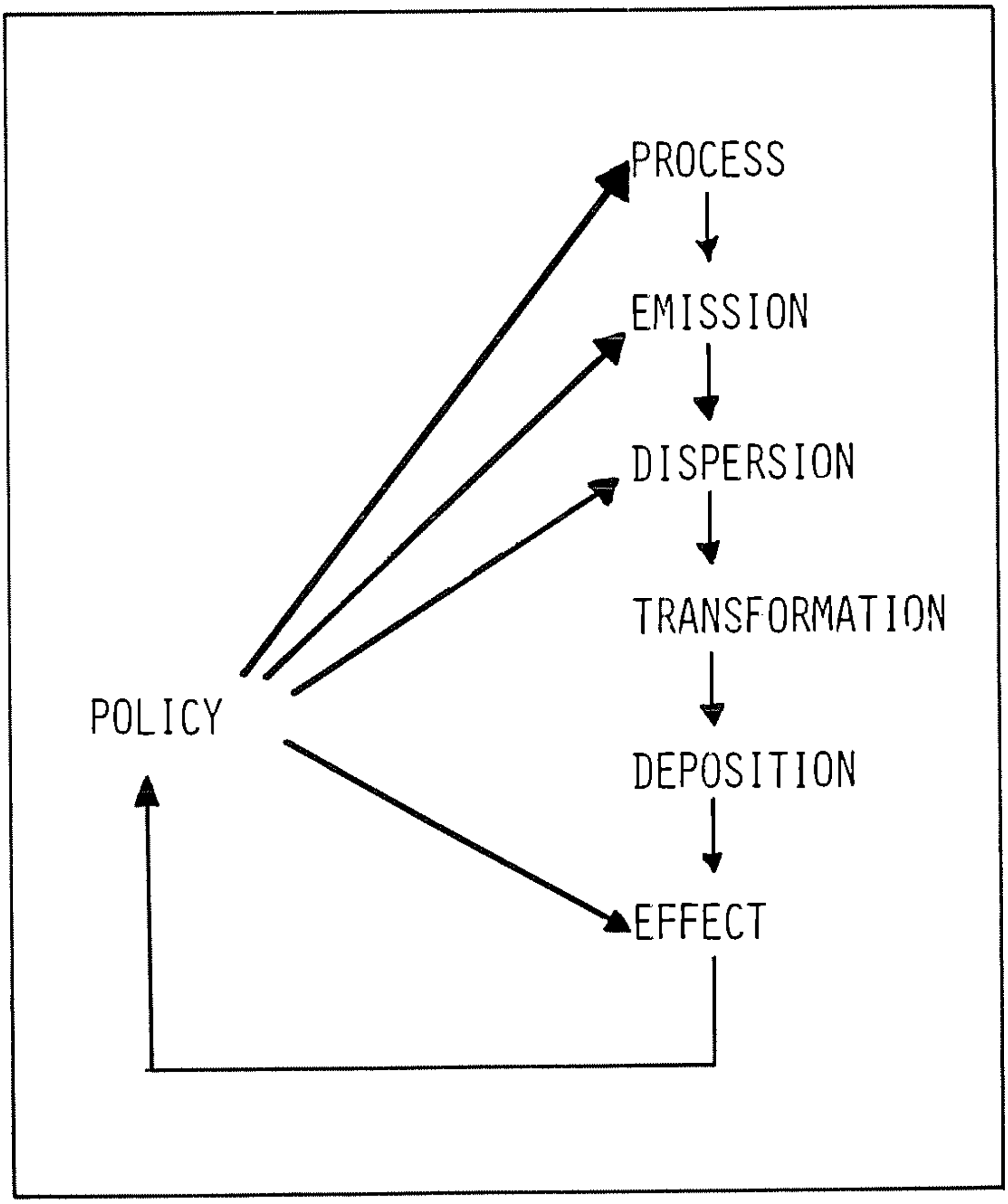


Fig. 3 A summary of National Governmental and Non-Governmental Institutions which are involved in air pollution and acid deposition studies.

GOVERNMENTAL: MIN. OF ECON. AFF.(P)
AGRICULTURE(P)
ENVIRONMENT(P)
TRANSPORT(P)

RIVM(P+R)
KNMI(R)
ECN(R)

NON GOVTAL: TNO(R)
KEMA(R)
SHELL(P+R)
HOOGOVENS(P+R)

P= POLICY, R=RESEARCH

Fig. 4 Two typical situations for the dispersion of air pollution close to source (a) a stable surface layer during the night and (b) an unstable mixed layer during daytime.

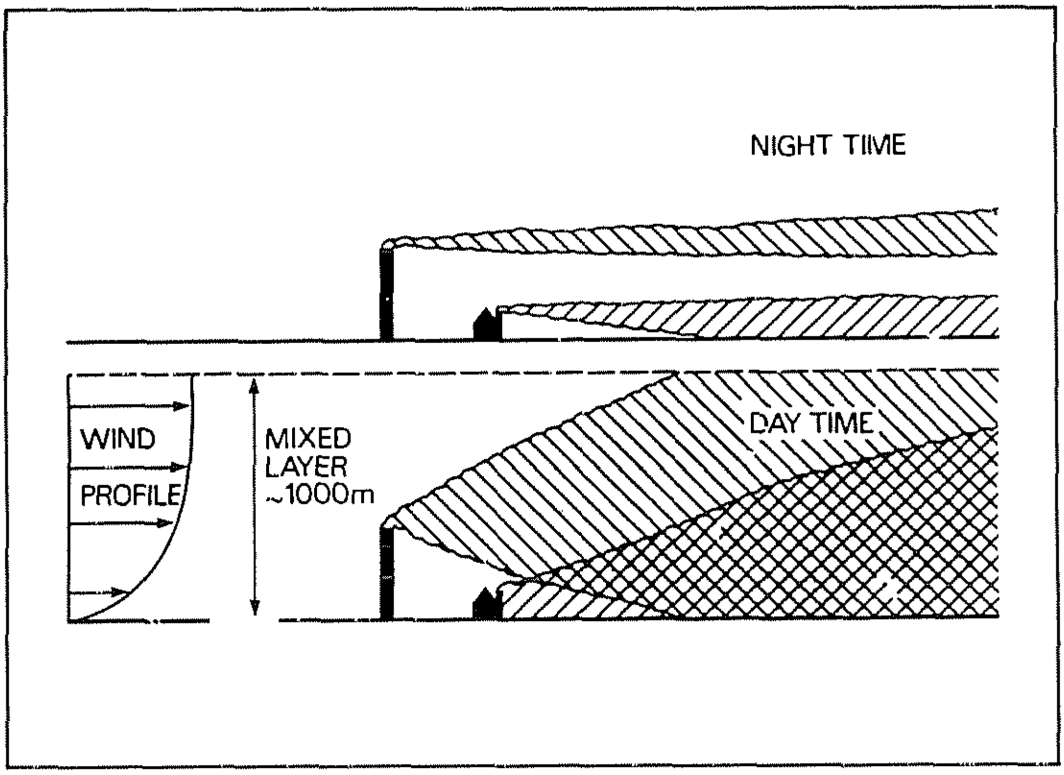


Fig. 5 Division of the atmospheric boundary into a surface layer, a marine layer, a mixed layer and a cloud layer. (Source: ref (2)).

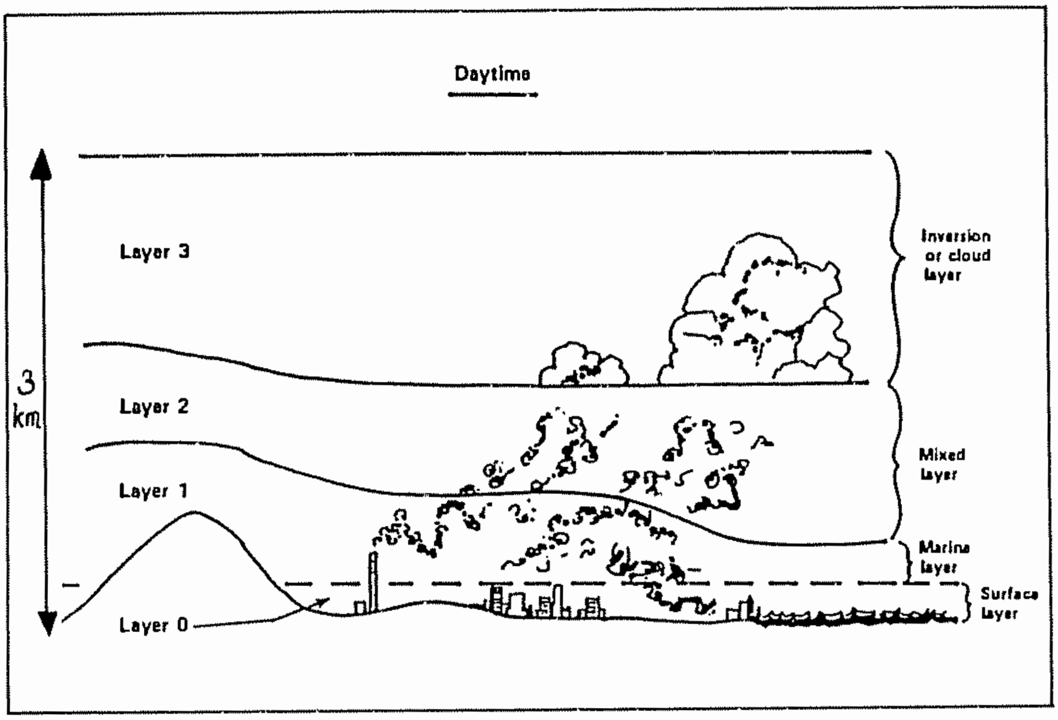


Fig. 6 Results of a calculation with a Box model (Brice and Cox (3)). Development of gas phase and deposited ozone with time. There are no emissions after Day 4. The integrated NO_x emissions are also shown, together with an analytically calculated curve for depletion through deposition only.

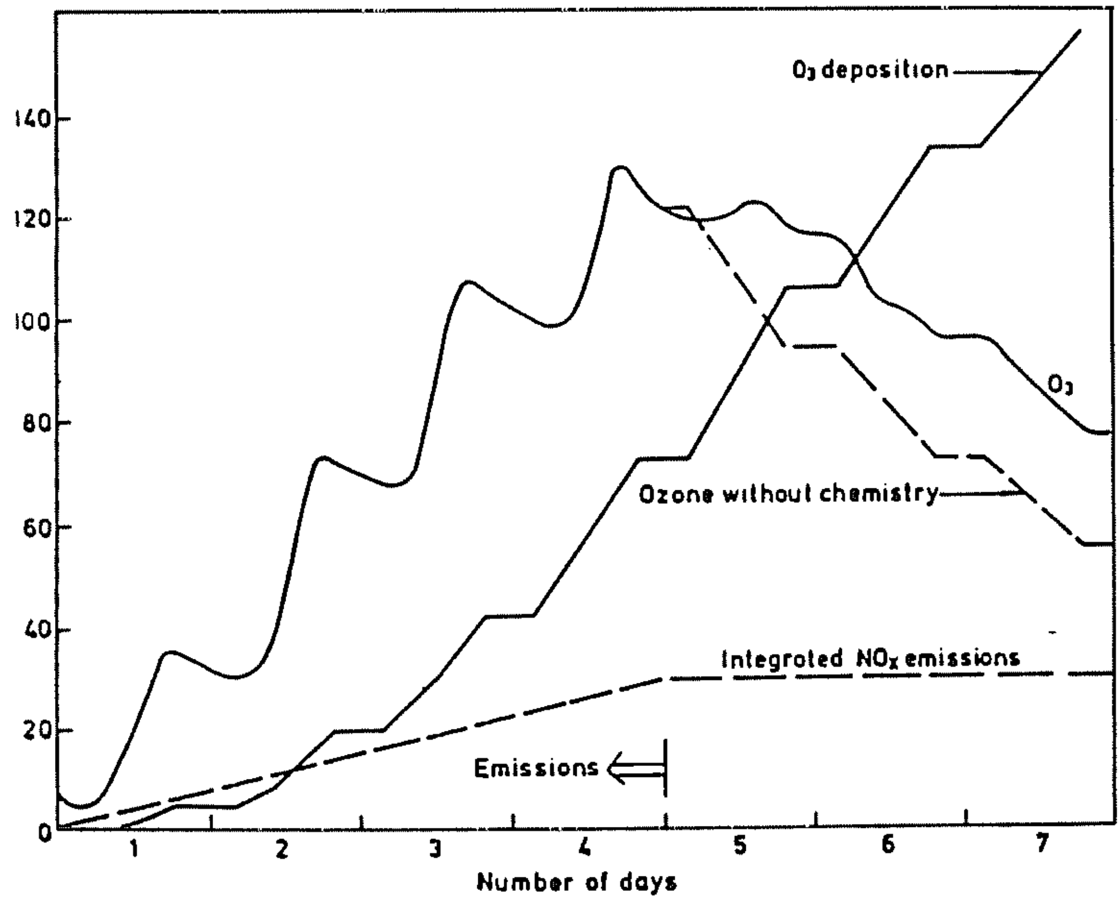


Fig. 7 Trajectories ending in Soissons (France). The trajectories indicate that there is a large divergence at the different heights: the 850 mbar trajectory depicts the motion of air at an approximate altitude of 1500 m.

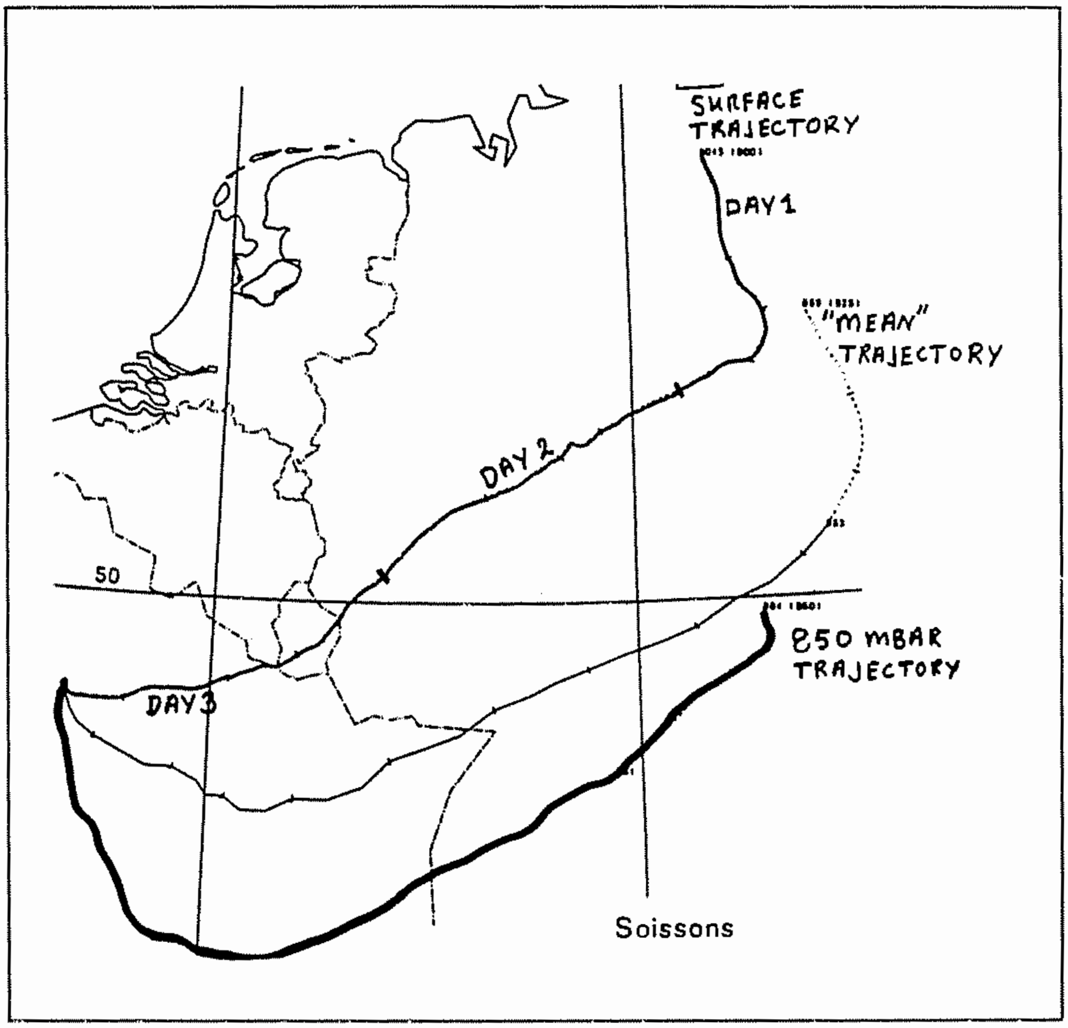


Fig. 8 Annual dry deposition of sulphur over Europe from man-made sources in Europe. (Source: ref (7)).

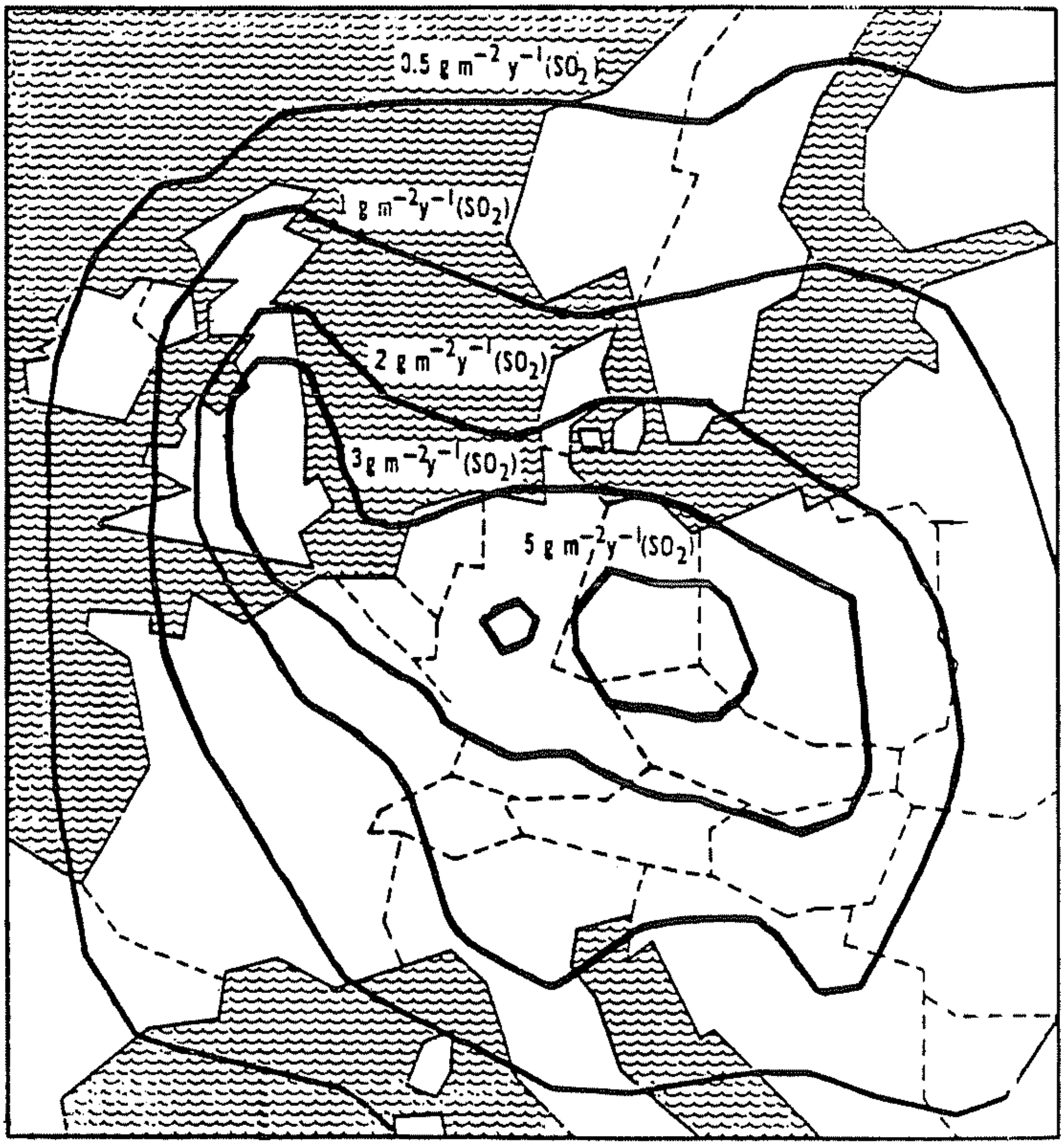
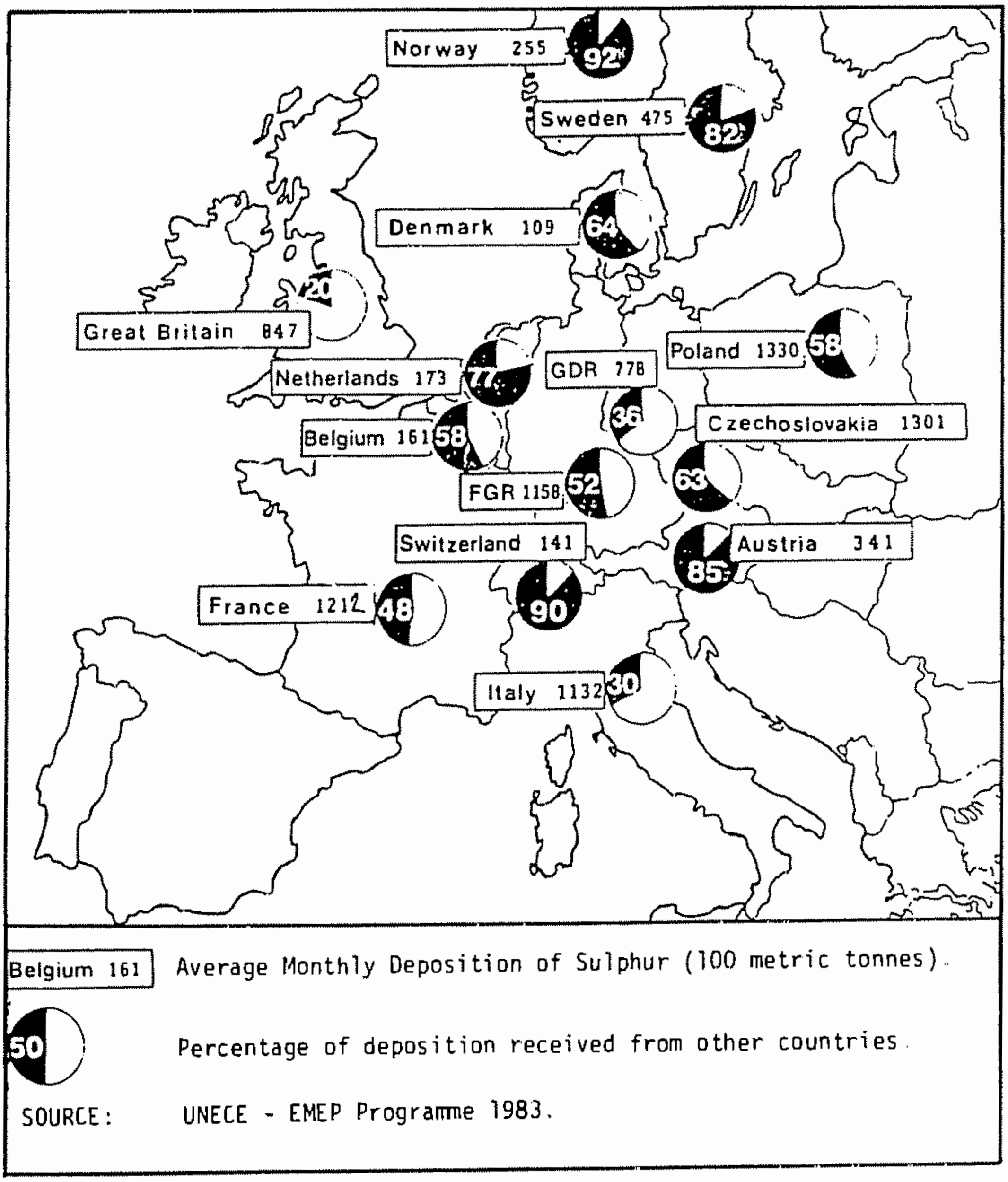
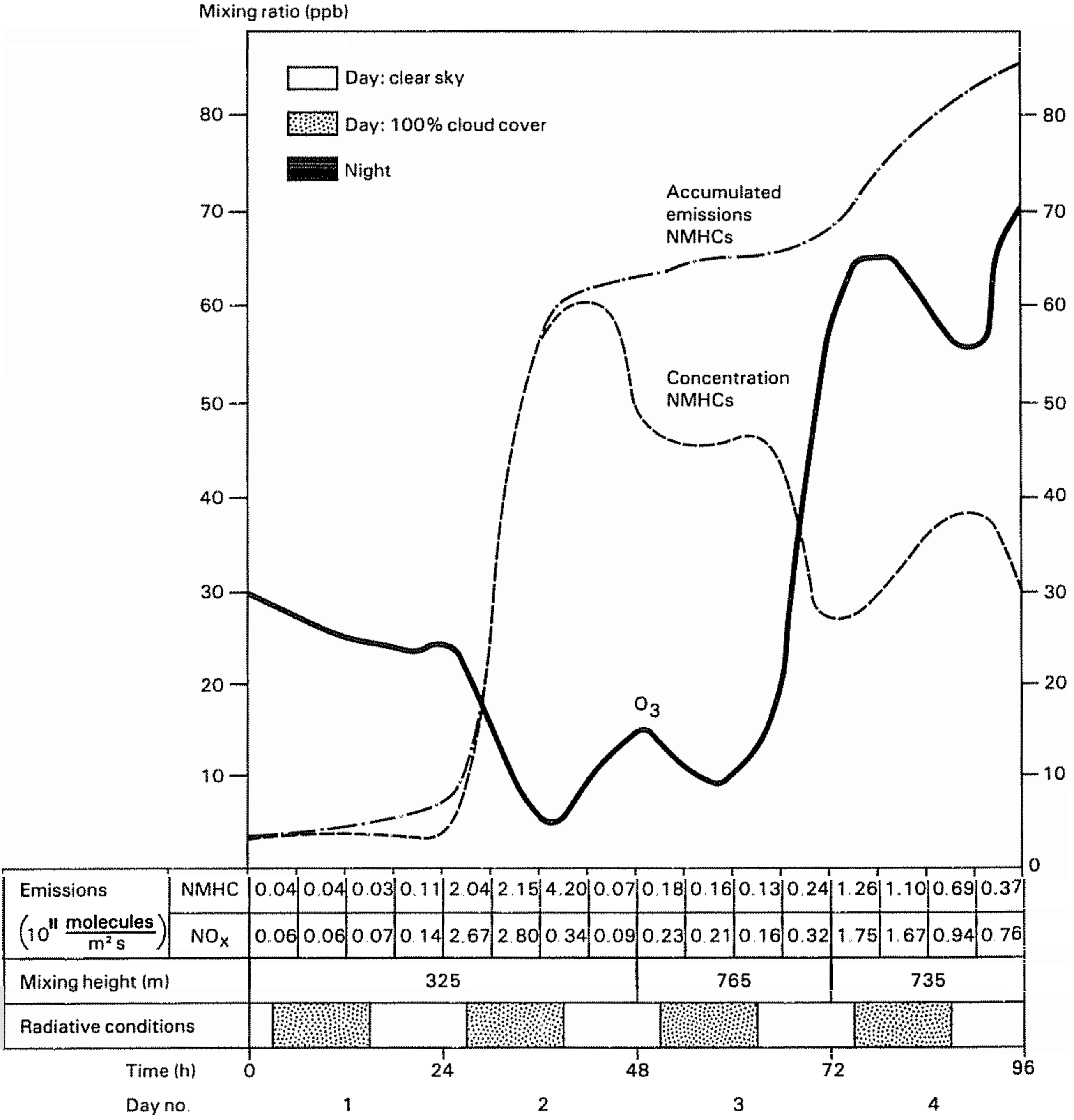


Fig. 9 Deposition of total sulphur in Europe based on the estimated emissions in 1980.



SOURCE: UNECE - EMEP Programme 1983.

Fig. 10 Time development of pollutant concentrations and emissions for the trajectory arriving near Langesund at 1200 GMT, April 12. The concentration of O_3 and NMHC and the accumulated emission of NMHC are shown as curves. The emission fluxes of NMHC and NO_x and the mixing height are shown in numbers below the curves. The radiatieve conditions are also indicated.



Emissions $\left(10^{11} \frac{\text{molecules}}{m^2 s}\right)$	NMHC	0.04	0.04	0.03	0.11	2.04	2.15	4.20	0.07	0.18	0.16	0.13	0.24	1.26	1.10	0.69	0.37
	NO_x	0.06	0.06	0.07	0.14	2.67	2.80	0.34	0.09	0.23	0.21	0.16	0.32	1.75	1.67	0.94	0.76
Mixing height (m)		325								765				735			

Note: NMHCs = non-methane hydrocarbons

Fig. 11 Region and grid of the acid deposition and oxidant model to be developed by KNMI and RIVM (Netherlands).

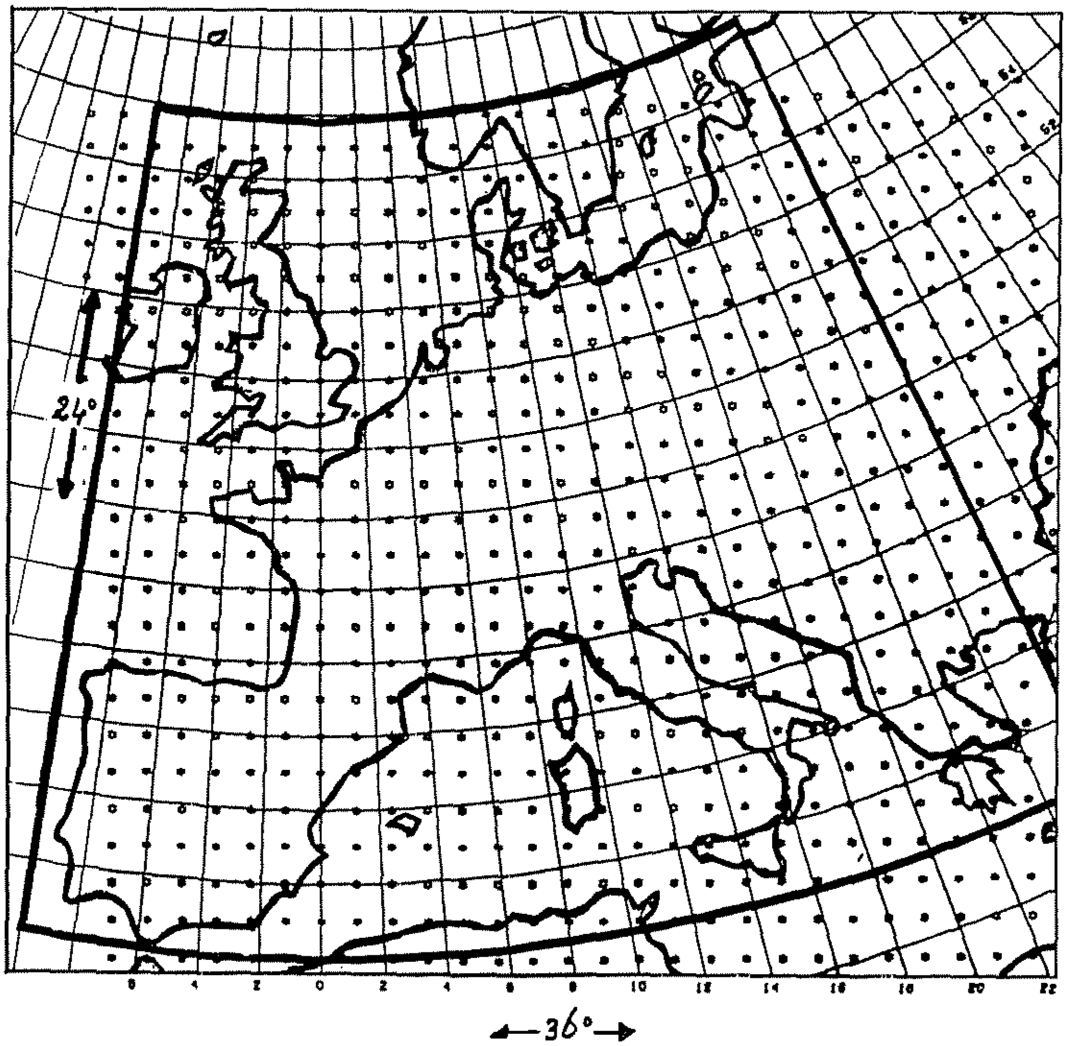


Fig. 12 Typical values of deposition velocities of a few of the more important air pollutants in combination with current terrain types.

Terrain Type	Roughness factor(a) (cm)	Deposition velocity(b) (cm/s)					
		O_3	NO	NO_2	CO	SO_2	$SO_4^=$
Cropland and pasture	20	1.20	0.1	1.2	0.0006	0.70	0.20
Cropland, woodland and grazing land	30	1.20	0.1	1.2	0.0025	1.00	0.20
Grazed forest and woodland	90	1.10	0.1	1.4	0.0014	1.20	0.40
Ungrazed forest and woodland	100	1.48	0.1	1.5	0.0045	1.50	0.50
Swamp	20	1.00	0.1	1.0	0.0008	0.14	0.35
Metropolitan city	100	2.00	0.1	1.8	0.0050	1.50	0.30
Lake or ocean	0.01	0.10	1.6	0.6	0.0005	1.10	0.50

(a) From Sheih et al., 1979.

(b) From McMahon and Denison, 1979.

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"REVIEW OF ATMOSPHERIC PHOTOCHEMISTRY"

Presentation by

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ABSTRACT

The phenomenon of photo-oxidant air pollution was first recognised in Southern California, where studies showed that it was a result of photochemical oxidation of hydrocarbons and NO_x pollutants. Subsequently it has been shown to be part of a general phenomenon of atmospheric chemistry, the details of which have been worked out over the past 10-15 years. The more important chemical steps in the mechanism for hydrocarbon oxidation, for NO_x conversion, and ozone formation have been characterised and the factors relating structure and reactivity established. The detailed chemistry of trace gas behaviour in background and polluted atmospheres is presented and some problem areas highlighted.

I would like to start by thanking CONCAWE for inviting me to come and talk to you today. I plan to present a talk with a fairly chemical bias to it, in which I hope to outline to you the photochemical processes which occur in the lower part of the atmosphere. I will cover both the boundary layer close to the region where the pollutant gases are emitted and also the background atmosphere after the pollutants have dispersed from the source regions. I believe, and I hope to influence you in that respect, that the latter is something we need to be looking at in atmospheric pollution today. The photochemistry that I will be talking about in both these two regions of the atmosphere is very closely related. The realisation that photochemistry is important for determining the fate and composition in trace materials in the atmosphere goes back to the 1950's with the discovery of the phenomenon of photochemical smog in the Southern California air basin.

What is the chemistry involved in this process? Fig. 1 shows the variation with time during the day of the concentration of a number of trace species in the atmosphere in Los Angeles county. The significant species are the primary pollutants, namely the hydrocarbons and the nitrogen oxides which are emitted into the atmosphere in the early morning hours. The subsequent chemical decay of these pollutants gives rise to ozone, a secondary pollutant, which is the product of photochemical reactions. The oxygenated organic species which are produced as a result of the oxidation of the hydrocarbons are also revealed. The concentrations of each of these species that you see is actually a balance between production and removal. So this familiar pattern was discovered by observations in the atmosphere. In order to try and find out what was going on, experiments were conducted in the laboratory to try and simulate the chemistry of the atmosphere. It was found fairly early that species concentration changes could be quite readily simulated by near-ultraviolet photolysis of nitrogen oxides and typical hydrocarbons such as isobutene.

This led to a large amount of experimentation in which the relationships between the so-called primary pollutants and secondary pollutants such as ozone were explored. This was to some extent successful, but in many ways unsuccessful because it led to a rather narrow view of the phenomenon of what was going on. The reason for this rather narrow view is that the atmosphere is not just a box, and various other transport phenomena, time dependant emissions, and reaction rates impinge on the problem. These factors can better be accounted for in numerical simulation models containing elementary chemical reactions which describe the phenomena in more elementary terms. I hope to show you the essential features of these mechanisms and how they help us to understand the phenomenon.

I have talked so far about ground-level pollution, but the other interesting facet of this problem is that it seems that smog formation is an extension of something that is going on generally in the atmosphere and can actually be viewed in a simpler fashion if one looks at what is happening in the background atmosphere.

The production and distribution of ozone in the atmosphere is shown in Fig. 2. This gives a schematic diagram of the lower part of the atmosphere, the troposphere, which extends in the tropics from the surface up to about 15 km. Above the troposphere is the stratosphere, where most of the ozone that is present in the earth's atmosphere resides. The troposphere can be divided also into the boundary layer, and the background troposphere, which is, some of the time, coupled rather closely with the boundary layer. Ozone is present throughout the atmosphere. The main source of ozone is the stratosphere, where it is produced by the photodissociation of molecular oxygen. The photodissociation of molecular oxygen requires short-wave length radiation smaller than 260 nanometer (nm) which is not present in the atmosphere below the tropopause. At the top of the troposphere the wave length is limited to about 280 nm in the ultraviolet.

The ozone in the background troposphere originates in two ways: firstly from the transport of ozone down through the troposphere into the background troposphere and secondly from the photodissociation of NO_2, which will be described later. In the background troposphere ozone does absorb light but the photodissociation of ozone produces atomic oxygen which just recombines again with molecular oxygen to form ozone. However, once in the troposphere, the ozone eventually diffuses down to the ground where it is removed by the dry deposition process.

There is, however, a very important ramification of the formation of ozone in the troposphere, and that is that a small proportion of the ozone dissociates to produce atomic oxygen in the excited state. The reactions that result from that excited atomic oxygen reacting with water produce hydrogen-containing free radical species like hydroxyl and these are coupled in a rather complicated chemistry. Fig. 3 gives details of the photochemical processes of the photodissociation of ozone to produce a reaction of the excited atomic oxygen and produce hydroxyl radicals. The hydroxyl radicals are then coupled to the hydroperoxyl radical by the interconversion of the radical through reaction with carbon monoxide and ozone. This essentially leads to a steady state concentration of these radical species when the atmosphere is irradiated by sunlight. The steady state concentration is maintained by these cyclical reactions and then the radicals can act as an oxidizing attack species for species like hydrocarbons and sulphur compounds. This provides a scavanging mechanism for these species in the atmosphere.

Another reaction of the hydroxyl radical of importance is reaction with atmospheric methane. And this brings in a whole new section of chemistry which we need to understand in order to describe the steady state concentrations of the radicals in the unpolluted atmosphere. The reaction of hydroxyl radicals with methane produces firstly a methyl radical which then adds one oxygen and forms this organic peroxyl radical. These processes are outlined in Fig. 3. The organic peroxyl radical can then react with another HO_2 type radical species and form a hydro-peroxide which eventually is converted either by photodissociation or by reaction with another hydroxyl radical into formaldehyde. The formaldehyde then photodissociates and feeds back another radical into the system. So here we have a cyclical reaction involving several species which converts the OH radical through these organic radicals back to the hydroperoxyl radical which is then converted back to the OH.

The radicals are removed from the system only by recombination with each other so the two radical centres recombine to form water or hydrogen peroxide.

Another very important component in this system is nitric oxide. When nitrogen oxides are added to the system they have several effects on the radical concentration. The first thing that happens is a very fast reaction takes place which converts HO_2 species, which are rather less reactive than OH through to the reactive OH species. The nitric oxide upsets the balance between the OH, and the HO_2 providing more of the reactive OH species. Nitric oxide plays a similar role in the oxidation of the organic peroxyl radicals bypassing the hydroperoxide stage, straight through to formaldehyde. There is also a very important process involving NO_2 which actually removes radical species from the system, converting NO_2 to nitric acid. If one sets up a model of these photochemical reactions one can calculate the steady-state concentration of the free radical species.

As well as affecting radical chemistry, NO_x actually also a very fundamental effect on the ozone concentration in the lower part of the atmosphere because of the following reactions:

$$(1)\quad NO_2 + h\nu \xrightarrow{J} NO + O$$

$$(2)\quad O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$(3)\quad NO_2 + O_3 \xrightarrow{k_3} NO_2 + O_2$$

The first one is the photodissociation of NO_2. This is the only source of atomic oxygen in the lower part of the atmosphere below the troposphere. The recombination of the atomic oxygen produces ozone. This occurs very rapidly but the system is balanced by the fast reaction of the other photofragment NO with ozone to produce NO_2 again. These reactions are occurring all the time in the sunlit atmosphere and with a time constant of about 1 or 2 minutes in the normal daylight situation, and the ozone concentration at any particular place is related to the ratio of the NO_2 over NO by the ratio of rate constants k_1/k_3. The NO_x - ozone relationships are summarised in Fig. 4

Any other process which converts NO to NO_2 in parallel with reaction 3 will leave one net O atom or O_3 molecule. The important radical species which, in fact, effect this conversion of NO to NO_2 are HO_2 and the organic peroxy radicals. So this is the fundamental source of ozone in ground-level polluted atmospheres.

How do those organic peroxy radicals arrive? Fig. 5 shows a hydrocarbon oxidation scheme comprising generalised steps which are used to describe the NO to NO_2 conversion and the oxidation of an organic compound. Although they may differ in detail for the different types of organic compound, generally the pattern is very similar for different species. This is that there is an attack by an OH radical on the organic to produce another radical, which may occur by abstraction, as illustrated here, or by addition. The radical adds on an oxygen to form a peroxy species which reacts with NO to give NO_2. The RO radical can react further, e.g. with oxygen, to produce the HO_2 radical plus a carbonyl compound. The HO_2 then reacts with another NO to regenerate the OH and produce NO_2. This is a chain reaction in which total number of radical species is maintained because the OH is regenerated. In the overall reaction a molecule of hydrocarbon plus two molecules of NO are converted to an oxygenated species plus two molecules of NO_2. When this process is superimposed on the NO_2 photolysis system this leads to production of two ozone molecules.

In order to determine the rate of ozone production in either a polluted or an unpolluted atmosphere one has to determine the rate of production of these RO_2 radicals from the rate at which the hydrocarbon reacts with OH radicals. This is shown in Fig. 6. To evaluate the rate we need to know something about the rate coefficient for the reaction, and in this quantity resides the so-called reactivity component, i.e. is the reactivity of the hydrocarbon. We also need to know the total concentration of radicals. The OH radical is coupled to the total concentration of radicals by the radical partitioning or interconversion reactions. We also need to know the concentration of the hydrocarbon, which is a function of the emission and the dispersion and the location relative to the sources. Fig. 7 shows the overall scheme. Essentially, what we have is a radical pool in which the radicals are interconverted. The hydrocarbons are essentially flowing through that pool as they are being oxidised by the generalised scheme, and at the same time NO is being oxidised to NO_2 which is then producing ozone. The magnitude that the radical concentration in that pool depends on the magnitude of the radical sources and the radical sinks. So, what I am going to do now is just to have a look at what those radical sources and things are.

Examination of the radical sources and sinks provides a clue as to the influences on ozone production in a chemical sense. Firstly, as we saw, production of OH radicals occurs through ozone photolysis throughout the atmosphere. We also have a source through hydroperoxide photodissociation but since most of the hydroperoxide is originally derived from the radicals anyway, it is not really a net source. A very important net source is photodissociation of formaldehyde, which is produced in the break-down of virtually all organic matter in the atmosphere. The higher aldehydes and ketones which derive from hydrocarbons are also photodissociated in the near ultraviolet and provide a source of radicals. There is also a source of radicals that is related to nitrogen oxides. This is the photolysis of nitrous acid, which is formed from reactions involving nitrogen dioxide and NO and H_2O.

Looking at the radical sink processes, the most important ones involve nitrogen oxides. The reaction of OH radicals with NO_2 to make nitric acid provides a major sink. Also, the reaction of the organic peroxy radicals with nitrogen dioxide to form peroxyacetylnitrates (PANs) is an important sink.

Finally there is interesting reaction between RO_2 and NO which forms nitrate esters and which occurs in parallel to the main NO_2 forming pathway:

$$RO_2 + NO \text{ ---- } RO + NO_2$$

$$\text{---- } RONO_2$$

The nitrate esters are stable both photochemically and thermally and so act as a true sink for radicals in the same way that nitric acid does. Nitrate formation is favoured particularly for hydrocarbons of chain lengths greater than C_5.

There are several radical sink processes not involving NO_x, but these are only important in the background atmosphere when NO_x levels are very low. Clearly, we need to know the elementary rate coefficients for all reactions which provide sources and sinks for radicals in order to do an adequate calculation of overall radical concentrations.

Next we examine the sources of atmospheric hydrocarbons which determine the concentration term in the rate of peroxy radical formation.

In Fig. 8 are listed several representative types of hydrocarbon or volatile organic species. The first one is methane, which is the major hydrocarbon component in the atmosphere. This has both natural and man-made sources, which have been identified as enteric fermentation from wild animals and also from domestic animals, and emission from swamps and natural wet lands (rice paddies are considered a man-made wet land). Natural gas leaks are also a significant source of methane as are combustion sources. There is also a small natural source from the oceans.

In the next category we have the light paraffins. There is certainly an aerobic biological source of light paraffins, which has been observed at various locations. We also have some release from natural gas leaks, solvent and fuel evaporation, and refinery emissions. I put a question mark on the natural sources of olefins. Olefins are certainly present in nature and, since they are volatile, it is likely to be a natural source. There is certainly a well-defined vehicle exhaust source of olefins and probably some refinery and petro-chemical emission. Again, I put a query on natural sources of aromatics, I am sure that aromatics are present in natural systems, but there is very little information on which to go on as far as natural sources of aromatics are concerned. The man-made sources of aromatics are very well defined and fairly well known to most of us.

The final classification is the terpene and isoprene hydrocarbon species which are the most widely characterized natural emissions of volatile hydrocarbons. Isoprene certainly is emitted in large amounts from many broad-leaf trees and terpenes too, from plants and various conifers. Emission rates of hydrocarbons from most of these sources is very poorly defined. The magnitude of the sources, because of their diversities, is one of the most severe problems facing us at the present time in trying to quantify the budgets of these species in the atmosphere.

The next issue that I would like to deal with is the idea of the chemical basis for hydrocarbon reactivity. The reactivity of a particular hydrocarbon resides in the rate coefficient for the rate of production of the RO_2 radicals. It is actually a little bit more subtle than that because there are other factors than purely the magnitude of the rate coefficient that can influence hydrocarbon reactivity as manifested in the system producing ozone. These are listed in Fig. 9.

The first of the factors is the rate constant of OH attack. Second is the number of NO_2 to NO conversion steps which follow that initial OH to HO_2 attack. Thirdly, the reactivity may also reflect in the nature of the products formed, i.e. how photochemically. reactive they are.

We know quite a lot about rate coefficients for hydrocarbon + OH reactions, mainly because of the fairly timely recognition of this as an important factor and also due to the development of techniques for determining elementary rate coefficients for fast free radical reactions with organic species. So we have a fairly good data base here. Fig. 10 lists some hydrocarbons from the typical categories already highlighted. An important point is the very large range of reactivity when measured on this criterion. The rate constants are for 25°C and atmospheric pressure. I qualify that because some of them, e.g. the reaction of OH with methane, has a fairly strong temperature dependence, so the rate coefficient could vary by several factors in the temperature range that is encountered throughout the global troposphere where the methane is distributed. That is why I have put a lower limit of 4.5 years on the life-time for methane, which is based assuming an average hydroxyl radical concentration of 1×10^6 molecules per cc, considered to be representative of the sunlit surface atmosphere.

Moving down the list we find ethane is fairly unreactive, having a life-time of 48 days in the atmosphere. Propane is a little bit more reactive; hexane in fact becomes quite a reactive hydrocarbon with a life-time of about 2 days under those average conditions.

The alkenes are much more reactive than the alkanes in this table; isobutene has a life-time of only a few hours in the atmosphere. For the aromatics we have again a rather large range. Benzene is fairly unreactive, but xylene and highly substituted side-chain aromatics are much more reactive. Finally, we look at isoprene as a typical terpene; these, in fact, are extremely reactive compounds with very short life-times in the atmosphere and their direct effects are very much confined to the source regions.

The second factor that I highlighted on reactivity is the stoichiometry for NO to NO_2 conversion. I have indicated the origin of this by looking at the scheme for the photo-oxidation of normal butane. This is shown in Fig. 11. The first attack by OH produces the secondary butyl peroxy radical which then undergoes an NO to NO_2 conversion producing the 2-C_4H_4O radical. This radical either breaks to produce an acetaldehyde molecule plus an ethyl radical or reacts with O_2 to form the ketone plus an HO_2 radical. The HO_2 then is converted directly back to OH. So if we go round this latter cycle we have two NO to NO_2 conversions so that will produce two ozone molecules per cycle. However, if the other competitive path-way occurs we get formation of acetaldehyde and then the further oxidation of the ethyl radical through an analogous scheme but with an additional NO to NO_2 conversion in the oxidation of the ethyl peroxy. So here we have three NO to NO_2 conversions so three ozone molecules are formed in the cycle. Clearly this factor should be taken into account when one is looking at reactivity.

The influence of products on ozone formation occurs because of the effect that products have in modifying the balance of the sources and sinks of the radical species, thereby influencing the OH concentration. For example, alkyl peroxy radicals can react with nitric oxide by the two paths, one converting NO to NO_2 and completing the chain producing OH, the other one producing the alkyl nitrate which essentially acts as a radical sink. So alkyl nitrate formation essentially reduces NO to NO_2 conversion and also removes radicals, and both these factors reduce the rate of ozone formation.

The second effect, of course, reduces ozone formation not only for that species but also for any other species because of the effect on the total radical concentration. Radical concentrations may however be increased due to the formation of products which photolyse rapidly. producing more radicals. For example, alpha di-carbonyls tend to dissociate more rapidly than formaldehyde which is again more rapid than the substituted aldehydes which are in turn more rapid than the ketones.

Other factors being equal, ozone formation will be faster in mixtures where alpha di-carbonyls are formed as products, compared with a system that is forming substituted ketones as product. A typical example here is the role of aromatics, because the breakdown of the ring of aromatic species like toluene and xylene in fact produces the alpha di-carbonyl species as fragmentation products from the oxidation, which can, in fact, enhance radical concentration.

Peroxyacetylnitrate is a member of a family of compounds formed when the acylperoxy species recombines with NO_2. These compounds are not very stable and they dissociate again by the opposite route to that by which they are formed. In fact, an equilibrium can exist between the peroxyacylnitrate and its precursor species. Now, in competition with the formation reaction is the reaction of the peroxy radical with NO down the usual route which converts NO to NO_2. This produces a methyl radical which then goes on to be oxidised to HCHO. The life-time of PAN in the air is determined by the balance between these reactions and one can write a fairly simple equation here which shows that the overall removal rate for the PAN is a function of the ratio of NO to NO_2 (see Fig. 4). The laboratory studies allow us to evaluate the parallels and we can calculate that the life-time of the PANs due to the thermal decomposition, which on whether it is day or night or what the NO and NO_2 ratio is doing.

It is clear that the life-time of PAN is rather complex. One of the interesting facts is that it can be very long-lived once it gets out from the boundary layer into a low NO_x situation and relatively low temperatures. Thus it can act as a transporting medium for NO_x from the source region.

The concentration field for ozone in the boundary layer near the ground is determined by several factors. It is a balance between mixing of ozone from the background and from other unpolluted regions, photochemical production by in situ photochemistry from the precursors, homogeneous removal of ozone by reactions in the gas phase, and also dry deposition to the ground. So in order to determine the ozone concentration at any place in time or space one needs a model to describe each of these components that enter into the ozone balance. The chemistry element needs to address accurately the following three functions: it needs to describe accurately the NO_x ozone photostationary state and it needs to describe accurately the combination of the rate constant and the hydrocarbon concentration and its variation with time as the reactivity of the mixture changes with the hydrocarbon content. We also need to define the steady state concentration of the OH radical. This is a function of the source and sink terms which we need to know fairly accurately and the partitioning of the radicals between the different types as a function of time. At the present time I think that it is fair to say that quite a large factor in the differences that are evident in the results of model calculations of ozone arise from the differences in the formulation of the chemistry.

These factors appear in the shape of the ozone isopleths describing the relationship between the hydrocarbon and NO_x precursors and the amount of ozone predicted to be formed in the photochemical reactions. It is important to iron these differences in order to formulate reasonable control strategies on the basis of the isopleths.

Finally it is of interest to return to the situation in the background troposphere with reference to Fig. 13. Global tropospheric ozone is an important factor for ground level ozone because a large fraction of the ozone that is normally measured on the ground in fact originates from the background troposphere by downward transport. So if one is looking for changes in ground level ozone you certainly want to know what is happening to the background ozone. In recent years there is evidence that the ozone concentration in the background atmosphere at least at mid-latitudes in the northern hemisphere is on the increase in a fairly substantial way. The question is whether background O_3 is being influenced by emissions from the surface. We have seen that certainly emission of NO_x species into the atmosphere provides us with the additional source of oxygen atoms in the lower atmosphere. This can provide a net source of ozone which complements that which is occurring higher up in the stratosphere. The emission of hydrocarbons or organic species has been established. Methane is fairly unreactive and, in fact, with a life-time of at least 4 years it diffuses throughout the whole of the troposphere and is converted eventually to formaldehyde and to CO through photochemical oxidation. If NO_x is present this will provide a net ozone source.

Most of the non-methane hydrocarbons will be oxidised fairly rapidly and produce ozone in the boundary layer. Under situations of cloud cover or no sunlight or any other factors which may reduce the free radical oxidizing capacity in the atmosphere, they will diffuse through into the background troposphere. The long-lived ones like benzene and ethane have been regularly observed at high altitudes, so certainly transport of that carbon into the background troposphere does occur.

If the nitrogen oxides combined with the oxidation products of some of the non-methane hydrocarbons in the form of PAN are transported into the background atmosphere, subsequent release at the nitrogen oxides in this region provides a mix in the background atmosphere which can react in exactly the same way as in the boundary layer, producing ozone in the troposphere. The quantification of these processes is one of the main problems that is being addressed in tropospheric chemistry to-day.

The atmospheric photochemistry that has been described is the chemical approach to the identification of the sources, sinks and budgets of ozone and related related gases. Fig. 14 summarises the technical points and some research requirements.

The tools that we use to try and advance that science are: programmes of atmospheric measurements in order to define concentration fields, quantification of emission and deposition rates, laboratory measurements of the kinetics and mechanism of the chemical processes involved; and also modelling studies in order to address both detailed local and also global behaviour of species in the atmosphere.

Now, in the troposphere, and also the boundary layer, the important points of focus at the present time are on ozone production and on acidity, i.e. the incorporation of transformation products of hydrocarbons, nitrogen oxides and sulphur oxides. The OH radical plays a central role in the formation of these products.

There are a number of points that are being addressed at the present time. Firstly, what are the underlying causes of the increase in methane and carbon monoxide in the troposphere that has been noticed in recent years? Secondly, how far from sources does man-made NO_x affect ozone in the troposhere? Thirdly, what fraction of man-made non-methane hydrocarbon escapes into the background atmosphere? Fourthly, what is the origin of organic acids in background acidity? The measurements of acidity in precipitation in remote areas show that, in fact, the acidity in rain water and cloud water is largely determined under those situations by organic compounds.

The research requirements in order to attack these problems are rather large. We need efforts to establish the concentration of the major hydrocarbon species in the near field and the far field with respect to sources. Quantitative determination of the sources and sinks of OH and other radical species in the atmospheric photochemical system are required. Establishment of the relative importance of the different forms of NO_x which can exist in the atmosphere is important, as well as investigating the formation of organic acids from photochemical and non-photochemical routes. We need to develop models describing the transport in and out of the boundary layer and to develop models to describe photochemistry in both polluted and unpolluted air.

Fig. 1 Variation with time of the concentration of trace species in the atmosphere

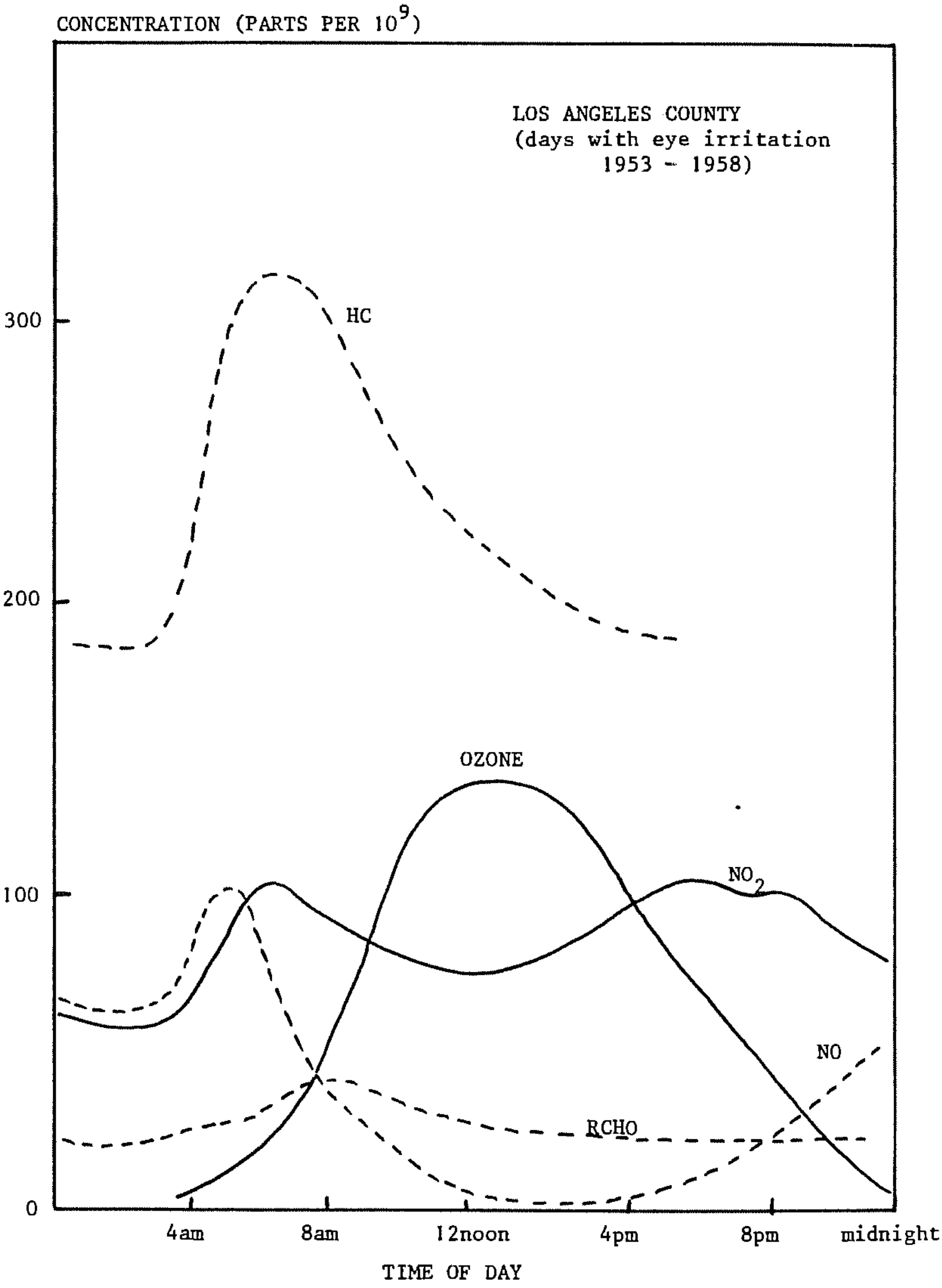

Fig. 2 Production and distribution of ozone in the atmosphere

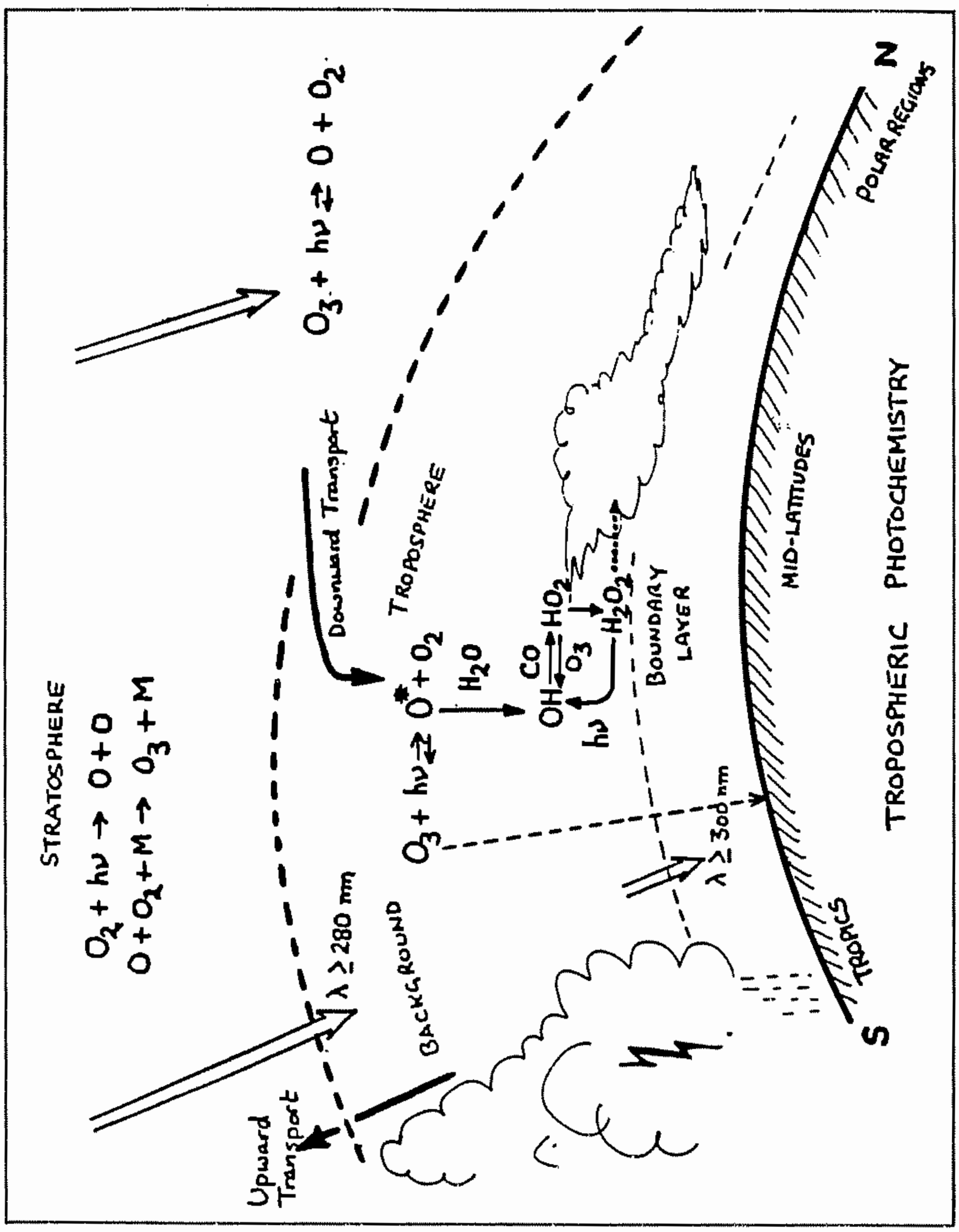

Fig. 3 Chemical and photochemical reaction in the background troposphere

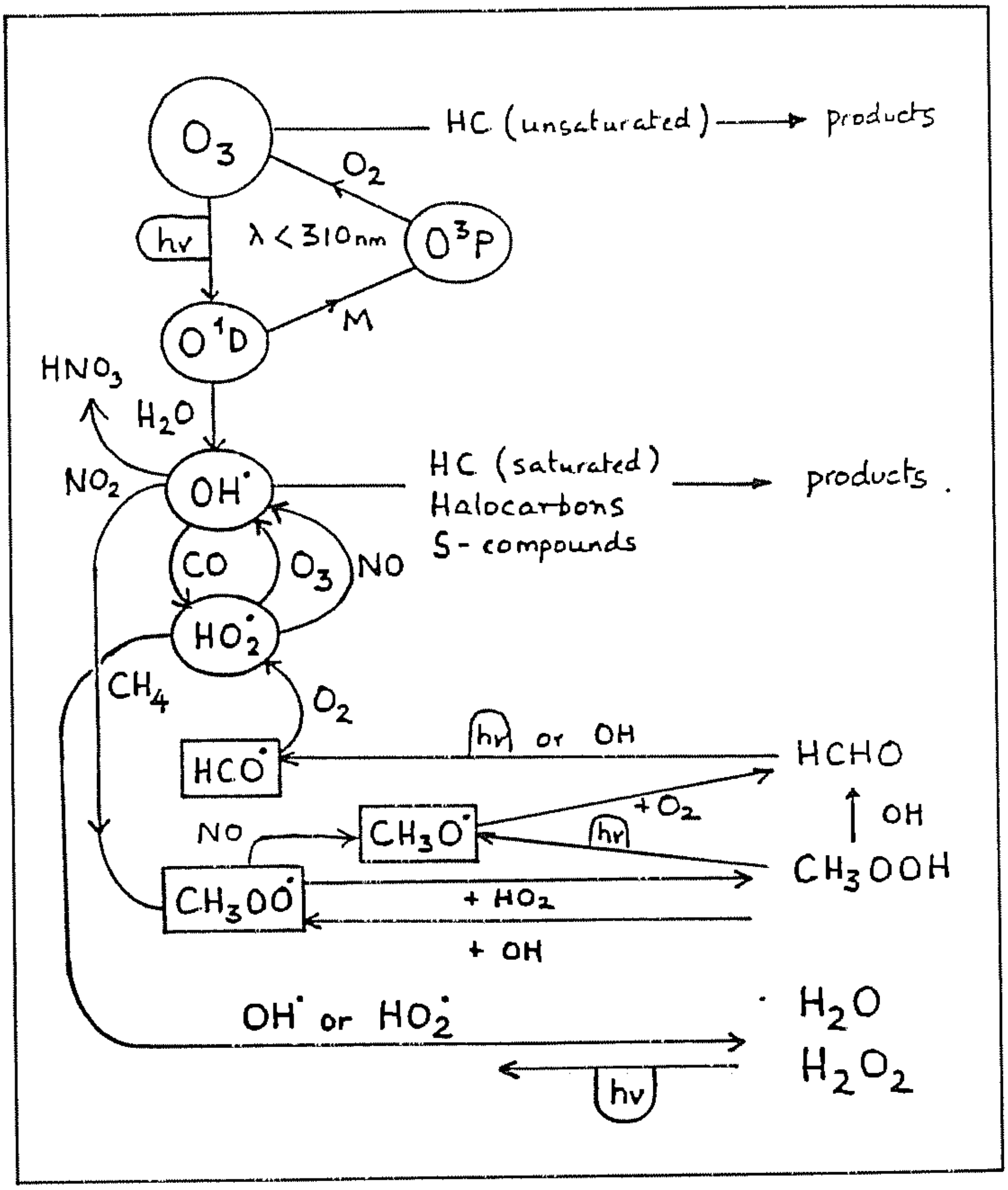

Fig. 4 Photochemical ozone

Natural ozone: 20 - 40 ppb
Originates in stratosphere and from
in-site tropospheric photochemistry
Destroyed at Earths' surface

Photochemical ozone: 60 - 120 ppb in polluted air

Origin of photochemical ozone:

Photochemical reactions involving NOx and hydrocarbons in which NO is oxidised to NO_2 and hydrocarbons to aldehydes, CO etc.

Ozone production:

$$\begin{array}{lll} NO_2 + hv = O + NO & J & \\ O + O_2 = O_3 & k_2 & \text{(fast)} \\ NO + O_3 = NO_2 + O_2 & k_3 & \end{array}$$

When R, = R_3 $[O_3] = \frac{J}{k_3} \frac{[NO]}{[NO]}$

Reactions driving $[NO_2]/[NO]$:

$$\text{Hydrocarbon} \longrightarrow RO_2 + NO \longrightarrow NO_2 + RO \longrightarrow \text{aldehyde}$$

<u>Fig. 5</u> Hydrocarbon oxidation scheme (ambient temperature and pressure)

$$\boxed{\begin{array}{lllll} OH & + RH & \rightarrow & R & + H_2 \\ R & + O_2 & \rightarrow & RO_2 & \\ RO_2 & + NO & \rightarrow & RO & + NO_2 \\ RO & + O_2 & \rightarrow & HO_2 & + R'_2CO \\ HO_2 & + NO & \rightarrow & OH & + NO_2 \end{array}}$$

Net $\underline{RH} + 2O_2 + 2NO \rightarrow R'_2CO + H_2O + 2NO_2$

<u>Fig. 6</u> Rate of peroxy radical formation

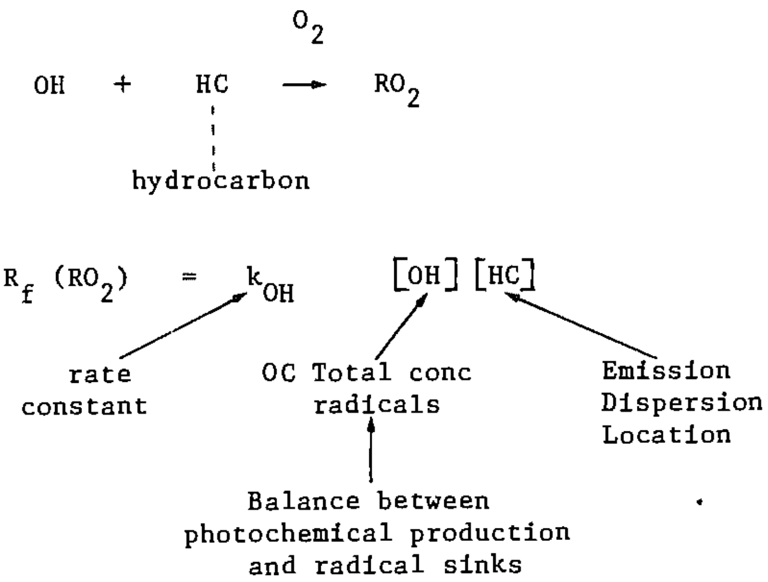

Fig. 7 Overall schematic for ozone formation

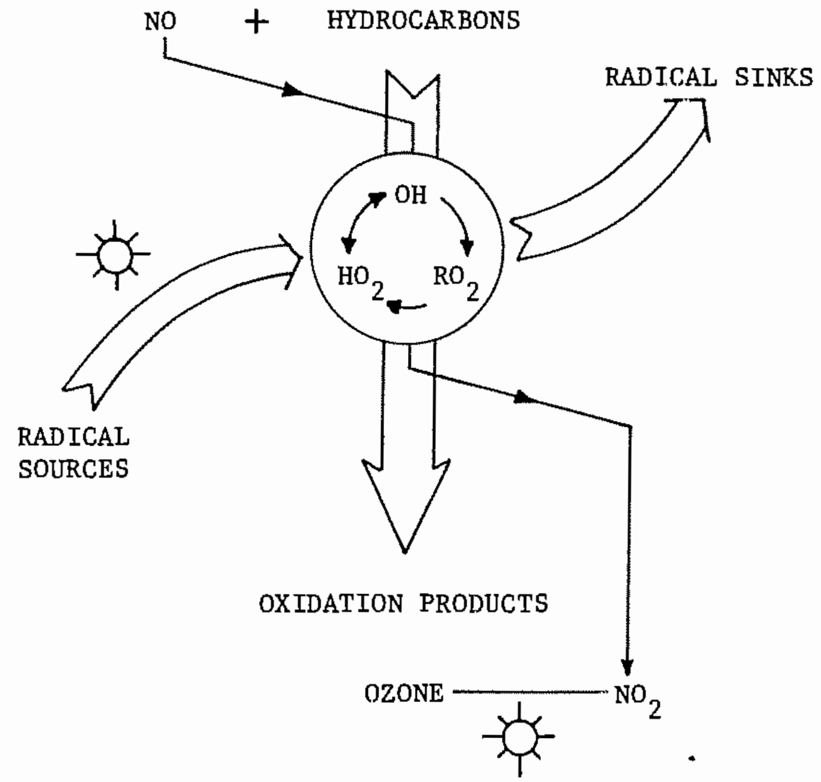

Fig. 8 Sources of atmospheric hydrocarbons

	NATURAL	MAN-MADE
methane CH_4	enteric fermentation (wild animals) swamps, natural wetlands oceans	enteric fermentation (domestic animals) rice paddies natural gas leaks combustion sources
light paraffins $C_2 - C_6$	aerobic biological source	natural gas leaks solvent & fuel evap. refinery emissions
olefins	?	motor vehicle exhaust petrochemical industry
aromatics	?	motor vehicle exhaust solvent & fuel evap.
isoprene (C_5H8) terpenes ($C_{10}H_{20}$)	trees (broadleaved and conifers) plants	-

Fig. 9 Chemical basis for hydrocarbon 'reactivity'

The 'reactivity' of a particular hydrocarbon species in respect of OZONE formation is determined by:

- magnitude of the RATE CONSTANT for OH ATTACK
- number of NO NO_2 CONVERSION STEPS following
- nature of the PRODUCTS formed

RATE CONSTANT FOR OH ATTACK

This is of prime importance since it determines the relative lifetime of the hydrocarbon

i.e. how quickly it degrades (with accompanying ozone formation)

and how far it will be transported from the source region.

Fig. 10 OH rate constants and typical atmospheric lifetimes of hydrocarbons

Hydrocarbon	Rate Constant* $cm^3 s^{-1} \times 10^{12}$	Lifetime* days
Methane (CH_4)	0.007	> 4.5 (years)
Ethane C_2H_6	0.25	48
Propane C_3H_8	1.0	12
Hexane C_6H_{14}	6.5	2
Ethene C_2H_4	8.5	1½
Isobutene C_4H_8	60.	< ¼
Benzene C_6H_6	1.0	12
O-xylene C_8H_{11}	13	1
Isoprene C_5H_8	80	< ¼

* At 760 Torr pressure, 25°C

* Assuming average (OH) = 1×10^6 molecule cm^{-3} (4×10^{-8} ppm)

Fig. 11 Degradation pathways in the atmospheric photo-oxidation of n-butane

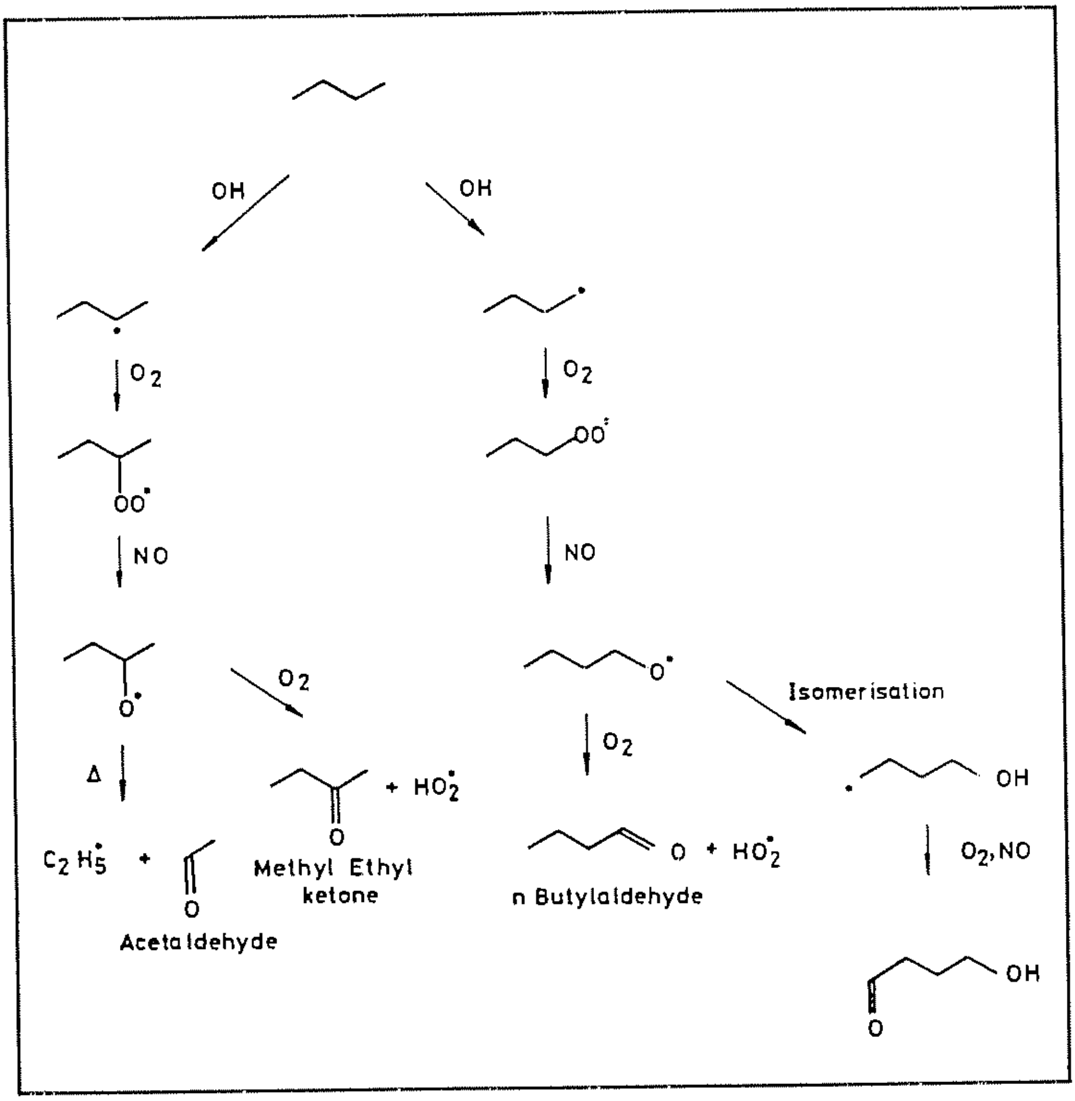

Fig. 12 Thermal decomposition of PAN

$$CH_3CO.O_2NO_2 \overset{+M}{\rightleftarrows} CH_3COO^{\bullet}_2 + NO_2 \qquad k_{12}, k_{11}$$

$$CH_3COO^{\bullet}_2 + NO \longrightarrow CH_3 + CO_2 + NO_2 \qquad k_{13}$$

$$\frac{d\ln[PAN]}{dt} = k_{12}\left\{1 - \frac{1}{\dfrac{1 + k_{13}[NO]}{k_{11}[NO_2]}}\right\}$$

$k_{12} = 4.0 \times 10^{15} \exp(-13040/T)\ s^{-1}$

$k_{13}/k_{11} = 2.3$ (1 atm, 298°K)

Lifetime due to thermal decomposition (in hours):

	Day (25°C)	Night (15°C)
Urban:	2.7	2.8
Rural	0.7	∞ ($[NO] = 0$)

Fig. 13 Tropospheric photochemistry

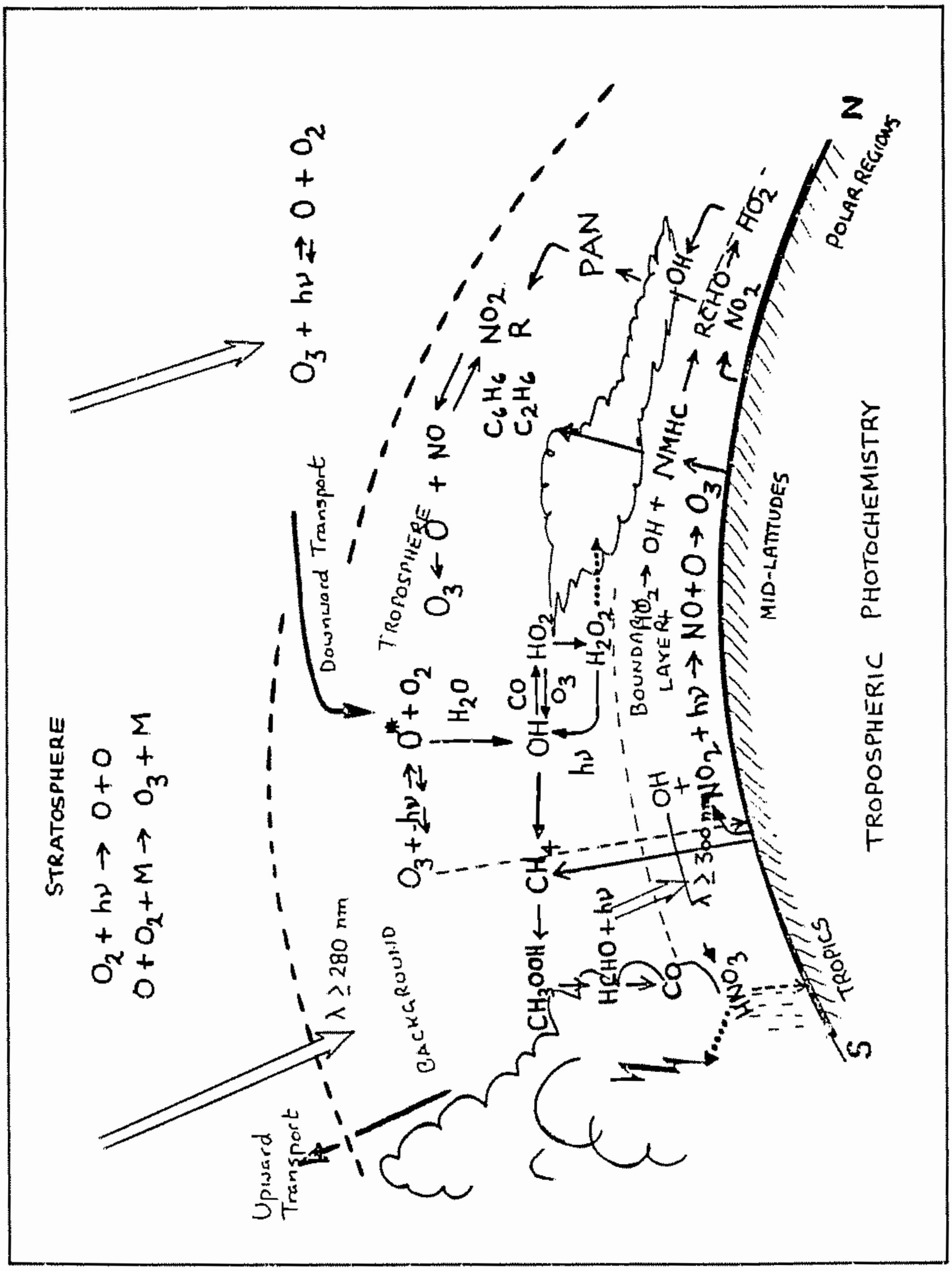

Fig. 14 Ozone sources, sinks and budgets

Atmospheric photochemistry - identification of sources and sinks, and creation of ozone budgets

- Atmospheric measurements
- Quantification of emission and deposition rates
- Laboratory measurement of kinetics and mechanisms
- Modelling studies

Troposphere and Boundary Layer: ozone, acidity and OH concentration are the important points of focus.

? - What are the underlying causes of CH_4 and CO increase

? - How far from sources does man-made NO_x affect O_3

? - What fraction of man-made NMHC 'escape' into B.G.

? - What is the origin of organic acids in B.G. acidity

Research Requirements

- Establishment of conc of major HC species in near and far field
- Quantitative determination of the sources and sinks of OH and other radical species
- Speciation of NOx
- Investigate the formation of Organic Acids from photochemical and non-photochemical routes
- To develop models describing transport in and out of the boundary layer; to develop models of the B.G. (averaged) troposphere.

QUESTIONS AND ANSWERS ARISING FROM DR. VAN DOP'S AND DR. COX'S PRESENTATIONS

Question	Is there a simple answer Dr. Cox to the question how to control the formation of ozone on this very complex chemistry.
Dr. Cox	I think that from what we know now there is not a simple answer to your question: first you have to make a decision about what problem you are addressing to because, if you want to change something to affect ozone in one part of the atmosphere it may have no effect in another part of the atmosphere and vice versa One really does have to look at exactly what aspect one is trying to control and whether it is ozone or visibility or PAN or eye irritation and so on. So I think the short answer to your fairly short question is no there is no simple answer.
Question	I would like to ask you about the contribution of the ozone transported downward to the ambient air from the troposphere.
Dr. Cox	I have been involved over a number of years with measurement of ozone at ground level and we have seen very strong evidence - and others have too - of a very large effect of downdraft ozone from high altitude at the ground. Under some meteorological conditions which are actually quite well charactarised by meteorologists, ozone concentrations at the order of 100 parts per billion near the ground have been observed in the U.K. and many other parts of the world on a handful of occasions over the last five to ten years. So I think that there is actually quite an important contribution to groundlevel ozone from the troposphere but the timing of it is a complicated factor. It is not a constant contribution.
Question	In southern Germany where the measurements are going on since two years, several times a year, concentrations such as 100 parts per billion in the ambient air are found and I think they occur also in remote areas and during the early afternoon hours in urban areas. Would you exclude that such concentrations are due to man-made production of precursors? That is, would you say such concentrations are only from downward transported ozone?
Dr.Cox	From my experience I would say that the observation of those concentrations of a 100 part per billion alone, doesn't give any indication of its origin. The sort of evidence that we have, I'm just thinking now of two separate occasions of observation of high ozone some years ago in the U.K. during our measurements: one of these particular observations, which I was quoting in connection with downdraft from upper airs, the concentration of other polluted species in that airmass, in particular the halocarbon species, the fluoro-carbon 11 and 12, which one can actually use as a rather handy tracer for clean and polluted air, under those conditions reached extraordinary low levels. On another occasion when we have seen elevated ozone concentrations in the ground-level air the atmosphere showed different chemical characteristics, very high levels of these type of trace materials that we associate with an air that has in its very recent history been contaminated by man-made chemicals.

Question Dr. Cox, where can terpenes be put in the list of radical formation constants you showed in your presentation?

Dr. Cox The terpenes are linked with isoprene. Their reactivity is of the same order of magnitude. They have very rapid reaction with radicals.

Question Mr. van Dop, in the different modelling systems you have shown, is it easy to put rain-out and wash-out into that model? I believe that for Western Europe, which in general is a very wet area, it must be a very important factor in the pollutant transport representation.

Dr. Van Dop Each of the above models contain some formulation to calculate the wet deposition process. However, this can be done in various degrees of sophistication. Current models contain formulations which are very incomplete and unjustified, mainly due to lack of data, or lack of possibilities to evaluate these data.

Wet deposition in Western Europe is indeed an important process, since measurements indicate that roughly 50% of airborne pollution is deposited by precipitation.

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"POSSIBLE CAUSES OF FOREST DAMAGE IN GERMANY"

Presentation by
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~~Institut für Bodenkunde, Freiburg, BRD~~

ABSTRACT

The study of the symptoms and the development of the decline phenomena in silver fir, Scots pine, European Beech, and Norway spruce stands in Europe shows that in all these cases the phenomena - although exhibiting some common features - differ considerably between species and between regions. Therefore, it is assumed that there are different types of disease or decline occurring under varying combinations of multiple stress factors. Using this approach, the possible causes of forest damage are discussed, with special regard to the progressive decline of Norway spruce.

POSSIBLE CAUSES OF FOREST DAMAGE IN GERMANY

The first step towards evaluating forest damages should be a careful study and description of the symptoms, especially of their spatial distribution and temporal development. But already when doing this, different approaches are possible. One is to say we observe the appearance of a new type of damage called 'Waldsterben' which is spreading out more or less suddenly and affecting more and more species. Certainly there are a lot of common features like premature senescence and shedding of leaves causing more transparent crowns.

A different approach tries to differentiate between symptoms, species, and regions with the aim of classifying different disease types. Different types of disease should be related to varying combinations of stress factors. I think the latter approach is more useful to find out what's going on in our forests, which are well known for their great variability of site factors. I will show you different types of decline and evaluate the possible causes.

Before starting this I would like to underline that it is not just the trees that are affected by stress factors but the complete ecosystem. The ecosystem includes trees, all vegetation, and soil, i.e. the rooting substrate. The whole ecosystem receives wet and dry deposition of compounds which might effect the trees directly but which might influence the soil development as well. From there root growth and tree growth can be affected, too. We have to keep in mind this always.

'New-type forest decline' started in Germany with silver fir (Abies alba). Silver fir decline has been observed since the beginning of the 70's. I would not like to discuss this for too long because such a decline has been described already many decades ago. Furthermore I would like to mention a few forest tree diseases which are well known to be caused by specific biotic or non-biotic factors. A well-studied example is the Dutch elm disease which seems to be lethal to this species. Many insects are observed to produce defoliation or growth anomalies of the crown. Weather conditions are mostly involved in the epidemic spread of such diseases. As an example I refer to the infections of spruce and pine forests in southern Germany in 1983/84 with needle cast fungi. They cause browning and shedding of part of the needles.

Well-known non-biotic factors are wind throw and ice or frost damage in exposed stands. Another example is the damaging effects of salt along the highways.

At the other hand there is no doubt that air pollution may reach dangerous levels, not only in the vicinity of coal-burning plants but also in forest areas remote from sources of emissions.

As I said before, we can distinguish between certain types of damage symptoms. In the following part of my talk I would like to discuss first a widespread type of decline which occurs mainly in stands of Norway spruce on acidic soils at higher altitudes in the mountainous regions in Central Europe. The typical symptom is yellowing of the older needles of trees of any age. The youngest (current) needles normally remain green until the following year, then turn yellow at the time of bud development. This kind of damage has developed since about 1978 in the Black Forest as well as in the Bavarian Forest or in Northern Germany. Two years ago it was evident also in the Vosges Mountains in France. This means there is evidently an astonishing spreading. From the helicopter you can see that the forest is no longer green, you find it yellow and grey, yellow from the chlorotic older needles, and grey from the dominating growth of epiphytic lichens. As these lichens are known to be rather sensitive SO_2, the concentrations of this pollutant cannot be high in the affected regions. We will come back to this later on.

If you look at the branches, on the upper side the needles are more affected than on the lower side. This has been observed from the very beginning and seems to show that there is some influence from solar radiation. You may find similar symptoms in other species like silver fir, European beech, and Douglas fir. These symptoms are similar to magnesium deficiency, symptoms which have been known for a long time.

Now I would like to give you a short survey of what we found in our studies of this type of forest damage. We did this study in the Southern Black Forest and we looked at the soil chemistry, nutritional status of the trees, damage symptoms, and air pollution data. As shown in Table 1, there is a clear difference in the total content of calcium and magnesium in the soil of the healthy and the sick stands. This holds true also for the available (exchangeable) fraction of magnesium and calcium. All the soils are very acid but the difference between healthy and damaged stands is very clear as to the amount of available calcium and magnesium. If we look at the needles of the tree we must compare the element contents with the well-established limit values for good or bad growth. From Table 2 it can be seen that the supply of nitrogen, phosphorus, and potassium is optimal. But we have a very low content of magnesium in the damaged trees, already in the green current needles and even more in the older ones. We can also see that there is some difference in the micro-element zinc which is also low where we find this low magnesium content. All the other elements do not show any significant differences. If we look at toxic elements we cannot find any influence of aluminium, lead, or cadmium. Sulphur contents show that we are below the level of medium or higher input of SO_2 from the air. The data presented indicate that damaged trees show clear nutritional disturbances. Looking at other parts of the trees, especially fine roots, which might be influenced by toxic substances from the soil, we do not find any difference in the contents of the concerned elements in the roots (see Table 3). But the needles show it very clearly. This means that needle analysis is a much better tool than analysis of the roots. Certainly, roots accumulate high amounts of aluminium and heavy metals. That's one way to protect the organism from negative influences. Furthermore, we know that conifers can withstand very high concentrations of aluminium, and also manganese, without any damage.

From these data we have seen that there is something wrong with the nutrient supply. I will come back to this. But first I would like to present a few data which characterise the air pollution situation in the Southern Black Forest (see Table 4). It can be deduced that all values for SO_2 are relatively low and are minimal for NO_2. But ozone comes up to about 100 microgram per cubic meter, which is about 50 parts per billion, and maximum values are considerably higher. This means ozone might reach the level where injury could happen. The total input of nitrogen and sulphur is rather low, which corresponds with the values given above. The nitrogen input remains below 20 kg per hectare and sulphur is also around the same order of magnitude. The input of protons, this means acidity, shifts around 1 keq, which is a moderate input.

From these data, I think it is difficult to postulate any strong direct influence of air pollutants to tree growth. In this context we must come back to the soil chemical data showing that low base saturation. The natural soil development under a cool humid climate certainly leads to acid poor soils, especially if we already have parent material with low contents of calcium and magnesium, which is the case in the granite sites of the Southern Black Forest. Acid rain in Central Europe should be occurring already at about 50 years. This must have an additional effect on soil acidity. Due to this development, the actual supply of nutrients, especially of magnesium, is so low that deficiency symptoms are widespread and can be demonstrated by soil and needle analysis. Thus, a large part of the new type of forest damage involves some nutritional disturbance.

The problem is why these deficiencies occur just now. They were known also in former time but never over such a large area. And why is this occurrence so widespread in different parts of Europe and maybe also other parts of the world?

We have to look for an inciting factor. Soil development must be considered a long-term predisposing factor that might have changed only slowly within the last decades. The acidity of the rain has not show a rising tendency due to certain reductions in SO_2 emissions. But there has been marked increase in NO_x emissions within the last two decades. If these compounds play a role as precursors for the formation of ozone, a recent change could have occurred. Therefore, we speculate that ozone and other photo-oxidants might be involved in this picture as a triggering (inciting) factor. This will be discussed again later.

Before doing this I will present a few results of field experiments in which we tested our nutrient deficiency hypothesis. In a large number of fertilisation experiments we applied just the nutrients which seemed to be lacking following soil and foliage analysis. As an example, data from 'Elzach' trial will be presented in the following. This spruce stand shows the described disease symptoms very clearly (see Plate 1). The site characteristics are also typical for this kind of damage. The altitude is 900 metres above sea level (m.a.s.l.), with a mean yearly precipitation of 1600 mm. The soil is an acidic brown earth developed in periglacial solifluction layers derived from granite with very low magnesium and calcium content. Table 5 illustrates the extremely low base saturation in the rooting zone. The nutritional status of the non-treated trees (Table 5) is characterised by optimum levels of the macro-nutrients nitrogen, phosphorus and potassium, but low contents of calcium and zinc, and a strong deficiency of magnesium. This holds true for 1983 and 1984 as well. In Spring 1984 part of the trees received a quick-release magnesium fertiliser. This improved the magnesium status of the trees considerably as can be seen from the needle analysis data of the fertilised trees in Autumn 1984. A great part of the yellow needles have greened up (see Plate 2).

A series of similar fertilisation experiments has also given positive responses. In relation to the varying soil properties at other sites, potassium or manganese are the deficient elements. After application of the corresponding fertiliser, such deficiencies have also been overcome (see Plates 3 and 4). These results point out that nutritional disturbances play a major role in the development of particular forest damage types.

Sometimes it is said that nutrient deficiency alone cannot destroy stands on such a large scale as is to be seen nowadays. This opinion simply is not true. If you look throughout subtropical regions with man-made forests (plantations) which have a high need of nutrients, you can see many cases of declining stands, sometimes totally broken down. Examples are zinc deficient plantations of Pinus taeda and Pinus elliottii on latosols in southern Brazil, calcium deficient plantations of Pinus radiata on marginal soils in South Australia, or plantations of the same species in Chile which failed to grow due to heavy boron deficiency. On all these sites appropriate application of mineral fertilisers resulted in a satisfactory growth of the trees.

Let us come back to the different disease types occurring under varying levels of stress factors. One widespread type has been described above.

Now I will briefly with an other type, which is also observed over large areas. It is a light to moderate, sometimes heavy, shedding of older needles, which makes tree crowns less dense. In spruce varieties with secondary branches hanging down by nature, the so called comb spruce, these defoliated parts of the secondary branches look like silver tinsel (in German lametta), from what the symptom has been named. It is certainly a rather unspecific symptom and it is also not a new one. There are photos published decades ago showing such a shape of the tree crown, even carrying the remark 'a perfect spruce tree'.

Until now, there have been no clear relations between the degree of needle loss and the current incremental growth of the tree. Several studies demonstrate that there is no growth reduction if the needle loss does not exceed 30-35%. This is well understood because the oldest needle age classes have already a negative net assimilation potential: this means they do not contribute any more to biomass production.

Furthermore, it is important to mention that generally no nutritional disturbances are seen where moderately 'defoliated' conifers are concerned. Such findings are not surprising taking into account that this type of damage evidently appears on any kind of soil or parent material. It is found on shallow limestone soil with low water-holding capacity, but also on acid loamy-sandy soils with mostly a very good water supply.

Therefore the question is: What set of stress factors might be responsible for this silver tinsel - needle loss - symptom? Natural site conditions show a great variation, but certain influences of different climatic stress cannot be excluded. This means frost shocks, droughts, or high solar radiation. In certain regions, or years, infections by needle-cast fungi are certainly involved. Referring to air pollutants, concentrations of SO_2 and NO_x are low in most of the affected regions. Ozone is not measured at many places, but might reach a level which is shown in Table 4 for the Southern Black Forest. So we come back to ozone and its possible contribution to the new-type forest damage.

The effect of ozone on forest trees is very well documented in the San Bernardino Mountains (California). The forest is composed of Pinus ponderosa, Abies concolor and a few other species, and if you look carefully then you easily will find damaged pines, the older needles yellow and shedding. The tree crown is not as dense as normally. All this has been studied for more than 20 years. The concentrations of ozone are considerably higher than those we measure in our country and the time of influence on the vegetation, during a growing season, much longer. There is no doubt about this direct influence of high ozone concentration on the trees. But even under this clear situation there is really no dying forest. They might have 1-2 percent of trees dying per year, finally killed by the bark beetles. The experts there are expecting a certain change in the species composition of the forest but no break-down as you can see it nowadays here in certain regions of Europe. This means that, even under these high concentrations, the effect on the whole ecosystem is evidently lower than the damage situation we can find in many forests of Central Europe.

There is another question: have ozone concentrations risen within the last years, i.e. within the period where we have seen the new type of forest damage? Unfortunately there are only a very few measuring stations which have records of ozone concentrations in the ambient air for a certain time. A critical review of all the data does not allow us to speak of a clear rise within the last years where these damage symptoms have developed. This means that ozone influence might be only a contributing stress factor under our site conditions.

On the other hand, there are many findings from which we might deduce a damaging effect on the foliage due to an interaction of ozone and acid fog. The cuticle and stomata may be negatively influenced in particular properties, cell membranes become more permeable and chlorophyll decomposition increases. This might lead to a higher leeching of mobile nutrients like potassium, magnesium, manganese, or zinc. These are elements which can be supplied in certain soils at a low rate only, due to soil chemical characteristics. We have demonstrated this for magnesium, and if a tree loses a little bit more of these nutrients from the foliage by leeching and cannot compensate this loss because the soil does not offer enough, then the tree must run into deficiency of specific elements. Summing up, the role of ozone in the development of the new-type forest damage in Europe does not seem to be a dominant factor, but it may contribute as one component in a complex picture of various stress factors.

Now I would like to refer back to my introductory section. I suggested that it is possible to distinguish between different types of damage, caused by different sets of stress factors. We have seen that the 'new-type forest diseases' cannot be related to only one dominant factor. However, there are damage types observed which are mainly caused by one well-known stress factor. Two types are demonstrated in the following series of slides.

One is the typical ozone damage in high radiation regions like California. Another type, well-studied for more than 100 years, is the tremendous damage of conifers caused by high SO_2 concentrations (annual means 80-150 microgram per cubic meter air). Under such conditions, especially in combination with climatic extremes occurring at higher altitudes, vast areas of destroyed spruce forests can be observed in the Ore Mountains (Czechoslovakia) and adjacent regions.

In both cases, the damage symptoms are very specific and quite different from symptoms we observe in our region. I will demonstrate this by pictures of cross-sections of needles which show the anatomical changes in the tissue. In Plate 5 a healthy spruce needle is presented. The needle in Plate 7 is from a fumigation experiment with SO_2. Parts of the mesophyll are destroyed, mainly near the stomata where gases enter the needle. A very similar type of destruction has developed in the pine needle under high ozone stress (Plate 8). Clearly different are the symptoms in spruce needles which were sampled in the Black Forest in magnesium deficient stands (Plate 6). Here you notice the collapsed phloem, whereas the mesophyll appears unchanged.

I would like to finish with a few words concerning heavy metals. Heavy metals are also said to contribute to the new type of forest damage. In my opinion there is no evidence for this, at least not in areas remote from strong sources of emission. Damaging effects due to high contamination of the biosphere with heavy metals like copper, zinc, or cadmium are well-studied in the vicinity of industrial plants like smelters or metal-refining factories. But in regions like the Black Forest element inventories and turnover data show that the input of heavy metals seems too low for direct toxic effects. However, forest ecosystems act as a sink, especially for toxic elements like cadmium and lead, due to the high filtering capacity of the tree canopy. This is particularly true for aerosols. The accumulation takes place in a characteristic way in the various compartments of an ecosystem. Longer-living organs, which are more exposed to the air stream like older branches and bark of the upper stem have higher contents of cadmium and lead. The same holds true for organic soil layers. If the deposition of essential metals (copper, zinc) rises a little, this may only mean an improvement of the partly insufficient supply of these trace elements. Anyway, no causal relation between heavy metal deposition and forest damage symptoms could be observed until now. On the other hand, increasing accumulation of heavy metals over centuries poses a potential danger because toxic thresholds may be reached in the long run. Then, acid soil solution could reach concentrations which have toxic effects on fine roots. An example is lead concentrations two orders of magnitude higher than normally found in the Harburger Forest, next to an industrial centre in the southern part of Hamburg.

Let me conclude by underlining a few important points. It is always the whole ecosystem, vegetation plus soil, which is affected by the deposition of pollutants. They can have a short-term effect on physiological processes of the trees but also influence soil properties over the long run. The level of stress factors varies considerable between regions and includes also climatic and biotic stresses. Hunting for a single factor which is causing 'Waldsterben' would be to follow the wrong track.

Nevertheless, a few dominant stress factors are certainly known, and there is no doubt that inadequate supply of nutrients plays a leading role in the development of widespread new-type forest diseases. Therefore the application of fertilisers helps to restabilise damaged forest ecosystems or to prevent the decline beginning.

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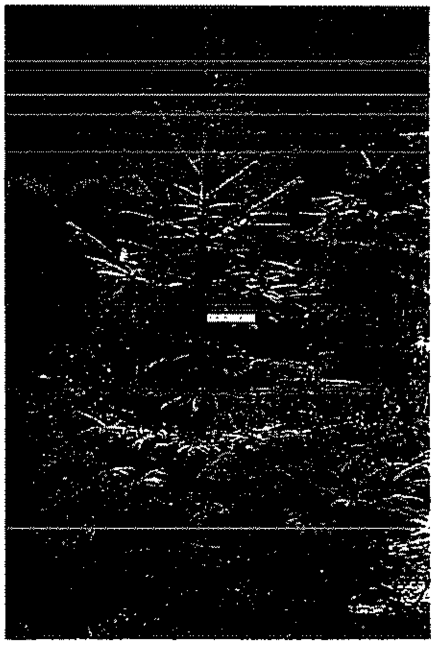

Plate 1 Fertilisation trial Elzach 10a. A spruce tree (control) in Autumn 1983 showing magnesium deficiency symptoms.

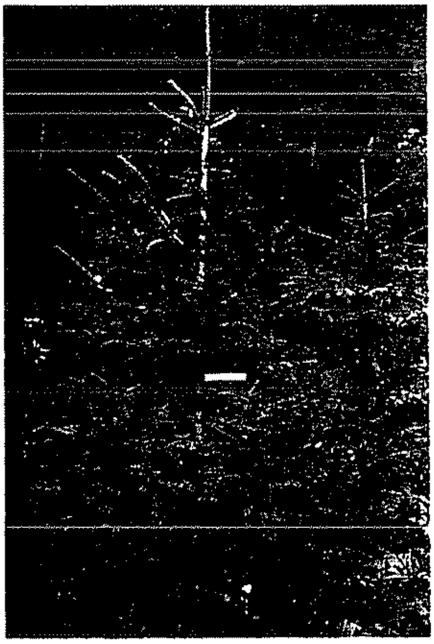

Plate 2 Fertilization trial Elzach 10a. The same tree in Autumn 1984 after application of magnesium fertilizer in Spring 1984.

Plate 3 Fertilization trial Saulgau 2. A spruce tree (control) in Spring 1984 showing potassium deficiency symptoms.

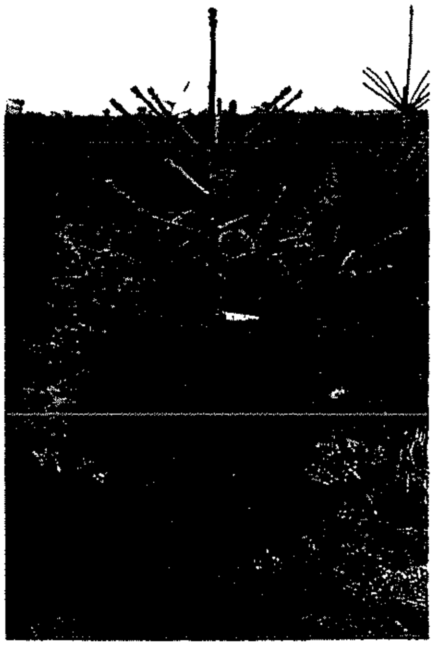

Plate 4 Fertilization trial Saulgau 2. The same tree in Autumn 1984 after application of potassium + magnesium fertilizer in Spring 1984.

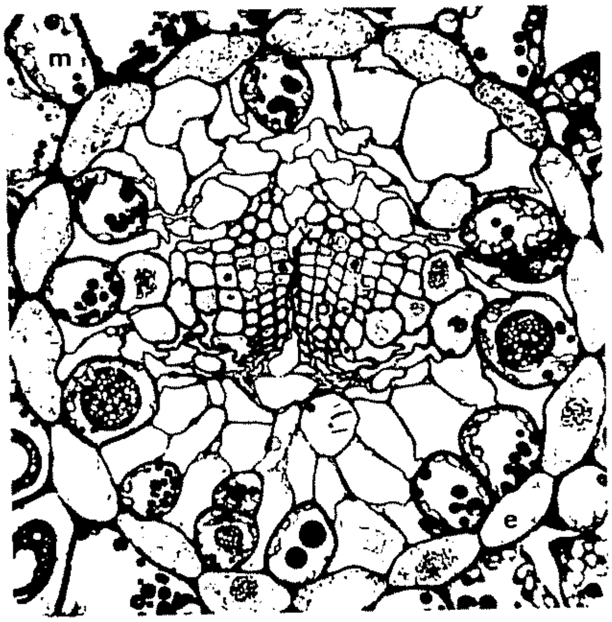

Plate 5 Vascular bundle of a healthy spruce needle (x 440 magnification).

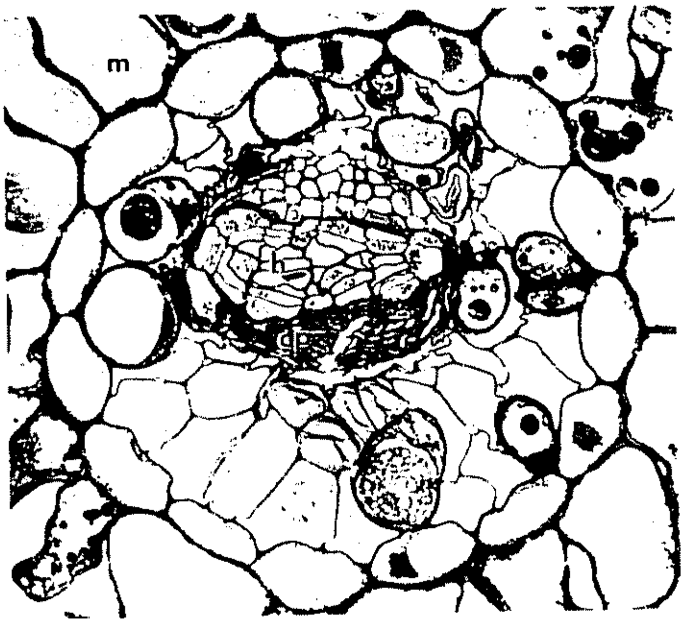

Plate 6 Vascular bundle of a yellow needle from a "forest decline"-affected spruce (deficient in magnesium), phloem collapsed, cambium hypertrophied and mesophyll intact (x 440 magnification).

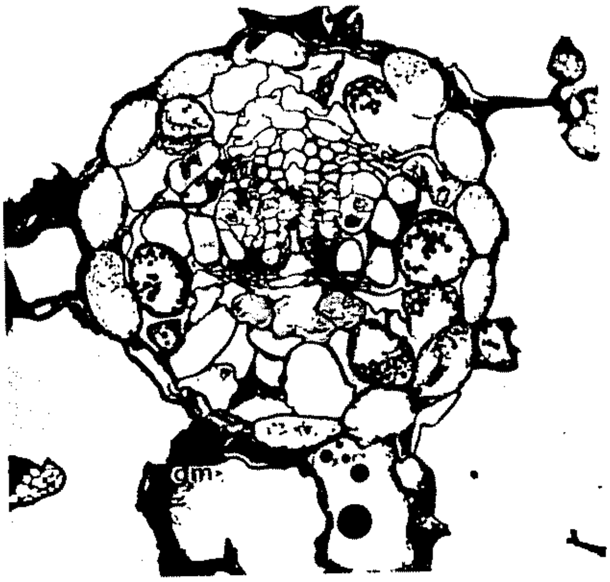

Plate 7 Sulphur dioxide-damaged needle, vascular bundle intact, mesophyll cells collapsed (x 320 magnification).

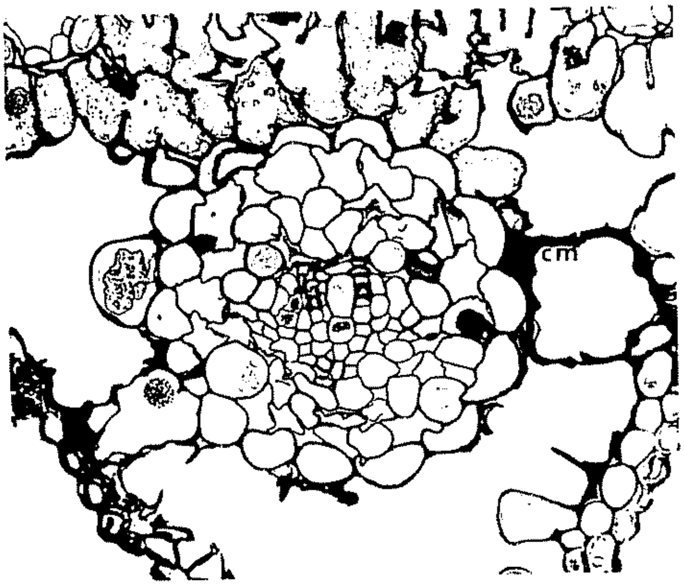

Plate 8 Ozone-damaged *Pinus strobus* needle (Appalachians, USA), vascular bundle intact, mesophyll cells collapsed (x 345 magnification).

KEY: x = xylem, c = cambium, p = phloem,
e = endodermis, m = mesophyll,
h = hypertrophied cambium,
cp = collapsed phloem,
cm = collapsed mesophyll.

Table 1 Soil data, Belchen area
Picea abies stands healthy (h) sick (s)

soil depth (cm)		total content (µmol/g d.m.)			
		Al	Ca	Mg	K
0–10	h	2820	25	270	780
	s	2940	16*	170	810
20–30	h	3100	24	290	870
	s	3220	16*	170*	830

soil depth (cm)		exchangeable (µeq/g d.m.)				
		Al	Ca	Mg	K	Mg/Al (mol)
0–10	h	52.2	11.6	5.1	2.7	0.147
	s	75.3*	4.6*	2.2*	3.2	0.044
20–30	h	43.9	6.8	2.4	1.6	0.082
	s	64.8	1.9*	0.8*	1.7	0.019

soil depth (cm)		pH $CaCl_2$	C%	N%	C:N
0–10	h	3.65	7.53	0.46	16.0
	s	3.56*	5.03	0.33	14.7
20–30	h	3.43	5.19	0.33	15.6
	s	3.81	3.41*	0.23*	14.9

* = Significant difference

<u>Table 2</u> Needle data, Belchen area.
Picea abies healthy (h), sick (s);
1st and 4th needle year class

	N	P	K	Ca	Mg
	mg/g				
1h	15,1	2,92	12,4	2,89	0,83
1s	13,9	2,63	11,2	2,10	0,35*
4h	10,2	2,31	8,1	3,19	0,64
4s	10,0	2,45	9,6	3,39	0,22*
	Mn	Fe	Zn	Cu	
	µg/g				
1h	405	50	33	3,4	
1s	522	51	23*	4,8	
4h	515	99	40	2,9	
4s	784	84	24*	4,4	
	Al	Pb	Cd	S	
	µg/g			mg/g	
1h	263	0,59	0,09	1,66	
1s	216	0,91	0,07	1,43	
4h	486	1,53	0,09	1,74	
4s	471	1,86	0,07	1,56	

* = significant difference

Table 3 Sirnitz, Picea abies

8 years old, h = healthy, s = sick;
samples fall 1983; n = 3 + 3;
current needles, roots < 1 mm ø

		N	P	K	Ca	Mg
		mg/g d.m.				
needles	h	14.5	2.02	6.35	2.32	0.51
	s	13.9	2.10	5.41	1.27*	0.24*
roots	h	11.0	1.98	3.61	2.75	1.17
	s	11.3	1.82	2.87	2.44	1.12
		Mn	Zn	Cu	Pb	Al
		µg/g d.m.				
needles	h	244	28	2.19	1.09	130
	s	218	14*	2.25	0.99	121
roots	h	221	146	12.8	17	6741
	s	263	148	14.0	15	7587

* = significant difference

Table 4 Atmospheric deposition load in the Southern Black Forest (800-900m a.s.l.)

Air concentrations (From OBLÄNDER u. HANSS, 1985)
Kälbelescheuer: 1984 monthly mean values (half hour average)

($\mu g/m^3$)	Jan.	Febr.	March	April	May	June	July	Aug.
SO_2	10	13	2	7	11	4	8	8
NO_2	1	2	0	5	5	4	4	2
O_3	64	98	84	76	80	86	77	84

St. Blasien	Winter 1983/84		Summer 1984	
($\mu g/m^3$)	Mean	Max.	Mean	Max.
SO_2	6	17	11	63
NO_2	6	18	10	47
O_3	74	144	106	231

Bulk deposition (From MIES, 1986)
Sept. 82 - Sept. 84, open land (o), throughfall (t)

	Kälbelescheuer		St. Blasien	
	o	t	o	t
N (kg/ha.a)	15.3	19.7	11.0	11.6
S (kg/ha.a)	15.8	24.8	10.6	21.4
H^+ (kmol/ha.a)	0.82	1.25	0.56	0.78
precipitation (mm)	1563	1153	1558	1021

Table 5 Fertilisation trial "Elzach 10 a". 12-year old Norway spruce stand; fertiliser (150 g $MgSO_4.7H_2O$ per tree) applied in spring 1984 (data from Hüttl, 1986)

Element contents of the current needles

Treatment	N	P	K	Ca	Mg	Mn	Fe	Zn	Al
	$mg.g^{-1}$					$ug.g^{-1}$			
control 1983	16.0	2.7	7.5	2.4	0.20	640	54	18	105
control 1984	16.2	2.5	8.6	3.0	0.32	690	43	20	95
fertilized 1984	15.1	2.6	10.1	2.4	0.56	740	40	24	85

Chemistry of the control soil at 20 - 30 cm depth

K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Al^{3+}	H^+	pH	base	K/Ca	Mg/Al
			$meq.100g^{-1}$				$CaCl_2$	sat.%	(mol)	
0.2	0.2	0.07	0.08	0.01	6.42	0.91	3.6	5.7	2.0	0.016

QUESTIONS AND ANSWERS ARISING FROM DR. ZÖTTL'S PRESENTATION

Question 1 Why are the effects on plants, such as you have just described for forests, not visible in urban or near industrial highly polluted areas?

Prof. Zöttl This is a question which arises quite often. If you look at the data than you certainly have much higher concentrations of SO_2, NOx, ozone and organic compounds in the urban areas, where you have traffic and all kinds of emission sources, and yet you do not find damage to trees growing in the gardens. You did find damage in former times where you had much higher SO_2 concentrations. For instance, in the big cities or in the Ruhr industrial region. In Munich no conifers could be grown in the centre of the city. But then they shifted from brown coal and other sources to gas and reduced considerably the SO_2 emissions. Lichens are invading and are now found in the centre of the cities again. This is an absolutely clear picture: in former times high SO_2 killing any conifer and only broadleaf trees which lose their foliage after one year able to grow. But still the urban levels of SO_2 and all other components are much higher than those we measure where the forests are damaged. I think the trees in the gardens are well fertilised and are well supplied with nutrients, and this makes them more tolerant to additional stress.

Van Dop If you allow me, may I comment on your question. Of course what's playing a role is that it takes some time for the chemistry to do its work. So, in a polluted area it takes time before NOx pollutance occur. And during that time they are transported far away from industrial zones. That may partially be an answer to your question too.

Question 2 In Germany there are many new theories regarding forest damage. A new theory mentions radiation from nuclear power plants poisoning the trees. What do you know about it?

Prof. Zöttl Yes there are many theories. Yesterday, 163 hypothesises, maybe today we have 164.

There is a study by Prof. Metzner (Tübingen). It is not yet distributed to the public but I have a copy. He finds certain weak points and there are a few points which should be considered in the future research. But I do not feel that this is really a hypothesis which explains the forest damage. The mapping which was done in the surroundings of power plants did not show relations to forest damage.

Question 3 Dr. Zöttl, in 1972 when I was on a visit in Upsala (Sweden) to the Forestry Department of the University, one of the assistants told me that in man-exploited forests, where wood production is a very important thing, each stem of each tree which is taken away takes with it x milligrams of calcium, x milligrams of magnesium, x milligrams of manganese. Is it too simple to say that this is partly an answer to forest damage?

Prof. Zöttl It is one of many factors influencing nutrient supply. All export of nutrient elements reduces the reserves in the soil. If you harvest the stem, the bole with the bark, the output is rising in certain elements by a factor of more than 3. This is part of the whole picture but certainly not the factor causing that what we can see nowadays.

Question 3 (cont'd) Has there been a change in management of forests over the last years that has caused this sudden change?

Prof. Zöttl The intensity of harvesting is higher now than it was in the past. This is also contributing a little. You can see it very clearly if you go to fast-growing man-made plantations in the subtropical region, where you have much higher need for nutrients and greater output by harvesting. They harvest trees after seven or 20 years whereas we wait 100 and 120 years. Thus within a relatively short time you can run into deficient situation of certain elements which are not highly offered in the soil. But this is only one of many factors and you can not from this deduce that only forest management is guilty of causing forest damages. At present, you find similar damages in natural stands, for instance mixed stands of European beech, white fir and spruce which are growing in optimum conditions. This means management methods alone are not the factor.

Question 3 (cont'd) So you still talk about the symptom: the nutrient deficiency. But what will be the cause of that because that's what we are asking, isn't it? I mean, what's the difference between 50 years ago and now?

Prof. Zöttl Well, the main question is why do we find this nutrient deficiency situation now spread out so widely within a very short time. That's more or less an unanswered question. The actual situation is clear. But why does this occur now?

Question 4 When you were at that part of the talk when you started introducing the tobacco leaf and you showed us the yellow spots on it and then you moved on to show us the changing levels of the various pollutants, and then you showed us the plots for ozone, the impression I got was the change in ozone was not all that high. Were you saying that that small changes could perhaps be a significant factor?

Prof. Zöttl I am not convinced. The San Bernardino forest is showing damage. But it's not a dying forest. The experts there told us they expect a certain change, a certain shift between the dominant tree species. Some are dying a little bit more, others less, because there are cedars and other species which are evidently tolerant. They do not show any decline. It's quite a different sensitivity.

Question 4 (cont'd) If I rephrase my question in a slightly different way, I mean what would you consider to be a significant change of ozone level in terms of looking for evidence of plant damage.

Prof. Zöttl The measuring stations in Europe show that in the higher altitudes the values shift around 30-40 parts per billion ozone, and there is no daily variation as these is down in the cities. Air chemists can easily explain this. High values of 125 parts per billion of ozone can occur, at which you touch the level where damage is possible. But in San Bernardino mean and peak values are higher and last longer during the year. There are experiments now under way. The results up till now are not very clear.

Question 5 The nutrient effect looks very spectacular and it is certainly very specific. Have you an idea how the tolerance of species of trees is then increased? Can that be, coming back to the same question, can that be demonstrated by fumigation tests?

Prof. Zöttl That's what we wondered and tests are under way now. There are several Institutes in Germany now running fumigation experiments and they keep the trees at different levels of nutrition. That's new. In former times they used a standard substrate which was mostly well supplied with all nutrients. In California, the effect of ozone is more on the agricultural crops, and the agricultural crops are always well supplied with nutrients. I asked colleagues there whether they find different reactions to ozone in plants which might have a different nutritional status. And they said, they find that if we have an over nutrition with nitrogen or so, than the plants are affected more. I must say we never find the situation in our forests because we are at the other end of the curve, if we have nutritional disturbances it's never over-nutrition, it's always a deficiency level. But this is a case they did not study because it does not occur in citrus or in soyabean or in cotton plants. Even now, where we certainly have a higher input of nitrogen to the forests, we do not find clear signs of an over-nutrition with nitrogen. What we find clearly, and it is well documentated, is a better growth, an improvement in growth on sites where the nitrogen reserves are very low. It is also an hypothesis that higher nitrogen input might lead to inbalanced nutrient supply. I only can say there is a huge data basis of foliage analyses which goes back about 30 years. We do not find over-optimal nitrogen nutrition. We are glad that the nutrition is better now than before. In Scandinavia, the foresters say that if they have an effect on the forest it is better growth due to higher nitrogen input. But you can reach a level where it is dangerous. This occurs in plantation forests in The Netherlands which receive extremely high ammonia input from adjacent production centers of animal manure.

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"US EXPERIENCE OF HYDROCARBON AND NO_x EMISSIONS CONTROL"

Presentation by
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~~Research Department~~
Paulsboro, NJ, USA

ABSTRACT

Ozone formation in the atmosphere is attributed to complex chemical pathways involving reaction of hydrocarbons and nitrogen oxides in the presence of sunlight. Thus, control strategies to reduce ozone levels involve control of hy~~drocarbon~~s and NO_x.

This review traces the development of hydrocarbon and nitrogen oxide (NO_x) controls as they relate to the control of high ambient concentrations of oxidants once observed in most US urban areas. First in California, then throughout the US, urban ambient concentrations of oxidants were observed which are associated with alleged health effects. This prompted legislation to control ozone and other ambient air pollutants. In Europe, the motivation for controlling ozone appears to have come from the association of ozone with forest damage at relatively lower rural ozone concentrations. Urban ozone concentrations are similar in Europe and the US; therefore, similar precursor controls should be effective. Since rural ozone levels in the US have not been subject to control, much uncertainty surrounds efforts to predict effects of proposed strategies on future rural ozone levels. Models in both the US and Europe that would handle transport of mostly urban precursor hydrocarbon and NO_x emissions and mixing with rural natural hydrocarbons to predict rural ozone levels are still in the early development stage.

Effective control strategy should begin with the largest sources. In the US motor vehicle emission controls of hydrocarbons and NO_x have been the backbone of ozone control strategies, beginning first in California in the 1960s, then becoming increasingly more stringent as technology was developed. Vehicle hydrocarbon emissions have been second most important for hydrocarbon reduction; controls have involved reduction in use, reformulation, and recovery.

Petroleum industry sources represented only about 10% of uncontrolled hydrocarbons and even less of NO_x, Recently, hydrocarbon emissions have been controlled selectively in high ozone areas. Controls in refineries have included better tank seals and increased monitoring and maintenance of valves and fittings. In

gasoline marketing, vapour recovery has been required for transfer operations from bulk tanks to tank trucks and to retail outlets. Vapour recovery in vehicle refuelling is in place in California and is under consideration as a nationwide requirement. Limits on gasoline volatility exist in California and are under consideration in other states and at the national level. Control of stationary source NO_x emissions has been limited to the few areas in violation of health-based standards for NO_x. Limits on refinery boiler and process heater NO_x emissions have been part of the control strategy.

Review of in-place petroleum industry hydrocarbon control techniques indicates that vehicle emission controls have had a larger impact on the petroleum industry through requirements to market unleaded gasoline than direct industry emission controls. Availability of unleaded gasoline was mandated when exhaust emission control catalysts were introduced. The unleaded gasoline mandate also carried restrictions on sulphur and phosphorus content and on usage of oxygenates and fuel additives. The more recent introduction of oxidation/reduction (three-way) catalysts that combine catalytic control of NO_x emissions with control of hydrocarbon and carbon monoxide is bringing pressure for low-phosphorus engine oils.

Concern about the performance of exhaust catalysts in service may bring about a complete ban on leaded gasoline to prevent catalyst poisoning through misuse of leaded gasoline in catalyst-equipped vehicles. Concerns about the effectiveness of evaporative emission controls may lead to gasoline volatility restrictions.

In the United States, regulations to reduce hydrocarbon and NO_x emissions to control ambient ozone have had a substantial impact on the petroleum industry. If further ozone control is necessary worldwide, regulations should take account of cost-effectiveness of alternative control strategies. Any policy must be based on sound scientific information and the application of value judgements that consider key social and economic factors.

<u>Editor's note:</u> *Due to procedural difficulties in obtaining clearances, the full corrected text of Dr. McCabe's speech was not available at the date of publication of these proceedings. It is suggested that readers wishing to obtain the text should contact Dr. McCabe direct at the Research Department, Mobil Research and Development Corporation, Paulsboro, New Jersey, USA. When the approved text is received CONCAWE will consider issuing it as a supplement to the current report.*

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"THE PHOXA MODEL"

Presentation by
Dr. P. Builtjes
Project Manager of the PHOXA Project
TNO Divisi~~on of Technology~~ for Society
Apeldoorn, The Netherlands

ABSTRACT

Several participants to the Seminar asked for more information on the PHOXA project. Dr. P. Builtjes, who was attending the Seminar as one of the representatives of EEC but who is also a PHOXA project leader, kindly accep~~ted to b~~rief the audience on the project scope, programmes and current status of activities.

THE PHOXA MODEL

What PHOXA stands for is photochemical oxidants and acid deposition model application. The real purpose of the project is to find out the effectiveness or cost effectiveness of possible abatement strategies. This project will run for about three years and it is split up in three parts: a data base branch, a photochemical oxidant branch and an acid deposition branch. The first year it started, in 1984, was used to set up a data base branch that included an emission inventory. That has already been talked about a lot at this Seminar. What we are trying to do is to set up an emission inventory for the Western part of Europe. That means starting from Ireland up to the Russian border and from the Alps up to the Southern part of Norway on a grid basis of a roughly 25 by 25 square kilometers. Now you can say: how can you do that? Yes, that was a point indeed! In principle there is an emission inventory, available for The Netherlands and Germany so there are official detailed emission inventories for Germany and The Netherlands and we try to make a guess based on open literature for the other countries including the Eastern European countries. The emission inventory, which is ready at this moment, contains, of course, SO_2 and sulphate, NO, NO_2, ammonia and hydrocarbons in nine reactive classes and, of course, it is split up into economic sectors like traffic, urban traffic, highway traffic and the different industrial categories, including natural emissions. What we plan to do within the next couple of months is as follows. For the photochemical oxidant branch, the SAT-RTM III regional transport model will be used to calculate in principle three episodes. I have to explain that a little. The original PHOXA project was funded by the German and the Dutch Governments. They paid mainly for the set-up of the data base and they covered the cost of doing an evaluation of a first photochemical episode. The European Community is paying for the second episode. The third episode is covered by a contract with OECD. So finally we'll have three episodes which have been evaluated against field data. Then we will carry out application runs, like looking to what would be the effect of the car regulations which are proposed by the European Community. In the acid deposition branch, we are a little behind the time schedule for the chemical oxidant branch, but there we will use episodic as well as long-term average models to calculate acid deposition, again using the same emission data base. Scenario calculations will also be carried out, hopefully at the beginning of next year, around April 1986. The total original PHOXA project, as it stands now, will be completed, by the end of 1986. There are a lot of Institutes contributing to that project. For example, KNMI is involved in the meteorological part and TNO, where I belong, is mainly responsible for the total photochemical branch of the project and has set up the data base and the emission inventory. Systems Applications will carry out some calculations and NILU, for example, is also involved in doing trajectory analysis for these specific episodes. If there are any other questions, I'll be happy to try to answer them.

Question	In applying the SAI model are you going to use some actual measured data of the pollution by ozone, hydrocarbons, and NOx?
Answer	Yes, not ground level, but higher then ground level. Normally, of course, what we have access to are ambient data at ground level. We have a whole process for selecting episodes, and we try to select episodes where as many data were available as possible. So at least two of the three episodes have some airflights. But of course what is mainly lacking, as is always the case, is the hydrocarbon field data. There are hardly any ambient data for hydrocarbons, and this has a relation with the uncertainty in the emission inventory for hydrocarbons. I agree fully with Mr. Van Dop's comment this morning that it is necessary to investigate the overall uncertainty in this application.
Question	As far as I know the hydrocarbon data from Germany originate from 1978. Aren't they outdated.
Answer	Mr. Löblich tried to set up an emission inventory for sulphur dioxide and NO$_x$ and Dornier was responsible on the PHOXA project for the emission inventory. TNO has a lot of experience in trying to make estimates for hydrocarbons. So in co-operation with Dornier, they set up an emission inventory for hydrocarbons for West Germany. At this moment I have, well not really on my desk, but nearly on my desk, an inventory for Germany for hydrocarbons split up into nine classes. The base year of the inventory is 1980, so we try to set up an inventory for 1980. Our first episode is in 1980. We have episodic specific figures, like the temperature dependence, the time of the day, which months, and whether it's a Saturday or a Sunday. We create an episodic-specific data base. If they used 1978 figures, if they did it correctly, they updated it to 1980. But I fully agree that the hydrocarbon emission inventory is the most difficult part of it. And if anybody can come up with better figures, I would like to have them.

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"EEC RESEARCH PROGRAMME ON AIR POLLUTION MATTERS"

Presentation by
P. Mathy
Directorate-General for Science
Research and Development
European Commission, Brussels

ABSTRACT

This paper reviews the research priorities and implementation of the European Communities research programme in the field of air pollution. As far as the scientific matters are concerned, only the headlines of the R & D Programme are presented in order to avoid overlaps with the other presentations, since a number of lecturers are involved in these R & D Programmes either in the Concerted Action or as contractors

1. <u>A review of the R & D programme in the field of environmental protection implemented by the Commission of the European Communities covering:</u>

   - history of the research programmes in the field of Environment;
   - objectives;
   - areas of research covered by the programme
   - ways of implementation (concerted actions; research contracts).

2. Research priorities; achievements and perspectives

2.1 Analysis, sources, transport, transformation, and deposition of pollutants

2.1.1 Background of the knowledge
2.1.2 The concerted action "Physico-Chemical Behaviour of Atmospheric Pollutants"

- Scientific content of the concerted action
- Results; perspectives; recommendations for future research

2.2 Ecological effects of air pollution

2.2.1 Background of the knowledge
2.2.2 The concerted action "Effects of Air Pollution on Terrestrial and Aquatic Ecosystems"

- Scientific content of the concerted action

2.3 Research contracts in the field of ecological effects; Research priorities

ACID DEPOSITION: RESEARCH PRIORITIES AND IMPLEMENTATION OF THE COMMUNITY RESEARCH PROGRAMME

1. PROGRAMMES AND GENERAL LINES

Most aspects of air pollution have been dealt with by the European Community research programmes more or less intensively since the European Community became involved in environmental research in 1972. Up to date, three Environmental Research Programmes have been carried out; a fourth one, which is the logical continuation of the previous one, has been submitted by the Commission to the Council of Ministers for adoption. It will cover the period 1986-1990.

The Community's research in the field of environment is aiming at:

- providing scientific and technical data to support the Community Environment Policy;
- addressing longer-term environmental problems, thus preparing the way for the development of preventive and anticipatory policies, taking into account foreseeable environmental trends; and to provide the means to evaluate the effectiveness of current environmental policies;
- serving as an instrument for enhancing further, at Community level, the co-ordination of national research activities in the environmental field, in order to improve the productivity of the overall effort through the encouragement of joint projects, the elimination of duplication, and the evaluation of gaps in research.

1.1. AIR QUALITY

Air quality is one of the most important areas to be dealt with within the general framework hereabove described. Although this field had been taken into account previously, the Commission reviewed the research priorities as a consequence of alarming reports on forest dieback in Central Europe and also as a result of the conclusions of the Symposium on Acid Deposition held in Karlsruhe in 1983. Influenced also by a general upgrading of priorities for research on acid deposition all over Europe and triggered by considerable public pressure, the Council of Ministers adopted in March 1984 a revision of the third Environmental Research Programme, allocating supplementary funds for research in this area. It is foreseen that acid deposition issues will reclaim the same priority within the framework of the forthcoming fourth Environmental Research Programme.

The general lines followed by the Commission in implementing the programme are as follows:

(1) promotion of the co-ordination of national research by means of Concerted Actions, but also by more flexible means, e.g. the establishment of ad hoc task forces to examine in greater detail specific, narrowly defined aspects;

(2) grating of selected research contracts, either for projects which will fill gaps in national research programmes or as contributions to well-defined major national research efforts (cost-sharing is usually 50%-50%).

Two Concerted Actions cover the "acid deposition" field:

(i) the physico-chemical behaviour of atmospheric pollutants (COST 611); and

(ii) the effects of air pollution on terrestrial and aquatic systems (COST 612).

Both Concerted Actions are managed by a Community-COST Concertation Committee constituted by the representatives of the Member States, while working groups are entrusted with the scientific tasks. The Commission of the European Communities provides the secretariat of the Concerted Actions.

In addition to the Member States of the European Community, a number of countries which are involved in the European Cooperation in the field of Scientific and Technical Research (COST) participate in the Concerted Actions:

- Finland, Norway, Sweden and Switzerland in COST 611;
- Norway, Sweden and Switzerland in COST 612.

This shows the interest of this type of action, even outside the Community, since these countries are not obliged to participate.

The objective of the Concerted Action is in principle limited to co-ordinating national research, national authorities remaining entirely responsible for the research carried out by national institutions or bodies. Thus the Concerted Action appears to be an adequate tool for analysing the experiences and the results acquired by European research institutions, and for assessing the state-of-the-art. As a result, priority objectives for future research can be established. To a very large extent, the granting of selected research contracts is based on the results of the Concerted Actions. The projects are selected in close co-operation with national authorities represented by an Advisory Committee.

2. RESEARCH PRIORITIES, ACHIEVEMENTS AND PERSPECTIVES

2.1. ANALYSIS, SOURCES, TRANSPORT, TRANSFORMATION AND DEPOSITION OF POLLUTANTS

2.1.1. Background knowledge

Among the primary pollutants, sulphur dioxide (SO_2) and nitric oxide (NO) are the most important ones. SO_2 is formed by oxidation of sulphur-containing substances (FeS_2, organic sulphur compounds) in fossil fuels and during processing of metal sulphide ores. Substantial amounts are emitted from volcanoes.

During all combustion processes, NO is formed by oxidation of nitrogen from the air, but also from nitrogen-containing organic compounds. NO and atmospheric oxygen are in equilibrium with nitrogen dioxide (NO_2). Nitrogen oxides are also formed naturally (e.g. by lightning, soil organisms, plants and oxidation of ammonia). In view of the rapid establishment of a equilibrium between NO and NO_2, nitrogen oxides are usually specified as NO_x.

Emissions of HF (from aluminium smelters, brick firing, etc.) are locally important. HCL is emitted in substantial quantities from waste incinerators.

A number of other species (e.g. H_2S, COS, $(CH_3)S$, mainly from natural sources, and chlorinated hydrocarbons, both man-made and natural), play a significant role in the overall bio-geochemical cycles, which cannot be discussed in detail, and are considered as precursors of SO_2 and HCL.

Hydrocarbons, CO and other volatile organic compounds, emitted from the natural sources and as a consequence of human activities, enter the atmospheric conversion processes described below and are important precursors of photochemical oxidants, together with NO_x.

There is growing concern about increasing emissions of NH_3 from agricultural activities in excess of the natural background, which may contribute regionally to acidification via nitrification processes in soil.

The problems related to heavy metals emitted together with particulate matter and deposited in areas remote from the emission site are at present subject to debate.

The primary pollutants react in the atmosphere with each other and with the normal constituents of the atmosphere, resulting in the formation of secondary pollutants. Many of these reactions need photochemical activation and involve short-lived species, in general radicals. The most important secondary pollutants are sulphuric acid, nitrous acid and nitric acid, ozone, aldehydes, peroxides and peroxyacylnitrates (PAN).

SO_2 is oxidised in the atmosphere by various direct and indirect mechanisms in homogeneous gas phase, liquid phase and on the surface of particles to the hexavalent state of sulphur and deposited as sulphuric acid with rain or as aerosol. The dry deposition of SO_2 also results finally in the formation of sulphuric acid and acidification.

A number of reactions lead from NO and NO_2, with other oxides of nitrogen as intermediates, directly to nitrous acid and nitric acid, subject to wet deposition. To what extent dry deposition of nitrogen oxides and subsequent oxidation contribute to acidification is not yet fully assessed.

In the homogeneous gas phase, during day time, a series of photochemical reactions occur, involving hydrocarbons, nitrogen oxides and a number of short-living radicals (HO, HO_2), and resulting finally in the generation of ozone, aldehydes, peroxides, peroxyacylnitrates (PAN), nitrous acid and nitric acid. The oxidising potential built up during day time reacts in the dark with reducing species, following different reaction mechanisms.

In addition to the reactions in the homogeneous gas phase, conversion of primary pollutants occur in the liquid phase (rain and cloud droplets) and on the surface of solid aerosol particles. So far, the various mechanisms are poorly understood. These reactions involve other intermediates, other oxidants (e.g. H_2O_2) and catalysts (heavy metals). It is clear, however, that the final products are mainly sulphuric acid, nitrous acid and nitric acid.

As far as transport is concerned, the overall emission/deposition balance over large geographical areas in Europe has been described with reasonable precision, as far as SO_2 and its conversion products are concerned. Information on the nitrogen oxides and their conversion products is still scanty.

In the light of the typical mean atmospheric residence time of acid and acidifying gases and their reaction products (1-2 days for SO_2 and NO_x and about one week for aerosols), acid deposition is rather a regional or mesoscale problem.

For mesoscale transport, the present state of knowledge does not provide sufficient predictive potential; this is due in part to the fact that plumes for single or diffuse sources may persist for rather long distances and conversion chemistry inside plumes is different from outside.

There is a lack of knowledge about the function of the ocean as source and sink of pollutants, and the global aspects of acid deposition (as part of the overall bio-chemical cycles of sulphur and nitrogen) are therefore poorly understood. Also the exchange of active species between troposphere and stratosphere needs further elucidation with particular emphasis on the role of N_2O produced in excess of the natural background due to increasing fertiliser use.

As regarding the mechanisms of deposition, the wet deposition with rain is easy to determine. All aspects of dry deposition (in the strict sense) are poorly understood, in particular the influence of the "roughness" of various surfaces. Some important aspects with regard to forest damage, such as "interception deposition" of small cloud droplets and fog water on trees located on mountain ridges, are difficult to assess quantitatively.

2.1.2. The Concerted Action "Physico-Chemical Behaviour of Atmospheric Pollutants" (COST 611)

2.1.2.1. Scientific Content

The scientific content of the Concerted Action on Physico-Chemical Behaviour of Atmospheric Pollutants includes the analysis of pollutants, the mechanisms and rates of the chemical and photochemical reactions, the characterisation of aerosols and the formation of particles, the pollutant cycles, and the transport and modelling.

In the field of the analysis of pollutants the activities focus on:

(a) the development of analytical techniques to determine main atmospheric pollutants or products due to their metabolism at low concentrations. Emphasis is given to the evaluation of compounds contributing to acid deposition, such as ammonia, nitric acid, hydrochloric acid and hydrogen peroxide in both gas and liquid phase (fog, clouds and precipitations), and to the analysis of precipitation chemistry to obtain data for acidity trends. The evaluation of the chemical nature of aerosols and their role in determining their acidity is also included;

(b) the improvement and standardisation of analytical procedures to detect and evaluate atmospheric pollutants, especially for NO_x, hydrocarbons and photochemical oxidants. Emphasis is given to investigations of the sampling procedures, which might seriously affect the analytical procedures for most pollutants and to prevent artifacts;

(c) development of analytical techniques for "new" pollutants which exert a recognised impact upon the air quality. This includes highly reactive species such as radicals.

The activities regarding the chemical and photochemical reactions encompass:

(1) laboratory studies designed to determine fundamental physico-chemical data such as rate constants, thermochemical constants, solubilities, absorption coefficients and photodissociation quantum yields, for potentially important reactions of atmospheric pollutants;

(2) laboratory studies designed to elucidate the kinetics and mechanisms of chemical transformation and oxidation of pollutants in the gas phase, in the liquid (aqueous) phase, and on surfaces such as are present in atmospheric aerosols and in the soil matrix. Such chemical studies are included regardless of whether the final product is gaseous, liquid or solid, but the physical mechanisms of aerosol production from the products is not included;

(3) critical evaluation of available kinetic, photochemical and thermodynamic data for atmospheric chemistry;

(4) laboratory studies relating to the formulation of test procedures for determining the kinetic data required to assess abiotic degradability of atmospheric pollutants.

As far as pollutants cycles are concerned, emphasis is put on investigation of the sources, concentration profiles, and sinks of gaseous and particulate pollutants and their cycles on a local, regional and global scale. The programme is confined to pollutant gases which are involved in chemical conversion processes in the troposphere and which have, or are thought to, have measurable environmental effects.

As far as pollutant sources are concerned, both natural and anthropogenic emissions are considered. In the investigation of sinks, work is concentrated on a quantitative determination of dry and wet deposition processes.

The causative chain between emissions and deposition of acid and acidifying substances is also being investigated.

Special attention is paid to the most important primary and secondary acidifying and acid gases. The most important primary acidifying and acid gases being sulphur dioxide (SO_2), nitric oxide (NO), and hydrochloric acid (HCL). The most important secondary pollutants formed from these primary emissions are sulphuric acid (H_2SO_4) and sulphates, nitrogen dioxide (NO_2), nitric acid (HNO_3) and nitrates, and ozone (O_3).

Although ozone is not an acidic substance, it is treated in the wider context of acid deposition since it plays an important role in SO_2 and NO_x chemistry and it most likely plays an important role in determining the ecological effects of air pollution.

The contents of the programme concerning Transport and Modelling is directed at:

(a) field experiments, stationary or using mobile stations like aeroplanes, including limited series of atmospheric measurements whose purpose is to investigate a particular physico-chemical process or group of processes occurring in the atmosphere, and investigations intended to demonstrate the existence of particular sources or sinks;

(b) modelling studies to describe the physico-chemical behaviour of atmospheric pollutants, including plumes and clouds, in the real atmosphere, in connection with measured data.

2.1.2.2. Results and perspectives

The Concerted Action on "Physico-Chemical Behaviour of Atmospheric Pollutants" was initiated in 1978. The achievements of this programme have been presented in several publications which are available to scientists. Many of these papers were published on the occasion of international workshops of symposia sponsored and organised by the Commission of the European Community. Detailed information concerning the scientific results of this Concerted Action are gathered in the final activity report of the Community COST Concertation Committee covering the period 1978-1983. This report is available on request from the Secretariat of COST 611.

Although it is quite impossible to give all the details in this meeting, it seems to me important to recall the main conclusions mentioned in this activity report:

- atmospheric conversions are strongly influenced and accelerated by oxidising compounds such as HO, HO_2, H_2O_2, as well as by reactive hydrocarbons;
- there is a considerable long-range transport of reaction products of atmospheric conversions, especially acidic compounds and oxidants;
- the development of new measuring techniques have made it possible to detect new substances, and advances in this area are considerable and are still going on;
- the formation of aerosols and their role in atmospheric conversion is of great environmental importance but is not yet sufficiently understood;
- the products of atmospheric conversions participate in pollution cycles and are transferred to soil, water bodies, biotic species and materials, and can affect human health;
- the conversion of primary pollutants into major acidic compounds has been intensively studied and, whilst mechanisms have been identified, the relationship between primary pollutants and acidic compounds is still quantitatively not clear;
- the reactions which lead to photochemical oxidants have been intensively investigated, but are not fully understood up to now;

- atmospheric transformations have also been studied through field experiments e.g. in the plumes of urban areas and power plants; the results are encouraging but too few to draw final conclusions about the validity of proposed mechanisms and rates occurring in ambient air;

- the rational drafting of air quality standards depends on a basic understanding of atmospheric processes.

As a result of these conclusions, the following recommendations were formulated:

- to proceed with this Concerted Action to reach a better understanding of physical/chemical conversions of air pollutants and the air chemistry involved;

- to give more attention to field experiments measuring conversions and reaction products in the free atmosphere, in plumes, clouds and fog;

- to ascertain the pathways of reaction products through the environment;

- to focus attention on the need to establish an international data base of measurements on species like O_3, NO_2 and PAN from representative national non-urban monitoring sites;

- to make use of modern analytical methods and measurement studies to develop and standardise new techniques;

- to encourage the development of mathematical modelling studies to assist in the interpretation and application of the results of studies contained in the Action;

- to continue to encourage high-quality laboratory studies of reaction mechanisms of relevance to tropospheric chemistry.

In order to establish a logical link between issues regarding the physico-chemical behaviour of air pollutants and the following considerations about their ecological effects, it is also necessary to emphasise that a comprehensive qualitative and quantitative knowledge of the chemical environment of ecosystems, especially forests, up to now lacking, is required. This particular gap is part of a more general one concerning the cycles of pollutants, for which some important pathways are insufficiently quantified (e.g. dry deposition of NO and HNO_3). In particular, dry deposition of nitrogen compounds should be seriously investigated, even if it is already thought that many forests probably receive more nitrogen under different chemical forms than in the past, leading perhaps to a long-term modification of the functioning of the ecosystems via perturbations of nutritional and physiological processes.

It is a matter of fact that the air concentrations of pollutants in ecosystems are not well quantified, although it is a prerequisite to the knowledge of their possible damaging effects on plant communities. With regard to some pollutants like SO_2, NO_x, ozone, the data are insufficient and sparse. For other pollutants such as PAN and hydrocarbons, organic lead compound, etc. the data are practically non-existant. As a result, it is difficult at present to investigate the role of these components in the functioning of ecosystems and, as a result, to assess the consequences of the presence of these chemicals on the status of the ecosystems.

2.2. ECOLOGICAL EFFECTS OF AIR POLLUTION

2.2.1. Background knowledge

2.2.1.2. Effects on the aquatic environment

As regards the ecological effects of acid deposition, the situation seems to be pretty clear as far as the aquatic environment is concerned. Water bodies with low buffering capacity are acidified by strong acids (H_2SO_4, HNO_3), directly affecting aquatic fauna or preventing the reproduction of aquatic organisms, with obvious consequences on the overall ecological balance. This situation is well known in Scandinavia, even if the quantitative aspects need further research, in particular the effects of acidic shocks, e.g. from melting snow. The role of indirect effects, e.g. by metal ions released from the bed-rock, also needs further elucidation. In Central Europe, the situation is less clear, It seems that the natural sources of acidification (e.g. from bed-rocks, forest themselves, etc.) could very often be more important than the man-made ones. It is important to take into account the buffering capacity of soils when assessing the risk that waters may become acidified.

2.2.1.2. Effects on agricultural productivity

With regard to the reduction of agricultural productivity, soil acidification plays a minor role, since an arable land this is usually compensated by liming and may also be less important than acidification due to nitrification. Direct damage due to SO_2 and oxidants is relatively well documented from laboratory studies, but reliable exposure/effect relationships are lacking, and sound estimates of crop loss in Europe are at present not possible.

Nevertheless, there is strong evidence for deleterious air pollution effects on agriculture crops in (or close to) industrial areas, where acute damage (visible effects) is well known. Such strong evidence does not exist for remote areas, although some risk to vegetation does exist. Some air pollution levels could lead to chronic damage (non-visible effects). This assumption mainly comes from measurements of air pollution in "rural areas", as well as from well known dose response relationships for single components. Owing to the lack of reliable information on field conditions, it has so far been difficult to assess this risk and the resulting effects from a biological and economical point of view.

Finally, natural factors such as climate, pests, etc., or individual sensitivity of plants will interact with pollution stress to modify plant response.

2.2.1.3. Effects on terrestrial ecosystems

It is difficult to disentangle the numerous publications, of variable quality, on forest dieback which have appeared recently. Many of them do not go beyond mere speculation, and various symptoms are often indiscriminately attributed to "acid rain". The real causes are extremely complex and poorly understood.

The direct effects of high SO_2 concentrations on trees, in particular conifers, have long been known. These may be at the origin of forest dieback in certain regions, e.g. in Northern Bavaria (Fichtelgebirge). Locally, increased concentration of the highly phytotoxic HF may also be responsible for calamities.

For the severe damage to forest ecosystems, only recently observed, in regions where ambient air concentrations of the classical pollutants are rather low, two main hypothesis are being discussed.

The first of them gives the main emphasis to a continuously increasing acidification of soil: direct damage to the root system including the symbiotic mycorrhiza, mobilisation of phytotoxic metals (in particular aluminium), leaching of nutrients, die-off of organisms which degrade organic matter, etc., impair the water and mineral balance of trees and lead finally to a breakdown of the entire forest ecosystem.

The second hypothesis, backed mainly by forest dieback observed in areas with low concentrations of sulphur-containing species, gives more emphasis to the direct effects of photo-oxidants, in particular ozone, on the vegetative organs of the trees.

We shall discuss these hypothesis with more details at a later stage, but we must mention here these two hypothesis were the basis for establishing the structure and the terms of a new Concerted Action implemented since March 1984.

2.2.2. The Concerted Action "Effects of Air Pollution on Terrestrial and Aquatic Ecosystems"

The main emphasis of Community research is on the ecological effects of air pollution. A new Concerted Action, decided by the Council on 1 March 1984, is being implemented, and efforts are being made to co-ordinate relevant research in Member States as well as in Non-Member States associated within the framework of COST agreement.

This Concerted Action covers:

- the effects on aquatic and wetland ecosystems;
- the effects on agricultural productivity;
- the effects on terrestrial ecosystems, in particular forests.

2.2.2.1. Scientific content

The main principle which has been considered in drafting the scientific content of this Concerted Action was to deal with the acid deposition issue by adopting a broad ecosystemic approach instead of isolating plants from their natural conditions as was done very often in the past. It is a matter of fact that the threshold concentrations of air pollutants which induce injury to trees or crops depend highly on a range of ecological factors linked to soil and climate conditions, as well as to the biological features of plants themselves. This clearly means that a reliable response of trees, crops or aquatic organisms, to air pollution could not be expected only from laboratory investigations but will derive mainly from field experiments.

Nevertheless, co-ordination work undertaken within the Concerted Action will also cover laboratory research under controlled conditions, as well as field research. Then several hundred projects will be progressively taken into account.

With regard to the air pollution effects on terrestrial ecosystems, particular attention is paid to forest ecosystems, but agricultural ecosystems are also considered. The functioning of the ecosystem is firstly considered under its main aspects:

- the cycles and the balances of mineral elements and energy flow;

- the relationships between the different factors of the ecosystems: soil, climate, biocenoses, including the natural long-term modifications of abiotic factors and their temporal (seasonal and occasional) and spatial variations which could induce temporary or permanent changes within the biocenoses;

- the effects of management practices on the functioning of the ecosystems;
- the mechanisms of the acidification and of the physico-chemical changes in the ecosystems;
- the water movements in soils and their relations with aquatic ecosystems.

The direct effects of air pollution are obviously of high priority and special emphasis is given once again to forest trees and stands of timber. The effects of dry and wet deposition, including the effects of acid mists and fogs, are considered, and in particular the effects of SO_2, NO_x, O_3, fluorides and ammonia, acting alone or in combination on:

- the anatomical structures, the mineral uptake and the physiological functions of plants;
- the growth, the productivity and the development of trees and stands of timber or agricultural crops;
- the symbiosis and parasitism phenomena;
- the flora and fauna community structure (diversity).

Third, the effects of air pollution on soils, leading to indirect effects on biocenoses are considered, and in particular:

- the effects of air pollution on the physico-chemical status of soils in terms of their nature and their characteristics;
- the effects on the enzymatic activities and microbiological processes in soils;
- the consequences of changes induced by air pollution of soils on anatomical structures, physiological mechanisms, etc.

The combined effects (synergisms and antagonisms) of the processes mentioned above are also important, e.g. the combined effects of management practices and the consequences of air pollution on biological processes in forest soils.

As far as the air pollution effects on aquatic ecosystems are concerned, the same kind of approach was adopted regarding the functioning of ecosystems as well as the effects on lakes and running waters, with a special emphasis on:

- the effects of wet and dry deposition on the acidity of water, in terms of the type and the characteristics of the catchments;
- the effects on water chemistry.

We adopted the wide ecological approach because we are convinced that it would be impossible to explain the recently observed impairment of ecosystems without taking into account the whole network of factors, biotic or abiotic which interfere within the ecosystem.

2.2.2.2. Achievements

Since this Concerted Action was initiated in March 1984, it is obviously too early to draw any final conclusion either on the state-of-the-art or on what should be the main need in the future. Nevertheless, a first analysis allowed the Commission to determine some basic gaps in the knowledge. As a result, this analysis was also the base for granting a number of research contracts to be implemented by scientific instructions in the Member States.

2.2.3. Contract research: priorities

As far as the assessment of direct air pollution effects on plants is concerned, the majority of studies posing the problem of deriving exposure/response relationships have been previously carried out mainly in closed chambers or in the vicinity of plants characterised by relatively high air pollution levels. These methods do not allow the establishment of reliable relationships consistent with field conditions characterised by rather low air concentrations of the classical pollutants and taking into account the ecological context. This means that there is a basic need to develop an appropriate methodology which could be used on the European scale and which could be used to scientifically establish the link between air pollution and plant damage, if any.

The open-top chambers provide such an opportunity. This methodology, already suitable for the assessment of damage to crop plants and applied with a great deal of success in the United States for more than 10 years, can be applied also to plurіannual plants, especially conifers. A common project dealing with open-top chambers involving not less than 20 scientific team representing most of the Community countries has been designed.

The hypothesis common to all the participating teams is simple; this is to check whether or not ambient concentrations of the main atmospheric pollutants in rural and forestal areas cause detrimental effects to agricultural crops and forest trees. This hypothesis will be tested by means of open-top chambers installed in sites remote from industrial and urban areas. These sites are characterised by relatively low average levels of air pollution (compared with those occurring in areas where visible injury undoubtedly attributable to air pollution). Agriculture crops of forest trees are grown in a set of open-top chambers with filtered atmosphere. Comparison is made with identical agricultural crops or forest trees grown in chambers with unfiltered atmosphere and with identical agriculture crops or forest trees grown nearby, in open field. (This is to assess the so-called "Chamber effect" on the crops).

The project is aimed at verifying the hypothesis at different European sites chosen in such a way that a representative range of ecological as well as air pollution conditions are covered (sites, pollutant exposure, climate conditions, etc.) In view of the necessity to generate comparable data, common experimental protocols will be applied by all participating teams.

With regard to agriculture, the establishment of this reliable exposure/effect relationships, necessary to estimate crop losses in Europe, will be complemented by specific research concerning the multifactorial effect of air pollution on plant production, product quality and plant metabolism. The special issue of the interference between air pollution effect and other biotic and abiotic stress (pests, meteorological events, etc.) will also be dealt with. With regard to the forest, at the interface between atmospheric chemistry and biological assimilation of pollutants, many aspects of deposition, especially dry deposition are poorly understood, in particular the influence of the roughness of various surfaces, the formation of pollutants concentrations gradients within the canopies, the influence of the micrometeorological factors which determine these gradients, the influence of the vegetation itself, the various forms under which the "interception-deposition" mechanisms can occur and finally the role of natural substances released by trees themselves (e.g. natural hydrocarbons) which probably play a role in the air chemistry of forests.

As already stated, figures on dry deposition in forest are very sparse, even for some important phytotoxic compounds as ammonium, ozone, etc. and as a result the effective doses are to a great extent unknown.

Referring, for instance, to the "ammonium hypothesis" recently recalled by NIHLGARD as being a plausible hypothesis to explain forest dieback, we have to recognise with the author, that direct uptake of dissolved ammonium as well as gaseous ammonia through the leaves is currently difficult to estimate, but it is likely that this uptake could play an important role in some areas. Similar comments could be made with regards to photooxidants.

Knowledge of the exposure, of its duration and of its frequences of occurrence should be considered as a pre-requisite to get a sufficient knowledge of the quantitative and qualitative dose to which plant might be subjected in their natural environment.

On the other hand, important gaps remaining in the area of the chemical phenomena which occur on biological surfaces, including leaves and barks, should be filled in order to get a better understanding of the first steps of mechanisms inducing direct damages or also leading perhaps to indirect damage via the important phenomena of crown leaching, throughfall and stemflow. Furthermore, the same comments could be made with regard to the physico-chemical reactions which take place in the leaves and involving air pollutants. Very little is known about the chemical reactions occurring on the leaves and into the leaves, even if scientists have some evidence of the formation of phytotoxic secondary compounds, as for example nitrosamines into the leaves or other toxic compounds on the leaves, perhaps washed down afterwards and transported to the rhizosphere via the stemflow and the throughfall mechanisms.

On the other hand, although it is unlikely that "acid rain" in the strict sense with ph above 3.3 causes direct damage to vegetation, since it has been known for a long time that foliar necrosis only occurs with lower ph values (rain characterised with such a degree of acidity is a rather rare event in Western Europe), the possible synergistic effects of acid rain or acid fog and mist and gaseous pollutants have to be considered, especially in mountains where acid fog events and high ozone concentrations alternate very often.

As a result, in addition of the direct effect of photooxidants on the physiological and biochemical functions of leaves, foliar leaching plays a role which is likely to be important. But so far, the consequences of this process on plants health have not been sufficiently investigated.

As far as the so-called indirect effects, through the soil, are concerned, acidification of soil, under some circumstances has been known for a long time. Some consequences of this acidification like mobilisation of phytotoxic metals, in particular aluminium, and leaching down of nutrients have also been highlighted to a large extent. In sensitive soils, e.g. mineral soils with low buffering capacity, acid deposition can lead to a reduction of the exchange capacity. Nevertheless, the geographical extent of these critical situations and the consequences for plant growth and diversity are not well known. In particular, the link between the impairment of the exchange capacity and the forest productivity would merit more attention in the short and the long term. On the other hand, the sources of acidification in forest soils are numerous. Sometimes, the anthropogenic inputs are minor when compared to the internal acid production. The relative importance of these different sources are subject to discussion and very poorly understood.

Finally, the consequences, for trees and timber stands of some modifications occurring at the rhizosphere level such as:

- the perturbation of microflora and microfauna;
- the over input of nitrogen or heavy metals;
- the long-term acidification of the upper layers;

should be carefully investigated in a range of representative ecosystems thought to be more or less susceptible to these modifications.

There are some of the main gaps which have been identified so far and for which research contracts have already been, or will be, negotiated.

3. CONCLUSIONS

In conclusions, it seems difficult to attribute the impairment of terrestrial ecosystems recently observed only to air pollution. A complex network of causes might be involved, including:

- some meteorological events;
- long term climatic episodes;
- pests and viruses acting as predisposing or secondary agents;
- forestry practices including former forestry practices like grazing or litter removal which are now abandoned but with possible remaining detrimental consequences up to date difficult to investigate.

The main point is probably to assess the relative importance of these factors, which are probably different from one situation to another. For example, air pollution should be regarded as a key factor. A direct experimental approach is required to check this hypothesis, at least with regard to the direct effects. This direct experimental approach should take into account particularly episodic peak emissions and episodic extreme climatic fluctuations. In particular it should verify the photooxidants hypothesis which is according to the experts, based only on circumstantial evidence at the present time.

Not only the deposition of classical pollutants like SO_2, NO_x and ozone should be quantified in forests but also other components like organic compounds or heavy metals. From this accurate knowledge of the chemical environment of the ecosystem with regard to the air, but also to the rhizosphere as well as from the knowledge of the long-term trends, a study of possible modifications of ecological balances could be undertaken with the final objective of assessing the consequences of these changes for the structure and the pattern of the ecosystems.

It is obvious that such a wide ecological approach cannot be fully developed in the framework of a two-year period (1984-1985). The on-going programme should therefore be considered as the first step towards the establishment of a real co-ordinated programme which could provide the scientifical basis for a complete explanation of the currently observed impairment of terrestrial ecosystems.

So far, more than one hundred shared-cost contracts have been negotiated with the scientifical institutions of the Member States, within the current programme.

A new call for proposal will be published in the Official Journal of the Communities as soon as we get the final decision of the Council of Ministers regarding the Fourth Environmental Research and Development Programme. This decision is expected at the very beginning of 1986.

"ATMOSPHERIC EMISSIONS AND THEIR EFFECTS ON THE ENVIRONMENT IN EUROPE WITH PARTICULAR REFERENCE TO THE ROLE OF HYDROCARBONS"

"THE DEVELOPMENT OF OZONE IN THE EUROPEAN ATMOSPHERE AND ITS IMPLICATION FOR THE ENVIRONMENT"

Joint presentation by

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THE DEVELOPMENT OF OZONE IN THE EUROPEAN ATMOSPHERE AND ITS IMPLICATIONS FOR THE ENVIRONMENT

PART I: Ir. L. Brader

About two years ago, Shell started to examine the so-called 'Acid Rain' problem, principally because of the wide-ranging statements that appeared in the various forms of literature. At that time soil acidification and forest damage were closed linked - you may recall the Ullrich theory. Matters have considerably changed, and this morning we have heard that over a hundred hypotheses have now emerged to explain forest damage. Nevertheless, the collection of the available information has been a useful exercise. My presence here is directed at conveying some overall impressions from the study.

Having listened to what has already been said I would agree that we are dealing with a problem that involves a very complex ecosystem. Plant roots extract from the soil water and nutrients; their tops also interact with the air and light above, and a multitude of factors may in one way or another affect their growth. Ecologists know that ecological studies are very complex and quantitative results are very difficult to obtain.

One conclusion from our study was that SO_x-related 'acid rain' alone did not explain all the reported damage on forests. For example, the match between the regions of reported forest damage and heavy acid sulphur deposition did not correlate sufficiently well, as has already been noted by previous speakers. Moreover, in recent years sulphur (SO_2) emissions have been on the decrease. The symptoms noted showed similarity to ozone damage published in earlier literature, and as a result we examined the possible implications of NO_x and hydrocarbon emission in particular with regard to the photochemical production of ozone in the atmosphere.

With regard to damage to buildings and the acidification of lakes, considerable information exists, and it is well accepted that SO_2 emissions are significant cause of deterioration. Lake acidification occurs in particular in regions where the soil associated with catchment areas cannot neutralise the deposited acidity. On the subject of agricultural crops, there has not been much discussion, although damage most probably occurs. Much work has been carried out to arrive at dose/effect relationships but it is difficult to be accurate if only because of the variations in crop sensitivity. However, ambient SO_x levels (e.g. in Central Europe) and ozone levels (greater than 100 $\mu g/m^3$) that can cause damage, have been reported. In the USA an estimate, reported by the National Crop Loss Assessment Network, of about 5% damage to agricultural crops is given.

With regard to forests much has already been said. Whether atmospheric pollution is a major cause or not, the ambient levels of SO_x and ozone are sufficiently high to explain an effect on forest stands. A multitude of factors can come into play to lead to their ultimate destruction when atmospheric pollution is combined with draught, soil acidity, lack of magnesium, aluminium toxicity and other factors. Of course, as forest damage develops there is further soil erosion, water retention capacity is reduced and other processes that further enhance the degradation process can ensue.

The last point I wish to touch on in this rather brief overview of the Shell study concerns the impact of pollutants when they occur together, e.g. SO_x and NO_x. If a plant is already affected by a source of stress, for example due to increased soil acidity, its response to the presence of additional stresses can, as shown by experiments, occur at reduced concentrations. As a result it becomes even more difficult to be specific about the levels that actually lead to damage. Research will certainly continue but whether the unequivocal clear cut relationships we seek will emerge is doubtful.

Having expressed some of the views that arise from our survey study I would now like to invite Dr. Briffa to continue with a description of our study on ozone in Europe.

PART II: Dr. F.E.J. Briffa

What I am about to say is fully described in the report (1) made available to this meeting. I also wish to acknowledge the significant contributions (2) made by my colleagues Dr. Selby, Dr. van Dop, and J. den Tonkelaar.

I intended to describe the study we carried out concerning photo-oxidants in the atmosphere and their development. When we were reviewing the subject of atmospheric pollutants/acid rain, the one area that needed a little bit more attention, especially if we wished to have an overview, was that associated with the development of photo-oxidants over Europe. By comparison quite a lot of work has been done in connection with the sulphur (SO_x) emissions and their long-range transport.

First I wish to explain the way the study was organised from a technical point of view. We needed NO_x and hydrocarbon (VOC) emission data, meteorological information and the results of modelling the atmospheric chemistry to examine their significance.

As we have heard this morning, the presence of hydrocarbons in the atmosphere assists the formation of more ozone and, as can be seen from the report, in a polluted atmosphere the equilibrium that exists between NO_2, NO and ozone is for practical purposes a simple one. The presence of hydrocarbons leads to more NO being oxidised to NO_2 with a consequent increase in the level of ozone. In reality it is, of course, also important to appreciate the time scales associated with the reaction leading to ozone, since the atmosphere is in practice a dynamic system.

The sources of our emission data are important, since the inevitably have a bearing on how valid the kind of results we've obtained are. For information on nitrogen oxides, we in fact were very grateful to get data from the Norwegian Institute for Air Research, who carried out an exercise to fill in on the NO_x emission data that was not available. The data for the volatile organic compounds was obtained from an OECD report. The information needed on VOCs from Eastern European countries was estimated (1,2). The meteorological data was provided by the Royal Netherlands Meteorological Institute who surveyed the weather patterns starting from 1976 up to 1983 (excluding 1977) with emphasis on the yearly interval between May to September, because that is the growing season, as well as being when you can expect to get good weather. Within the periods of what are described as anticyclonic, weather air trajectories were computed to meet very specific requirements to enable us to carry out the photochemical modelling. The remaining requirement was the use of a photochemical model which was developed at our own Shell Research laboratories (1,2).

The photochemical model was developed over a period of time and tested against published data derived from smog chamber studies. All the emission data was represented on a 150 x 150 km grid on the

European map. Each grid area had an average emission rate whether it was for VOCs or NO_x (Fig. 1). The numbers (Fig. 2) tell you what the VOCs to NO_x ratio for the different countries in Europe is approximately equal to. The numbers all hunt around the figure of 1.4.

With regard to the meteorological study, a considerable amount of work was done and will be published. The material presented here is a very brief summary. The table (Table 1) lists the more than 3 day anticyclonic periods. You can see of course why 1976 was such a good summer, we had some long sunny periods. The periods for the years examined amounted to a total of 250 days and if you consider the total number of days covered by May to September, that amounts to something like 25% of the time. Or to put it another way we certainly had a lot of good weather for producing ozone. This morning you heard Dr. van Dop explain that the generation of air trajectories for a given destination is not quite so simple and depends on the altitude of the atmosphere at which you decide to track an air path. At different altitudes the air path can be different and we were backtracking the airpath for 3 days. We did this by computing the trajectories at three different altitudes and chose trajectories where there was good correlation between airpaths at different altitudes. We picked on 5 destinations. Freiburg, and Nancy, because they're close to each other and at the time we started the study the reporting from the Black Forest region suggested more damage than at Nancy. It seemed interesting to see what differences the calculations might show up. Soltau, because it is in an agricultural area. De Bilt (The Netherlands) was chosen because there was local ozone data and is the location of the Meteorological Institute. Soissons was an additional location we picked on in France.

Now to come back to the trajectories, and to make the point about the need to be careful with respect to altitude and their choice. Trajectories calculated at three altitudes, for a given destination, show that air can originate from three very different locations. We restricted ourselves to those situations where the three trajectories were closely correlated. In this way uncertainty about the emissions that should be associated with a 3-day trajectory reaching a destination was minimised. In the course of the study we found ourselves doing a lot of other things, like examing the windroses associated with the different destinations for the predominance of wind directions.

You may notice that the Fig. 3 identifies an arrival time of 15.00 hours GMT. The reason for choosing a particular time is related to the development of ozone in the course of the day. Ozone tends to peak at between 14.00 to 16.00 hours (Fig. 4). Another reason is associated with the time when the depth of the atmospheric mixed layer is at a maximum.

The figures shown represent the three-day development of ozone concentrations along an air trajectory. The bars shown indicate the end of each 24 hours. The ozone levels shown are in parts per billions, and to make the transition to micrograms per cubic metre it is necessary to multiply by 2, approximately. The trajectory end values are generally above 50 ppb or 100 $\mu g/m^3$.

(1) Selby, K., "Computer Calculations of Ozone Formation during Anticyclonic Weather Episodes in Europe" Shell Research Ltd., 1985.

(2) Van Dop, H., den Tonkelaar, J.F., and Briffa, F.E.J., "A Modelling Study of Atmospheric Transport and Photochemistry in the Mixed Layer During Anticyclonic Episodes in Europe. Part I, Meteorology and Air Trajectories" - to be published.

<u>Fig. 1</u> Estimated hydrocarbon emission field (10^3 tonnes hydrocarbon/annum per 150 km x 150 km grid cell)

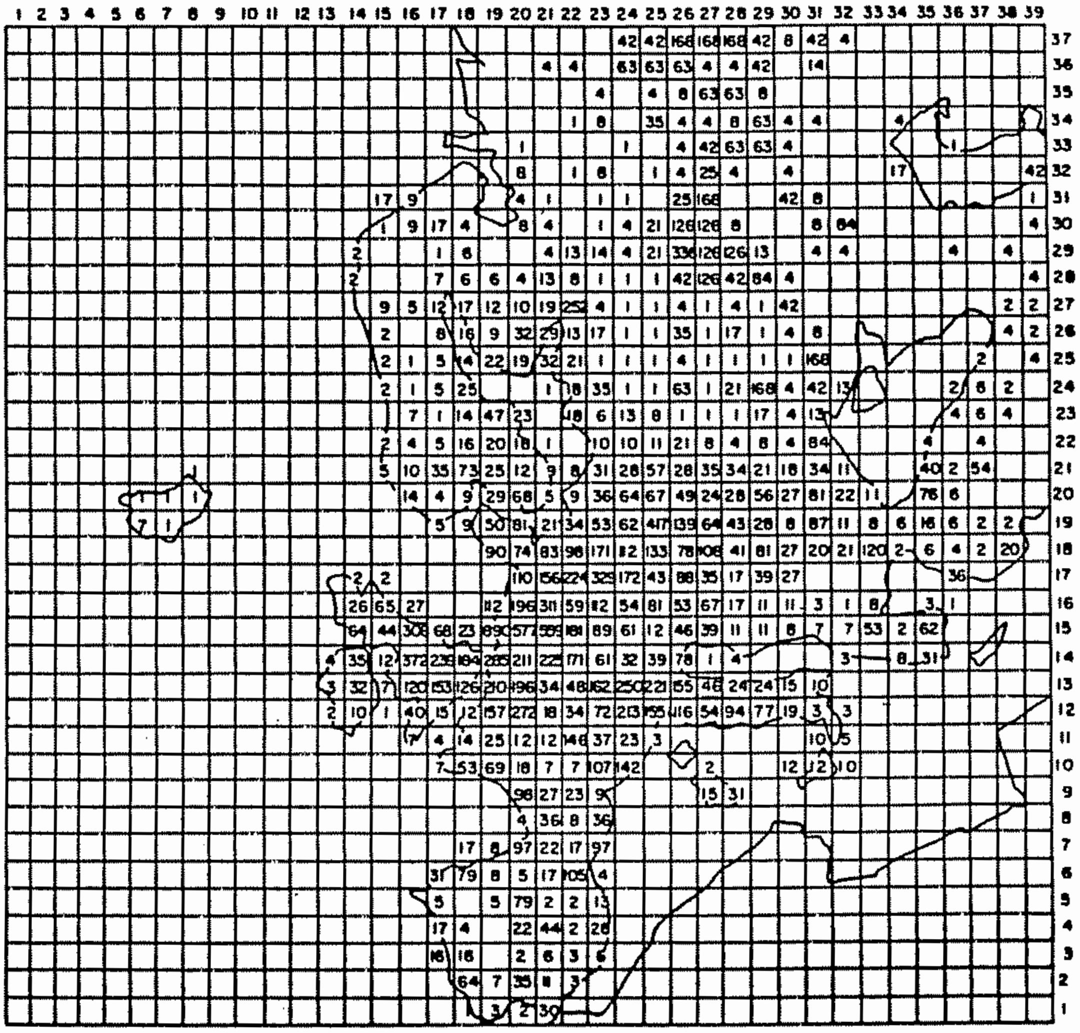


Fig. 2 Hydrocarbon/NO_x emission ratios for Western European countries

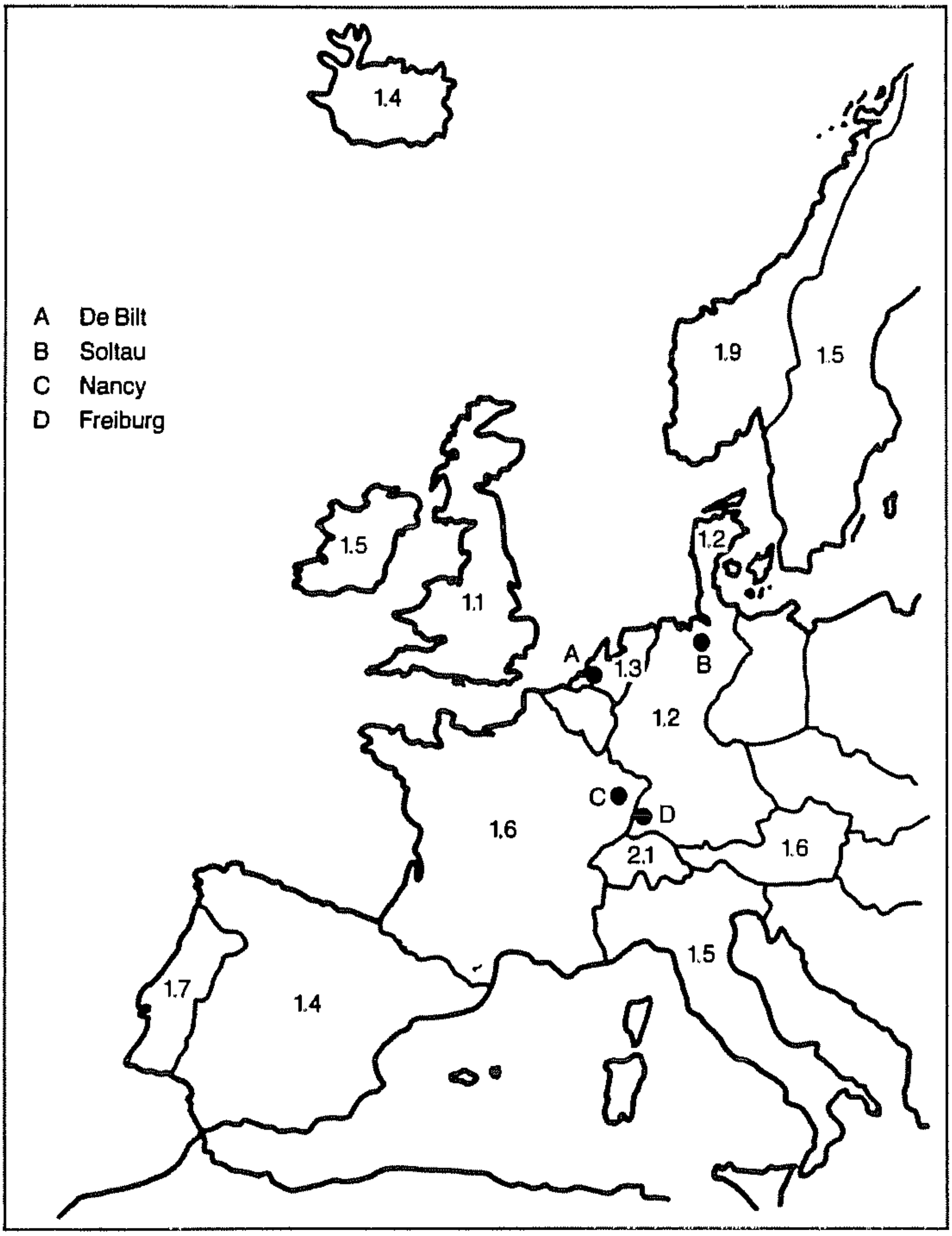


Table 1 Duration (in days) of fair weather periods during the summers of 1976-1983 (the number of 3-day episodes selected from each period is indicated in parenthesis)

1976	5(0)	10(1)	30(3)	24(2)	69(6)
1978	11(1)	9(1)	10(1)		30(3)
1979	4(0)	5(0)	5(0)	5(1)	19(1)
1980	5(0)	11(1)	4(0)	13(1)	33(2)
1981	5(1)	6(1)			11(2)
1982	6(0)	13(2)	8(1)	13(2)	40(5)
1983	19(2)	11(1)	18(3)		48(6)
Total					250(25)

Fig. 3 15.00 h ozone concentrations along 3-day air trajectories. Episode: 25-28 June 1976; 850 mbar trajectories

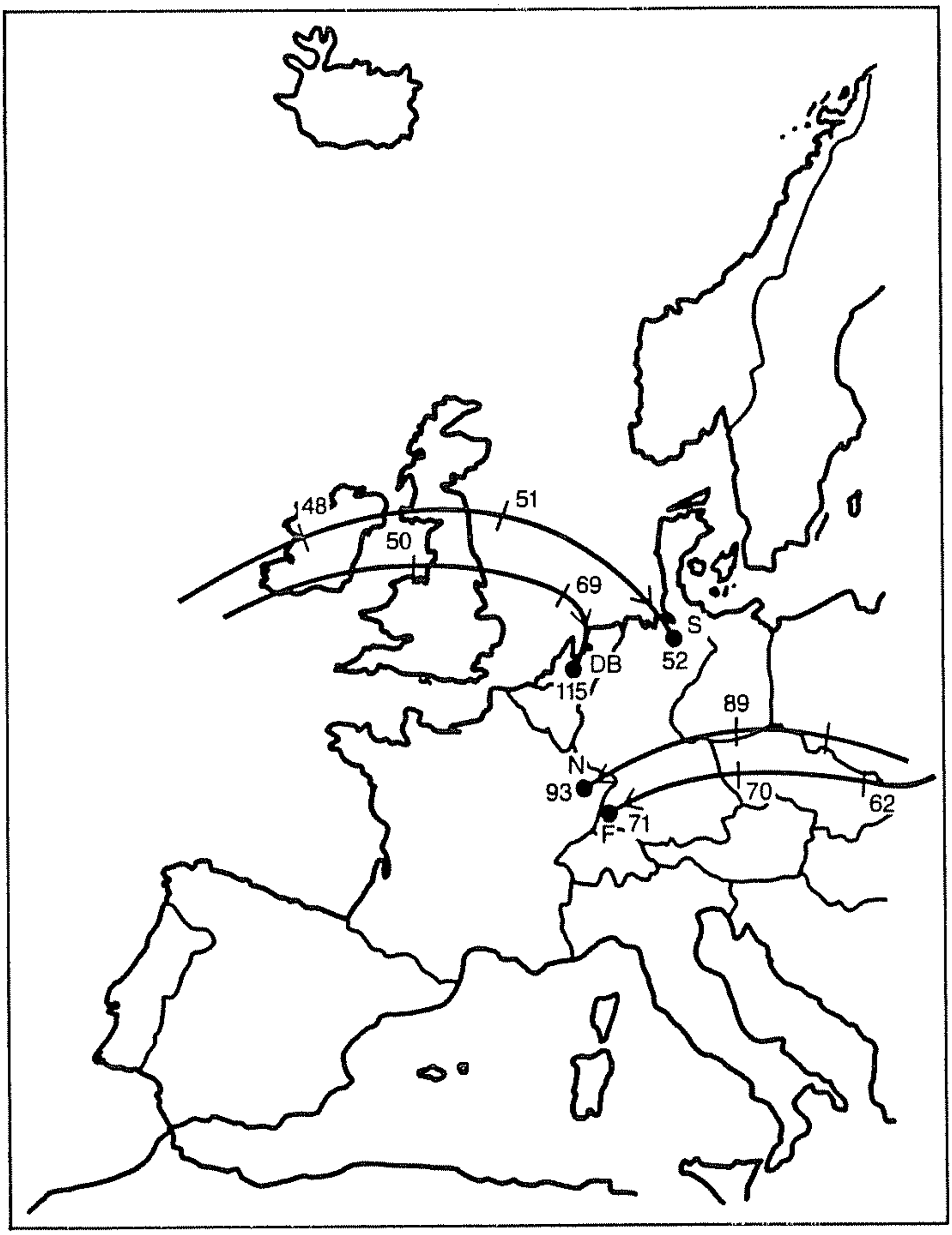


Fig. 4 Typical diurnal variation of O_3, NO and NO_2 concentrations

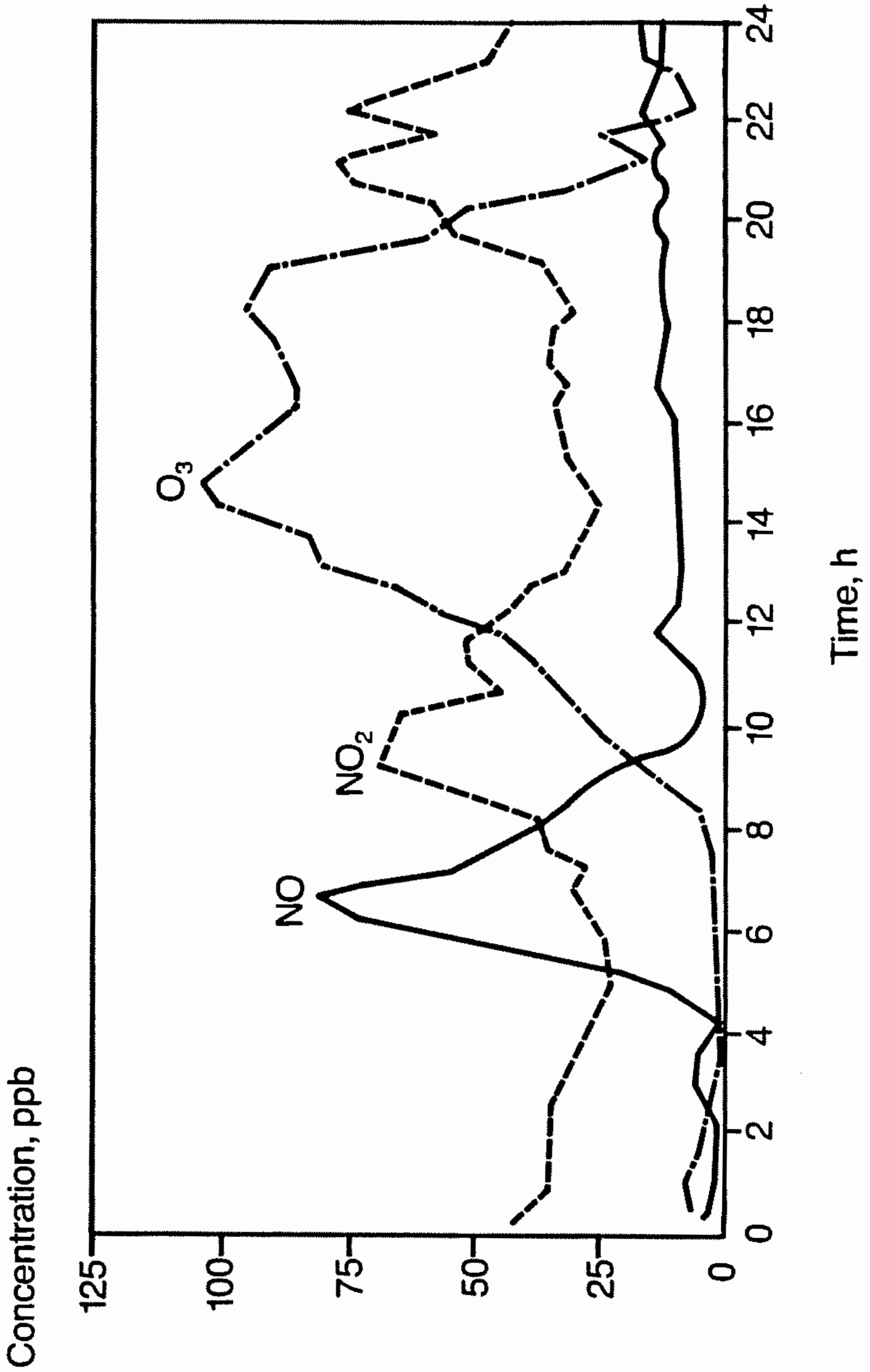


Fig. 5 15.00 h ozone concentrations (ppb) along 3-day air trajectories. Episode: 27-30 June 1978; 850 mbar trajectories

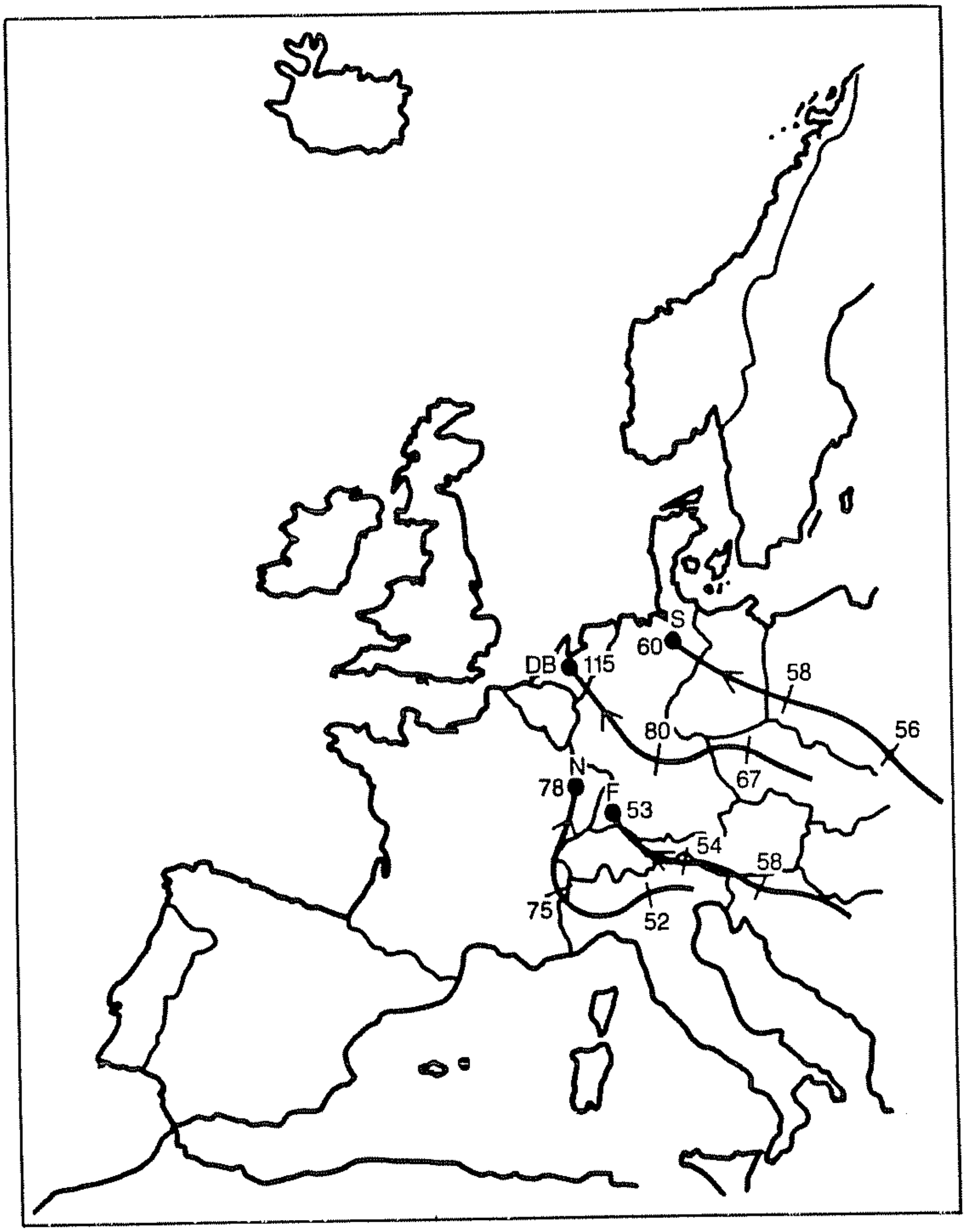


Fig. 6 15.00 h ozone concentrations (ppb) along hypothetical 3-day air trajectories. Destination: De Bilt (numbers in circles are concentrations at destination)

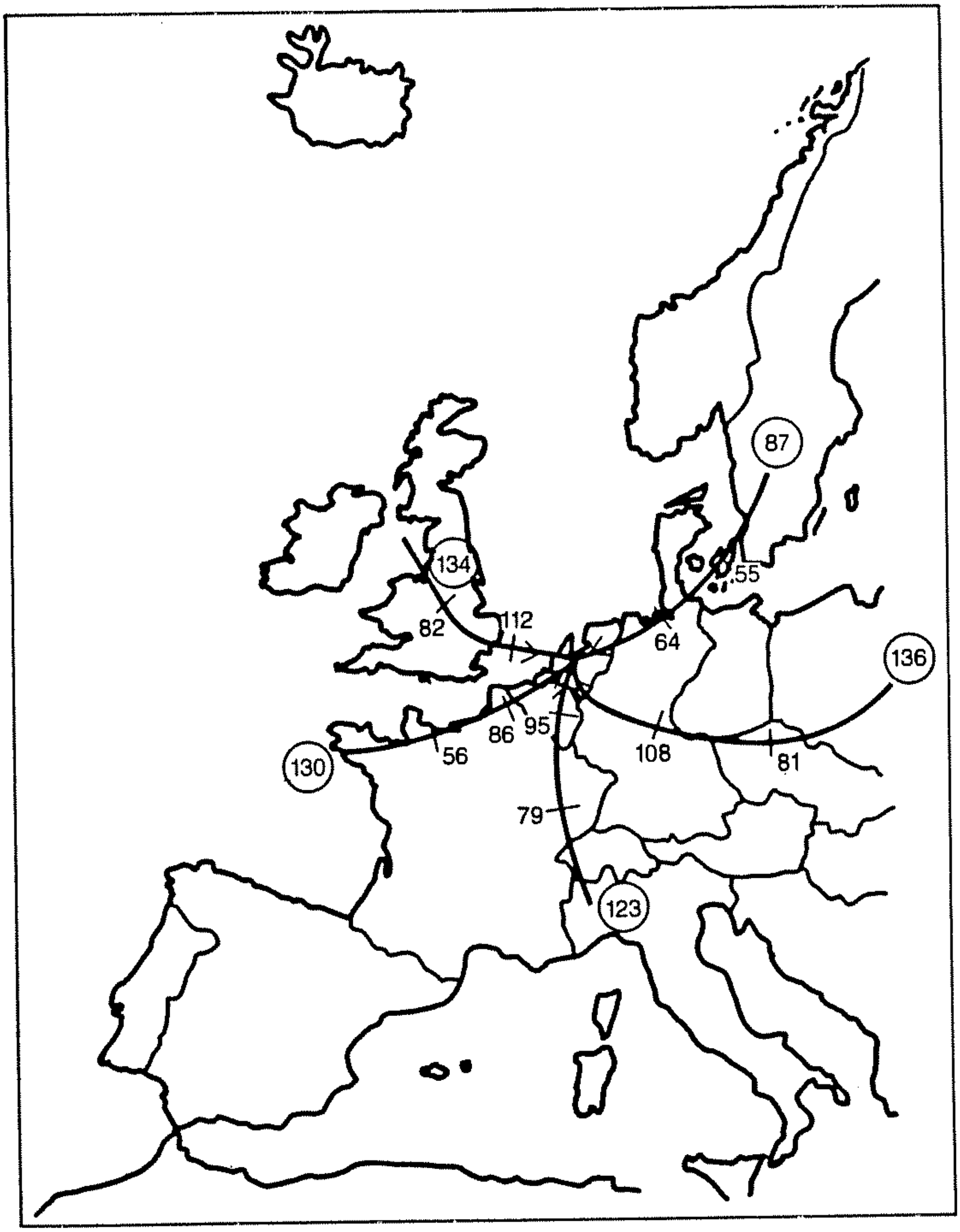


Fig. 7 Relationship between trajectory direction and ozone levels at destination: De Bilt

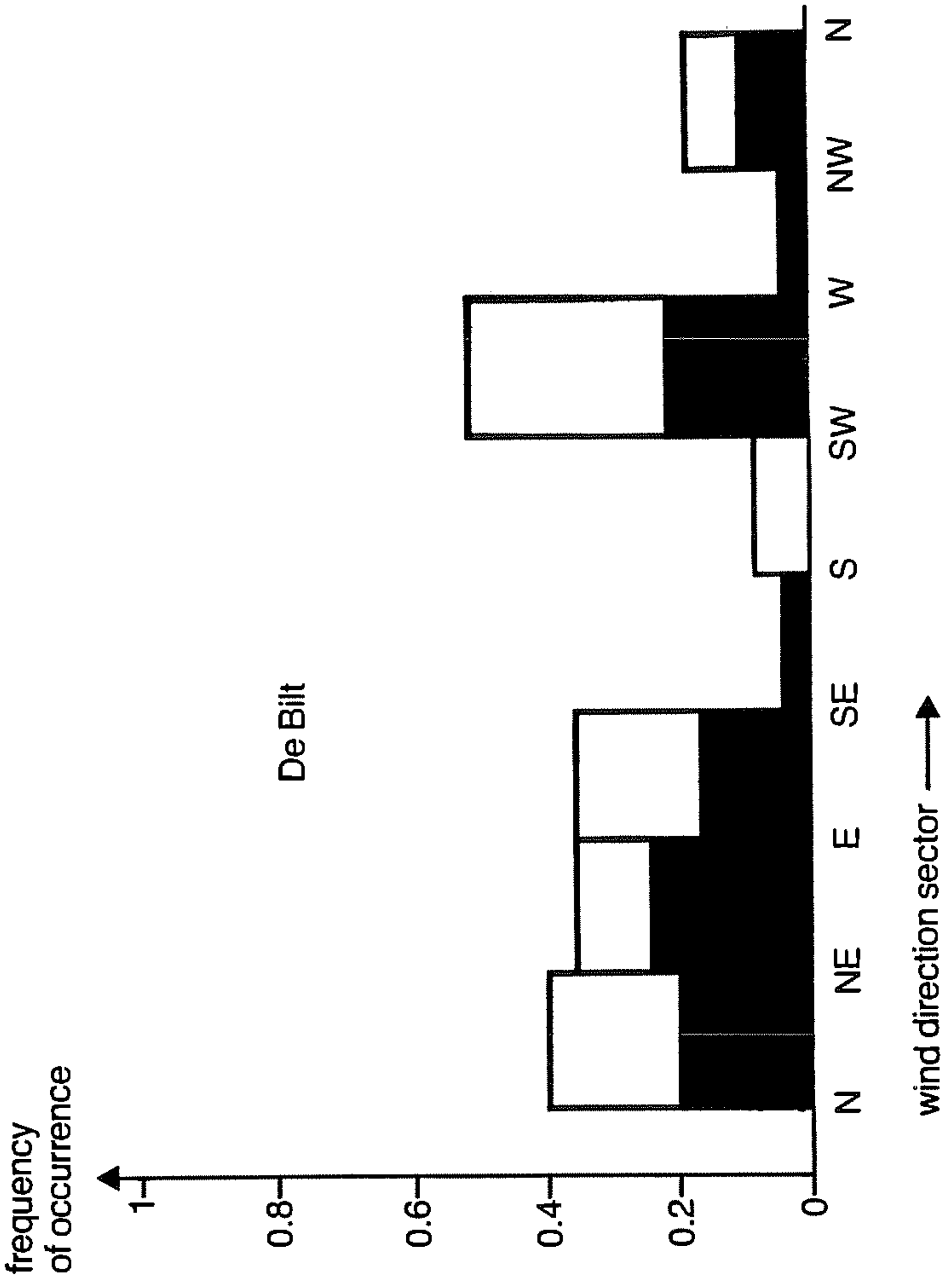
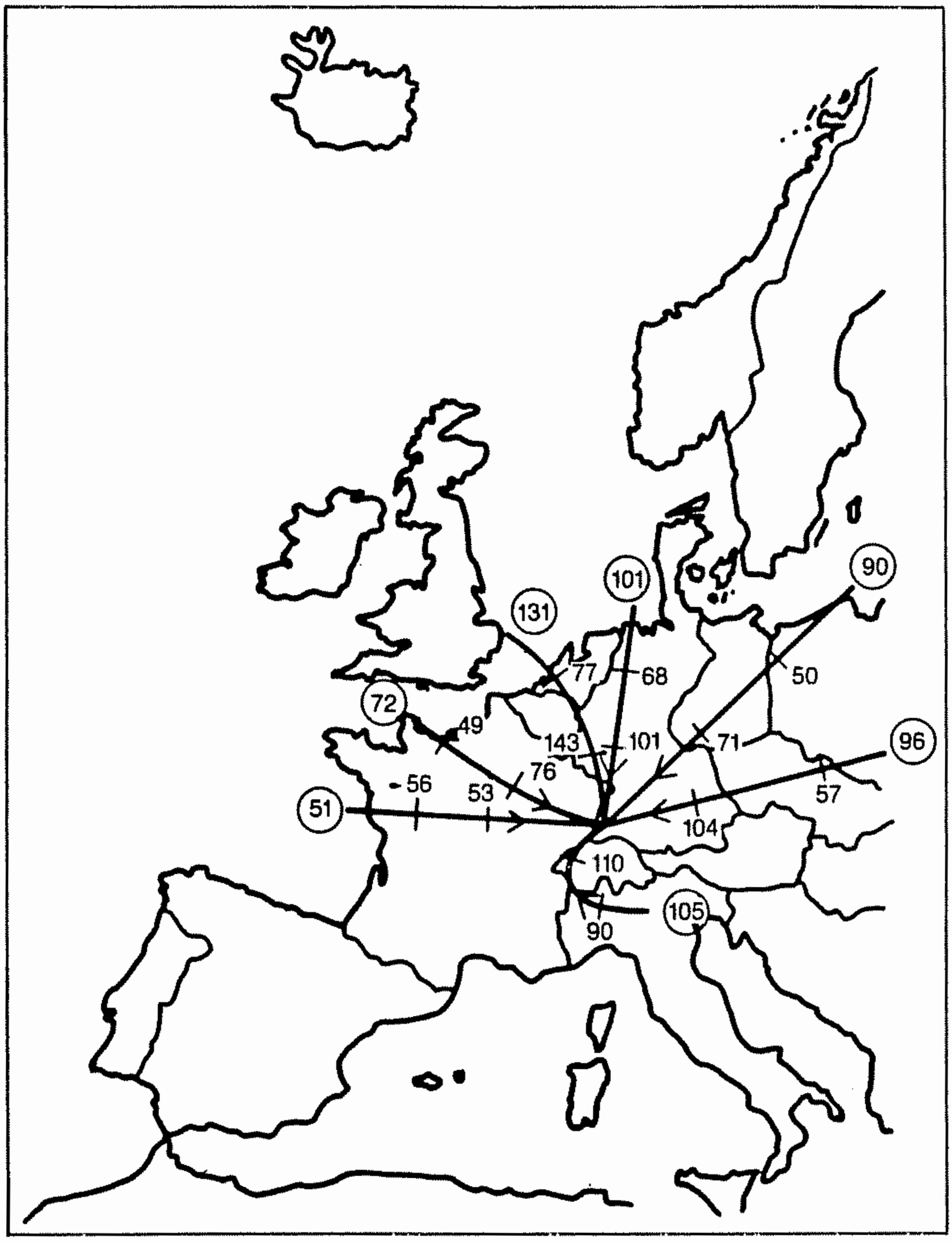


Fig. 8 15.00 h ozone concentrations (ppb) along hypothetical 3-day air trajectories. Destination: Freiburg (numbers in circles are concentrations at destination)



QUESTIONS AND ANSWERS ARISING FROM IR. BRADERS' AND DR. BRIFFA'S PRESENTATION

Question These are predicted values?

Answer These are calculated average values for the mixed layer of the atmosphere, at 1500 hrs.

We did look at reports of available ozone measurements from the various receptor locations but measurements are often near the ground, whereas we calculated an average figure for a height of about one and a half kilometres. One really needs the vertical profile at any particular location to be able to relate measured and calculated data. But by and large the numbers we've generated and the measurement trends over a period of time are compatible. For example, we tend to find that calculated ozone at Soltau was relatively low and when examined against local measurements available then that it was generally also relatively low.

Question I don't understand why you say Soltau is generally low.

Answer The term low is used in a relative sense, e.g., vis-a-vis the sort of level you might expect for example at De Bilt.

The trajectories arriving at Soltau for the episodes that we examined generated on average lower values than at some other receptor locations.

The direction of the air trajectories is an important factor, they vary with location, and are weather dependent. During a particular episode you can get, depending on location, winds from the east or the west. We do not have a general drift from one particular compass direction. It is interesting to look at the way the numbers build up.

The three-day trajectory for Soltau (Fig. 3) shows a level of 48 ppb of ozone is reached after the first 24 hours, and that the value achieved on arrival (3rd day) is not significantly higher (circa 52 ppb). The trajectory for De Bilt, over the same period, similarly reaches 50 ppb after the first 24 hours. However, as the Netherlands is approached the ozone levels increased and on arrival, the third day, reached a value of 115 ppb. The implication is that local emissions in the Netherlands make a significant contribution on the third day. The trajectories reaching Nancy and Freiburg during the same three days arrive from the East and the levels of ozone estimated to be present in the air on arrival are 93 and 71 ppb respectively. The differences in the numbers are again very much a function of the emission picked up by the air as it traverses the terrain along its path. It should be appreciated that having selected the dates the 3-day air paths to a destination are, except for computational error, determined.

Question I have some difficulties with the wind directions. I was always told the wind is coming to Central Europe from the west.

Answer During anticyclonic episodes the wind tends to circulate clockwise (in the Northern hemisphere) around the high pressure region. May I suggest that perhaps you are thinking about the Westerlies.

These air trajectories are computed for selected 3-day episodes during periods of anticyclonic weather.

Question Three special days, so three special trajectories?

Answer No. In our calculations a given destination is associated with one trajectory extending backwards in time over three days of travel. As stated earlier 3-day episodes during anticyclonic periods were chosen for examination. The air trajectory for a different 3-day period could be different and depends on the existing weather pattern. In three days air can travel over a 1,000 km., or depending on weather and location it may circulate with a much shorter range.

Question May I ask whether the reference to Freiburg is to Freiburg in the valley or is it Schauinsland?

Answer The resolution of our geographic grid was a 150 km by 150 km. The city simply identifies the location of a grid area.

Fig. 5 shows another plot for a different 3-day episode and illustrates the development of ozone from South Easterly and Easterly flows. It is interesting to note the changes of direction in the course of travel. The calculated development of ozone concentration is quite interesting. The ozone levels along the trajectories can be seen to reach almost the final value on the first day, or to continue to increase from one day to the next or to show a significant increase on the last day when the trajectory passes over a heavily industrialised area. It is even possible for the ozone level to be less, on the third day, than the value reached on the first day. The interpretation of the changes in calculated ozone levels shown in very much a function of the emission picked up along the route of the trajectory.

We have produced quite a number of these air trajectory ozone levels. Moreover windroses to identify the directional frequency of trajectories over the years during the episodes of high pressure over Europe have also been generated. Fig. 6 illustrates the development of ozone along five hypothetical trajectories. By superimposing the windroses for a particular destination over the hypothetical trajectories it is possible to obtain some insight to the relationship between the trajectory direction and ozone levels at a destination (see Fig. 7).

I should point out that the encircled values actually refer to the final third day value. The diurnal ozone development sequence along the trajectories are: 56, 86, 130; 82, 112, 134; 55, 65, 87; and 81, 108, 136.

Question Will the total concentration then be the sum of within the circles?

Answer A simple addition is not relevant. Each trajectory is associated with three days of travel, and in the case of Fig. 6 for example are hypothetical. However, the encircled third day values when examined against a windrose for the same destination would indicate e.g. how the third day value may be likely to fluctuate over a considerable period of time.

Fig. 8 is a calculation based on Freiburg. You can see, for example, that air coming down from the North West builds up to a maximum of 77 ppb, on the first day, increases to a maximum of 143 ppb, on the second day and then drops to 131 ppb, on the third day of arrival. The diurnal increase or decrease along a selected trajectory is very much a reflection of the emissions pick-up along the route of the trajectory. By combining these calculated results with the windroses over a period of years it is clearly possible to obtain some indication of the importance of en route emissions vis-a-vis a given destination.

The calculations also show that ozone does not necessarily increase from one day to the next. The results suggest that a build-up in maximum ozone level can be attributed to emission pick-up as a trajectory passes over an industrial region. Equally, the passage of an air trajectory over forested areas can lead to a decrease in the maximum ozone concentration. In the course of our calculations we tested out the extent to which the ozone level on a given day was influenced by local emission as opposed to the level of pollutants already present in the air from the previous day. And the feeling is that both are important.

Question Does that mean in other words that pollution abatement will be efficient in this case?

Answer The question is too broad. I'm simply reflecting the results of some calculations. The approach described demonstrates some ideas and would need to be developed to cover a much wider spread of locations in Europe. After all, we have taken four locations and it's first time we've seen these calculations done over such a span of time. Also, because we worked on the basis of a 150 x 150 km grid and provide ozone averages for quite a height the technique needs refinement. The feeling we have is that the results probably tend to underestimate actual measurements. Moreover, we assumed that the material is well mixed in the air, but as you know that may not be realistic. We do know that there are plumes, associated with cities, with much higher emission concentrations.

Clearly it is necessary to generate basic information on emissions which is on a much finer grid than a 150 km by 150 km. Also I do think that we need more accurate information on Eastern European emissions. The value of the work described is in demonstrating a way of achieving an overview on ozone development in Europe.

Question

Can you show one of these summary charts with the various numbers of ozone. Maybe the Freiburg chart (Fig. 8) is a good example, please. Do I interpret these numbers correctly namely, that the base level of ozone is about 50 ppb, in other words the pick-up from the East Atlantic was a number of say, 48.

Answer

Ideally, clean air is closer to 40 ppb.

Question

Well, that is my point. With respect to Fig. 15 of the report (1), the upper trajectory is 51, 44, 49 ppb. My conclusion is that there is still clean air in Soltau. There is no way to reduce it. It is clean air all the way, and there is no chance to reduce the ozone level by controlling man-made emissions. Now I am a little bit provocative, but on the other chart which I was referring to (Fig. 8), was a trajectory from the Gulf of Biscay going up to Freiburg without any significant change. In other words, there is no significant emission pick-up. Is that the conclusion?

Answer

On the basis of these calculations, and the direction associated with the trajectories you have chosen to highlight, the results do imply relatively clean air.

Question

Is it the right interpretation to say the base level is already so high that the man-made effect, in the rural area, is marginal?

Answer

To understand why the two hypothetical trajectories you refer to lead to low increases in the ozone level it is useful to examine the emission rates of VOCs and NO$_x$ assumed along the route of the trajectories you refer to; they are quite low and, as you say, do not add significantly to the base level.

Question

I think it would be very useful to compare your calculated data with the measured data at Schauinsland in the Southern Black Forest. Schauinsland has been a measuring station for many years and it is situated about in your calculated altitude. In addition to this I would like to mention that daily development of ozone concentrations in urban areas reaches typical peaks in the early afternoon. But in the remote forest areas at higher altitudes there is no such curve, it is a steady concentration which does not show any indication of going down to zero during the night. Relatively high values are kept during the night and they are kept also during winter time.This means daily variation in the forest damage areas in the higher altitudes is totally different from the daily variation of ozone measured in the cities and also the yearly variation is different.

Answer

We have compared the calculated estimates we produced with measurements made in the region of De Bilt here in the Netherlands and we will be publishing the results. The comments of Prof. Zöttl do not surprise me. I would suggest that the constancy in the values measured is probably related to the measurement altitude being above the nighttime inversion height (circa 200m) associated with the well-mixed layer of the atmosphere. As a result the higher layer is decoupled from processes associated with the layer near the ground surface where ozone is destroyed. Our calculated results refer to the time of day when the thickness of the well-mixed layer is approximately 1,500m.

Question Your data would indicate that the background ozone level is about 40 ppb. In the US our studies would indicate averages in the range of 80 to 90 ppb.

Answer It does vary with location and altitude and time of year on the surface of the globe. Increasing the value of the background ozone concentration would tend to increase our calculated estimates.

Question I would just like to comment on some measurement that were made over the area of London about two summers ago. These were measurements made by aircraft flights at an altitude of about 1.5 km above the ground in that region. If I remember rightly, we were examining air coming from a north easterly trajectory over the North Sea containing about 75 parts per billion of ozone. I'm not so sure where the air trajectory originated from, but certainly what we saw was a growth in ozone of about 20 to 30 parts per billion in about three hours travel time following passage over the London area out over the South coast of England, and I think, tie up very well with the kind of increase in ozone that you are predicting. The point is that the measurements were made at an altitude of 1.5 km which is where your trajectory calculation is actually applying to, I assume.

Answer It is the average in that height.

Question I would add that, if you look at the individual measurements which we made at the same time on that day you get a slightly more confused picture. The point I want to make really is that I think the model is probably as good as any other prediction at the present time for ozone. The other point I want to make is I think you have got to be extremely careful when relating this kind of model calculation to ground level measurements. As Prof. Zöttl has pointed out, even within the district of Freiburg you get a completely different view of ozone depending on where you measure it, that is, at hight altitude or in the valley. The ground is a sink for ozone and it influences what you measure.

Answer I fully agree. I would also add that one of the realisations we came to as we progressed through the discipline of the study described, is that the idea of averaging out emissions over a very large area is not an adequate procedure. We also need to know more about lateral mixing, I refer to emission plumes associated with industrial centres, as well as more information on vertical ozone profiles.

Mr. Chairman, Ladies and Gentlemen, I thank you.

6. PANEL DISCUSSION

Question I would like to know what is the ozone concentration of the clean air.

Van Dop The clean air ozone concentration is not a single number. It depends where you are on the surface of the earth, it depends what altitude you are. It also depends on the season. For mid latitude, northern hemisphere, in the summertime, the normal value is about 40 parts per billion. In the springtime, it's often maybe 10 parts per billion higher and in the wintertime it maybe 10 or 20 parts per billion lower.

The range of background concentrations in the northern hemisphere , mid troposphere might range between about 25 and 50 parts per billion.

Question You start from 40 and then you build up along the line until you reach 75 or 80. A three-day episode as you call it, under certain conditions. Are they special conditions? Does this mean that three days average, and how many episodes per year are enough to damage the forests? How can you relate this with the forest damage?

Van Dop The study which was undertaken by Shell has selected a number of sunny days, so, the study is only representative for these particular situations. The total amount of days which occurred in the investigated period was 250 out of approximately 1000. And I think this should be emphasized because 25% of nice summer days is an exception. The normal European situation is that the amount of nice fair weather days is something between 10 and 15%. So we have had in the last 8 years or so fairly nice summers. And we also know now by the results of the Shell study that there is a big correlation between high ozone levels, or higher than background ozone levels, and fair weather episodes. Apart from the fact that we have had much more fair weather than based on the climatic average, we also have had much more ozone than based on the climatic average.

Question Does this relate to the forest damage?
Is there anything we can say about the damage to crops due to ozone in terms of duration and concentration?

Brader It's very difficult, as I tried to say at the very beginning, to draw an exact quantitative relationship about certain factors of the damage occurring. On the basis of a whole lot of fumigation experiments, let's say where they have enriched the air with a certain level of ozone or with filter experiments where they have cleaned up the air. The conclusion is for certain crops species, and for trees some experiments have been done too, that if you have, and I give about an approximate level, if you have, let's say for a six week fumigation period, an average level of 7 hours a day above 100 micrograms, you can get significant damage. That means you see a significant growth destruction in that crop compared to another crop treated with the background level. Now how that exactly relates to the amount of forest damage seen, nobody can say. It can only prove that if you have a certain level, and if your level would be 150, you would already have damage in, let's say, about three weeks time or a shorter duration. So it's all a relation between quantity, time and level of ozone. We try to demonstrate that there is a definitely level, which is rather low in fact, which is only a little above the background level, which can be damaging. And this is very significant where one gets the feeling that ozone in some way or other is effecting the forests. I'm not saying that it is totally destroying the forests. I fully agree with Professor Zöttl. It's a complex of factors and it's maybe a chicken and egg situation: which was first, the ozone which started damaging, then the leaching of nutrients, or perhaps it's the combination with the acidity already weakening the tree, which again, if you have another combination of factors, I'm convinced that at a lower level of a shorter duration than even the 7 hours a day I referred to can already be damaging. But there is a strong indication, let's say it that way, and I doubt if you ever will have a quantitative proof that ozone reaches levels as indicated which can be damaging. That's the way I want to explain it.

Panel Chairman — I think Prof. Zöttl would like to add something.

Prof. Zöttl. — I would like to underline your comments. Ozone reaches levels which can be damaging and if we ask for how many percent the growth reduction would be, first we should distinguish between annual crops and forest stands. In US agriculture or horticulture respectively, they calculate with ozone damage up to about 20 percent as a very rough figure. This is already difficult to express if it is in citrus cultures because these are longer-living trees. And it is more difficult in forests where you have a more complex situation. The yearly increment of a tree depends highly upon the site's specific climatic conditions in this year. And if you have damaged trees which might have lower current increment it is very difficult to compare this lower increment with the non-damaged situation. In the long run you can determine how many trees are really dying. But here again you run into difficulties because mostly they will not die only by the effect of an air pollutant, at least not if the level is medium. Even if it is very high which is the case where you have SO_2 at high concentrations, you may have contributing factors like bark beetle, weather conditions and so on. Even in the Erzgebirge,Tchechoslovakia, where you have a long-term average of SO_2 concentration in the air of 120 microgram or more and peaks up to 2000 microgram, the Tchech colleagues say that the dying of the trees is additionally influenced by extreme climatic situations. Even there! And much more we must think about this if we have only a medium level of the pollutant.

Question — I would like to ask Prof. Zöttl what percentage does he think of dying forests is due to ozone? What do you believe is really due to ozone damage? How much of the German or the Central European forests? And an other question is: What do we know about ozone levels in other parts of the world, not in the States, not in Europe, but let's say in the Tropics? Tropical forests, Brazil? Is there only the normal average ozone level? Or is there a higher level? What do we know about that?

Prof Zöttl There is a certain development of the beliefs about the possible causes of forest decline. First, most have been concerned with acid rain and soil acidification and toxic aluminium or heavy metals. Then it came out that the so-called aluminium toxicity is more an antagonism which reduces uptake of magnesium and calcium. Later on the direct impact onto the foliage, the crown of the trees, has been considered with special reference to ozone. I look at this more critically since I have studied the forest damage in the San Bernardino Mountains in California and since I've been with Californian specialists in the Black Forest. In the last two years it has become evident that nutrient deficiencies are involved in many widespread damage types. And I think I have given a few examples of what we can do against this by application of fertilizers. Talking about ozone levels, in Germany now a quite dense network of measuring stations exists. In the United States we have less monitoring stations, at least in relation to the larger area. But there are very few records of data going back more than several years. Therefore we do not know enough how ozone levels have developed. This applies also to the Appalachian Mountains (Eastern US) where we see quite heavy destructions of red spruce forests and balsam and Frazer fir. Due to what? I do not know. But I'm sure that there are biotic factors very much involved.

Question A further question to Professor Zöttl about possible causes. He refers to the inciting factor. Some inciting factor which would be fairly widespread could have been simply climate which could have effected, for example, the soil moisture and linked with this nutrient findings which would have been fairly widespread and,as we've heard,Europe has had a sequence of fairly good summers. If one extends that could one find some correlation with longer-term history in terms of climatic changes and effects on forestry?

Prof. Zöttl Temperature and rainfall are easily measured and we know a lot about the influence of dry years to tree growth. Certainly weather conditions are contributing factors. But if you look at the German Federal Republic and the spread-out of certain symptoms in relation to the weather conditions than you will see remarkable differences between northern and southern Germany.

Question You have pointed to the many uncertainties related to the forest damage and also clearly indicated what makes these forest damages new in relation to what happened before. What also seems to have come out is the deficiencies in the soil. During the break, you mentioned that there is a lot of experience already in large-scale fertilizing of forests. And that one is now started on a large scale but in certain areas with adding magnesium, sulphate or potassium. If one looks at it now from the economy as a whole and one tries to draw conclusions from this, would you recommend that one now tries to fertilize by adding these minerals which are lacking and that industry concentrates on research? To put it in an other way: what would be your wish, realistic wish, which you could put forward to industry in connection with these damages?

Prof. Zöttl Forests fertilization is nothing new. In Germany there is about 80 years experience in forest fertilization. Still, many foresters don't like it. Because it's a little bit against the tradition which was very succesful with selection of the right species planting it or growing it at the right site. And believing that the demand of trees for nutrients should be relatively low. But in the 50's it was shown clearly that there many sites which due to their geological history, are really poor in nutrients, e.g. glacial outwash, sediments leached long time, which did not offer enough enough potassium, magnesium, or acid soils which did fix phosphate in insoluble form. It was also economically succesful when forest fertilization became a common method in silvicultural practice. Nitrogen fertilization was very successful in the 60's in old stands where only very reduced reserves of nitrogen were present. In the 70's, due to different reasons, forest fertilisation activities decreased in Germany. Then 'Waldsterben' began. Then the discussion about forest soil fertility started again. Now a new wave of fertilization is coming. Baden-Württemberg is spending a few million marks within two or three years for fertilization of the State forests. Private forest owners can apply for 70% subsidies of the price of fertilizer which they want to apply against 'Waldsterben'. As a scientist I must say it is a matter of fact that we have large areas of forest soils which do not supply enough nutrients to maintain a stable and vital forest ecosystem. Therefore, it is necessary and it is technically and economically possible to improve this situation. And if you look to other countries where there is a higher need for wood production and where you have intensively managed forest stands, fertilization is a common method and foresters know it and they do it and trees are happy. I am absolutely convinced that we must come back to a situation we already had 20 years ago when fertilization on specific sites was a common method. It is technically possible because most of the forest land has a very good network of forest roads so you easily can go through and blow the fertilizer into the stands. Where it is not possible you can fertilize by helicopter. It is not as expensive as you might think. And before planting a new tree culture you can easily apply the fertilizer before plowing the soil and planting the trees. This means it is technically and economically possible.

Let me now be an "agent provocateur". The fact was mentioned that we have had a higher nitrogen input for a couple of years. It is a common knowledge that until now most of our forest ecosystems were not optimal supplied with nitrogen. This means a rise of nitrogen input raises growth. This is the case in Scandinavia. Certainly if you extrapolate it, then you might come to a point where you reach an over-optimal or toxic level. But if the nitrogen fertilization level due to atmospheric input could be maintained more or less as it is now, this must influence positively the growth of forests where nitrogen reserves are low due to the history of the site. It might lead, at particular sites, to certain imbalances of nutrient supply. But to find this out, is quite easy by needle and soil analysis. And then it is also easy to correct it.

Question I'd like to ask a question to Professor Zöttl. It seems to me that the way one identifies that trees have a problem is by looking at their exteriors and then perhaps examining the needles. But we also hear that, of course, they have to get their nutrients from the ground. And so there is a sort of connection, if you like, in the process of what's in the ground getting up to the needles. And I wonder, isn't there some way of establishing to what extend or for how long a tree has been suffering. Is their no evidence within the tree trunk itself that is has been suffering? Whatever is going on at the pine and the lack of nutrient in the ground. Can't one take a section through these trees and establish they've been under stress for longer maybe than simply the evidence one sees on the exterior because of the yellowing of these needles?

Prof. Zöttl Foliage analysis has a long history. It goes back to the Swedish Professor Lundegard in the 30's. He found out that the central laboratory of the plant, that's the foliage, that's the needle, shows well if the tree is vital or not. For many years foliage analysis has been an excellent tool to look at the nutritional status of trees. If a tree is under stress, it should produce less carbohydrates, it should have a reduced current increment. This you can see from measurements of forest stands, which are deficient in nutrients. But we have measurements of forest growth from other sites and there is no general reduction visible during the time "Waldsterben" began.

Question Is ozone a satifactory measure of the photochemical activity or damage potential of the atmosphere?

Dr. Cox I think that the general consensus is that ozone is the major photochemical pollutant, but I think that we shouldn't forget the other aspects of photochemical pollution that have come to people's notice. The first one that I might mention, which has already been mentioned today, is peroxyacetylnitrate (PAN). I think that early experimental work in the US showed that this species was in fact a plant pathogen and that plant damage could occur to agricultural crops which are exposed to PAN. Another aspect is the eye irritation that has been experienced. And the eye irritation effects certainly can't be reproduced either by ozone or by PAN. I believe that the debate is still going on as to the cause of the agents that are involved in eye irritation. The third thing that I should mention is that the phenomenon that essentially brought photochemical pollution to our attention in the UK was the observation that in the summertime intense haze developed (which came to public attention about 15 years ago). It was discovered to be due to the build-up of sulphate and also nitrate aerosols in the atmosphere. Furthermore, it was found that there was a fairly high correlation of the sulphate aerosol concentration in the atmosphere to ozone during summertime conditions. It depends how you look at visibility but I think that many of us would say that clean air is an amenity that should be valued and it is a factor in making a judgement about control or abatement. I don't know whether anybody else has any comments on that.

McCabe I would agree with Dr. Cox's comments. I think that visibility is certainly a factor these days that has to be addressed - and is being addressed - in the United States, and you have the aerosol chemistry involved, aerosol chemistry and physics and also particulates: sulphates. But with respect to the ozone, in the US the emphasis has been on ozone because our ambient air quality standards are primarily on the basis of adverse human health effects. There has been a link at high concentrations of respiratory problems with high ozone levels especially for asthmathics.

Question According to Otto Kandler of the University of Munich, the new kind of forest damage in Germany can be explained entirely in terms of forest infections. His reasons for this claim are that the kind of forest damage does not correlate with air pollution concentrations. The damage itself is very patchy. And that suggests a biologic agent at work rather than an abiotic agent. And thirdly that the kind of damage that is observed has been observed for a long time and it can be attributed to viruses. Further, I understand that Frentzel, who is based at the University of Hohenheim, finds that every tree in the Black Forest is infected with viruses. How do refute this hypothesis, Professor Zöttl?

Prof. Zöttl Otto Kandler, one of the top physiologists in botany in Germany, is well known for strong and clear criticism of any hypothesis. He is certainly right when he finds a lot of weak points in many of the well-accepted hypotheses about the causes of forest decline. He is also right when he explains that the spread out of symptoms in spatial or temporal pattern looks as if it could be induced by a biotic factor. It really looks like it. And it is also well known that there are a lot of tree diseases caused by viruses, e.g. palm trees. Therefore I think it is really necessary that now an experienced group is doing research work to find out if there are viruses or other micro-organisms involved in the forest decline. The findings until now have been reported recently by Dr. Nienhaus from the University of Bonn who is probably the most experienced man on viruses and their effects on forest trees. He detected years ago a virus as the cause of a growth anomaly in larch. He says now that by analysing many trees at many sites almost everywhere we detect organisms, viruses or something else. But he feels this is mainly because in former years nobody looked for such things. Until now there is no relation, no hint that any new-type forest damage is caused by virus or other primitive micro-organisms. This was the status presented in the VDI-symposium at Goslar in June 1985.

You mention Dr. Frentzel from the University of Hohenheim. I do not know a scientific publication on this subject. He gave an interview to a leading German newspaper which was reported afterwards by international journals like Wall Street Journal, London Financial Times. And he said: I was going through the Black Forest sampling needles from fir, pine, spruce and beech, and everywhere I found viruses in declining trees. Then I went on to France in healthy stands and I didn't find viruses. My comment on this is the following. Two years ago the same author brought up findings that damaged trees have a lower stability of wood due to reduced lignification. But all the intensive research work done by wood technology institutes did not show such changes in the mechanical or chemical properties of wood.

Question I sense that many people maybe are having difficulties reconciling the very convincing nutrient difficiency hypothesis that we have described just today with some of the more traditional causes that have been put forward for tree die-back in Middle Europe. First the acid rain, acid deposition, ozone viruses and so on. I was on the same meeting which Professor Zöttl gave a paper in Goslar. And I came away with a very coherent idea in which the nutrient difficiency aspects were certainly key. I understood from other presentations there that this primary stress was simply exacerbated in some places and on some occasions by ozone which was able through the simultaneous presence of atmospheric acidity to leach out the minerals from the needles of trees that are already growing under very stressful condition on soils that were minerally difficient. And that this in turn was being made worse by the fact that the trees were being planted from stock that was grown in potting compost, in soil that was high in nutrients and hence the trees that were being planted out were being selected for the wrong reasons genetically. And I wondered if I've gone away with the correct impression. I wonder if Professor Zöttl would like to comment.

Zöttl I would like to underline that only part of the actual damage types can be explained by nutrient difficiencies. It may not always be magnesium, it can be potassium, it can be manganese, it can even be calcium. Leaching is a natural process in the element turnover of a forest ecosystem. Especially potassium is concerned because potassium is mainly a component of the cell sap, and can be easily leached. Our speculation is that a certain impact of photo-oxidants and interaction of acid fog might cause a higher leaching rate. Trees can compensate only for those elements which are supplied enough in the soil. And if there is already a low supply of magnesium which is leached at a higher rate from the foliage, the tree might run into a deficient situation. This picture is based on several facts. It has been shown that certain soils are low in nutrient supply. The nutritional status of the trees is deficient, which is demonstrated by needle analysis. If we add a fertiliser we have a positive reaction.

Question I would like to ask a question about methane. The various models and calculations and chemistry normally exclude methane because it is said that it is slowly reacting. But the fact is that there is a lot methane and it has its time to react. Is there anybody who can say anything about the effect of methane which is easily excluded but may well be of importance for the background ozone concentration?

Dr. Cox I think I touched on methane in the atmosphere this morning and indicated actually that it was a rather widespread component of the troposphere. I discussed the fact that it was long-lived. I mentioned the sources but didn't associate any numbers to them. I think actually, of all the hydrocarbons, the methane source numbers are probably the least uncertain. But that doesn't mean to say they're certain. The main sources of methane, in fact, appeared to be natural. One of the things that I didn't mention was the fact that measurements of methane concentration over the recent years have indicated that the gas, the concentration of methane, is actually increasing as a rate of between 1 to 2% per year. And this is an interesting finding and at the present time we don't know exactly why these methane increases are occurring. It could be due to the fact that the source term is increasing, that the methane emissions from natural or indeed man-made agricultural practices may cause an increase in methane emission. It may be that the sink term is decreasing. That is, the OH radical concentration for some reason is decreasing. I think that this is one of the unanswered questions that we need to address. How does it impact on ozone at ground level? My view of the situation is that methane itself is not an important component in ozone production on the time scales that we've been talking about in connection with these photochemical tropospheric models, etc. However, ozone at the ground is influenced by ozone in the background atmosphere. Methane is undoubtedly tied up with ozone sources and sinks in the background troposphere. Changes in the global burden of methane could certainly lead to changes in the ozone concentration in the background troposphere and for that reason I think we really need to know about it because if we're going to be measuring ozone in the surface atmosphere to look for trends as a result for perhaps making certain abatement measures then we want to know if we do see a trend, we want to know whether we can attribute it to those abatement measures or whether some more global phenomenon is taking place that is influencing the ozone that we measured.

Chairman We are just one hour over time, so it is indeed time we closed the session. In the first place, obviously , I would like to thank all the lecturers for their tremendous effort and their tremendous friendliness in the way they have presented their cases. Thank you very much. I certainly hope that with what we have heard we will be able to get our minds straight in the oil industry and see what we in our field can do about the problem of air pollution. Thank you very much again.