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REPORT OF THE FOURTH SESSION OF  
THE CO-ORDINATING COMMITTEE ON  
THE OZONE LAYER



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Co-ordinating Committee  
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Fourth Session

Bilthoven, 11-14 November 1980

REPORT OF THE FOURTH SESSION

No. 80-5747

I. OPENING OF THE MEETING

1. The meeting was opened at 10.00 a.m. on Tuesday, 11 November, 1980, in the offices of the National Institute of Public Health and Environmental Protection, Bilthoven, Netherlands. Mr. H. Cohen, Director-General of the Institute, welcomed the participants and wished the Committee a successful meeting. On introducing the Minister of Public Health and Environmental Protection, Mr. T. Ginjaar, he drew the Committee's attention to the importance attached to the ozone depletion problem by the Government of the Netherlands.
2. Mr. Ginjaar, on behalf of the Netherlands Government welcomed the participants of the Co-ordinating Committee on the Ozone Layer to Bilthoven. He said that the Netherlands Government, as one of the countries producing chlorofluorocarbons and aerosol sprays, could not and would not, ignore its responsibility in this matter. On the one hand, the effects of regulatory steps on the economy would be immediate. On the other, if no such steps were to be taken, major effects on the ozone layer, on human health and the environment, might occur. However, any decision taken should be based on the best available knowledge. In this connexion he referred to the excellent evaluations on all aspects of the ozone layer problem previously made by the Co-ordinating Committee on the Ozone Layer. He noted that exact and indisputable evidence of depletion of the ozone layer could not be given in the near future and it would be unrealistic to expect this. However, what could and should, be asked from the scientific community, was an assessment of the risks of serious ozone depletion by chlorofluorocarbons. He pointed out that the chlorofluorocarbon issue was not only important per se, but could well be considered as a test case for what could be achieved by the pursuance of environmental policies on a global scale. He finished by wishing the Committee positive and fruitful discussions, and a pleasant stay in Bilthoven.
3. On behalf of the Executive Director of UNEP, Mr. R.J. Engelmann, Deputy Director of the Environmental Assessment Service, extended greetings from both the Executive Director of UNEP and the past Chairman of the Co-ordinating Committee on the Ozone Layer, Mr. R.S. Mikhail. He said that he wished to place on record UNEP's deep appreciation of the hospitality of the Government of the Netherlands in offering to host this meeting and paid special tribute to the facilities which had been provided. He drew the Committee's attention to the Provisional Agenda and pointed out that if the meeting were to be successful, the co-operation and goodwill of all participants would be necessary. He invited the Committee to examine the paper "Assessment of Ozone Layer Depletion and its Impacts" UNEP/CCOL/4/5, a paper prepared for the CCOL by a UNEP consultant.
4. He also asked the Committee to note agenda item 5 concerning decision 8/7B of the Governing Council of UNEP regarding chlorofluorocarbons and said that the Committee's views on how best to implement this decision would be solicited. The representative of the European Economic Community at this point suggested that discussion on this item and item 6 be confined to scientific matters.

II.

DOCUMENTATION

- ... 5. A list of documentation before the Committee is reproduced in Annex 1.

III.

AGENDA

6. The following agenda was adopted:
1. Opening of the meeting.
  2. Approval of the agenda.
  3. Presentation by Committee members on their activities relevant to the implementation of the World Plan of Action on the Ozone Layer.
  4. Assessment of stratospheric ozone layer depletion and its impacts.
  5. Decision 8/7B of 29 April 1980 of the Governing Council of UNEP regarding chlorofluorocarbons.
  6. Recommendations for action.
  7. Any other business.
  8. Approval of the report.
  9. Closure of the meeting.

IV.

PARTICIPANTS AT THE MEETING

7. The meeting was attended by experts designated by the following countries, United Nations bodies and specialized agencies, and non-governmental organizations:

Governments: Denmark, France, Germany (Federal Republic of), Italy, Japan, Netherlands, Norway, Sweden, Union of Soviet Socialist Republics, United Kingdom of Great Britain and Northern Ireland and the United States of America.

United Nations bodies and specialized agencies: World Health Organization, World Meteorological Organization and the United Nations Environment Programme.

Intergovernmental Organizations: European Economic Community and Organization for Economic Co-operation and Development.

Non-governmental Organizations: International Council of Scientific Unions and the Chemical Manufacturers' Association.

- ... A full list of the participants is given in Annex 2.

V. REVIEW OF RECENT RESEARCH RESULTS AND ONGOING AND PLANNED PROGRAMMES RELEVANT TO THE WORLD PLAN OF ACTION ON THE OZONE LAYER

... 8. Presentations made by members on these subjects are given in Annex 3.

VI. PRESENT ASSESSMENT OF THE PROBLEM AND RECOMMENDATIONS

9. The background document prepared by a UNEP consultant on this topic was introduced and discussed. It was agreed that, rather than amending this paper, the Committee would proceed, as had been the case in previous years, with the formation of working groups to discuss various aspects of the problem. The reports of the three working groups were considered by the Committee and a consensus was agreed on a current assessment of the problem which appears below.

VII. ASSESSMENT OF OZONE LAYER DEPLETION AND ITS IMPACTS, NOVEMBER 1980

10. Ozone observations : The ultimate test of the ozone depletion theory depends on the detection of a long term decrease in global ozone, which in turn requires a continuous and comprehensive flow of reliable data from the ozone monitoring system. Ground-based measurements form an important element of the system, both on their own account and to provide the ground truth data for satellite based systems, which can provide more comprehensive information on both lateral and vertical ozone distribution. However, good ozone measurements are relatively difficult to make and their interpretation subject to many uncertainties (i.e. long-term instrumental drift) and high natural variability (i.e. synoptic, seasonal, solar, etc.).

11. Total ozone : During the past five years about forty Dobson ozone-spectrophotometers were upgraded and intercompared with either the world standard instrument located at NOAA-Boulder, Colorado, USA or a regional standard instrument. Some of the Dobson instruments have shown differences of more than 7% in their readings from these standards. Although shown by only a few instruments, these differences are disturbing, because they indicate the existence of stations generating data at times with large errors. A well kept Dobson instrument network is hoped to achieve an accuracy of  $\pm 3\%$  and its precision is estimated to be  $\pm 1.5\%$  for calculations of annual means. Drifting of instrument readings were also demonstrated and frequent (once in three to four years) inter-comparisons are considered essential.

12. Data obtained from the ground-based total ozone network are, in quantity and quality, still below requirements. About two thirds of the total number of stations are located between  $30^{\circ}\text{N}$  and  $60^{\circ}\text{N}$ , generating inhomogeneous and in some regions, not independent data. Calculations indicate, that increasing the density of ground based total ozone stations would not bring any significant improvement of the data. More even distribution, frequent instrumental checks and the regularity of observations could have a positive effect on the quality of the data.

13. From the existing ground based stations, approximately one third do not report regularly to the World Ozone Data Center, Toronto, Canada. Of the number reporting, a significant fraction (~40%) provides data derived from lower quality filter instruments. A new instrument has been developed during the last ten years by AES-Canada (Brewer) which has demonstrated differences of less than 1% with measurements from Dobson instruments. Its inclusion in the ozone measuring network supplementing or possibly replacing the Dobson instrument should be seriously considered. The advantages of the AES instrument were reviewed by the WMO meeting on Assessment of Ozone Observing Systems, Boulder, Colorado, July 1980.

14. Vertical Ozone Distribution : The predicted depletion of the ozone concentration at 40 km due to CFC releases is calculated to be about three to four times as great as the predicted depletion of the total ozone amount. Thus data from this level should provide the most sensitive information for ozone perturbations. This is another argument underlining the need of vertical ozone distribution data. Direct measurement of vertical ozone distribution from the ground are known to be inadequate as less than a dozen stations make weekly balloon ozone soundings and only a few have continuous records longer than ten years.

15. International intercomparisons of various types of ozone-sondes have been conducted twice in 1974 and 1978 and simultaneous flights are planned also for the summer of 1981. Efforts should be directed toward the continuation and improving of balloon ozone-sondes in parallel with the increase of indirect measurements of vertical ozone distribution by, for example the Umkehr method. So far Umkehr represents the largest set of data for vertical ozone distribution. This set could be especially useful for analysis of the 25 to 50 km region in the atmosphere. However, only about a dozen stations make them regularly. Recently a new "short Umkehr" multi-wavelength method has been developed and should be widely encouraged.

16. Satellite Measurements : The past ten years have seen the development of several satellite-borne instruments for measurements of both the total column and vertical distribution of ozone using a variety of experimental techniques. The instruments that have, or are, currently being used to measure:

- (i) total column ozone - are based on the techniques of Solar Backscattered Ultra-Violet (BUV, SBUV/TOMS) and Infra-Red radiance in the 9-6  $\mu$ m band (IRIS, MFR, HIRS-2). Although much of the data has yet to be processed, that data which has been processed and validated is proving to be most valuable (BUV data from 1970-1977). The differences between neon simultaneous BUV and ground based total ozone observation is about  $\pm$  5%.
- (ii) vertical ozone distribution - are based on the same basic techniques as for total column ozone, i.e. Solar Backscattered Ultra-Violet (BUV, SBUV) and Infra-red radiance in the 9-6  $\mu$ m band (LRIR, IIMS). In addition the technique of solar occultation in the ultraviolet region has been used (SAGE). As in the case of the satellite total column ozone data, only the BUV data has been validated and processed.

17. Within the next year the LRIR, LIMS, SAGE and first year of SBUV/TOMS data will be processed.

18. In future years satellites are expected to play an increasing role in the monitoring of ozone. Efforts to improve the accuracy and stability of the satellite system should be made in parallel with their continuation.

19. Rocket-borne ozone-sondes : Continuous rocket-borne measurements are necessary mainly for satellite instrument calibration. About sixty recent intercomparative flights should enable an assessment to be made of data derived from previous rocket soundings and should improve our understanding of the upper stratospheric ozone distribution.

20. Global Ozone Observing System (GOOS) : Careful assessment of the performance characteristics of the various ozone observing systems made at the WMO meeting in July 1980 in Boulder, Colorado, concluded that a continuous flow of reliable, total and vertical ozone data forming a coherent set, could be achieved by integrating the ozone observing systems using the satellite borne observing systems and a set of well maintained ground based stations. Co-ordinated ozone measurements based on the existing systems with increased calibration and integrating efforts and forming one Global Ozone Observing System was strongly endorsed by the meeting.

#### OZONE DATA ANALYSIS

21. The relatively large natural variability of atmospheric ozone makes detection of long-term trends difficult. Thus, the ground-based Dobson network indicates a statistically significant 5% increase in global total ozone between 1965 and 1970, a 2% decrease between 1970 and 1973, little change between 1973 and 1978, and a statistically significant 2% increase between 1978 and 1979. The 1979 value, comparable to those in 1970 and 1958 suggests the possibility of a solar cycle (11-year) variation in total ozone amount. There is no evidence of an overall statistically significant and greater than 2% total ozone change between 1958 and 1979. Any anthropogenic influence on ozone amount caused by chlorine compounds should be most apparent near 40 km, at a height where photochemistry dominates transport effects. It is as yet uncertain to what extent the Umkehr-derived 10% increase in the 32-46 km layer in north temperate latitudes between 1965 and 1970 is real (possibly due to the tendency for a greater ozone amount at sunspot maximum) and to what extent it is artificial, caused by the effect on the Umkehr method, of aerosols injected into the stratosphere at the time of the eruption of **Mt. Agung** (1963) and their subsequent decrease. In the same layer (32-46 km) there was a small (about 4%), but significant, decrease immediately following the Mt. Fuego eruption in 1974. The ozone concentration in this layer by 1979, had slowly reached the same value as in 1973/74.

22. There is a discrepancy between Umkehr-derived and ozone-sonde-derived ozone trends in the 16-32 km layer of North temperate latitudes, the Umkehr measurements indicating essentially no change in ozone amount between 1970 and 1979, the ozone-sondes an ozone decrease of a few percent. Thus, in this layer we cannot be sure of the actual ozone variation.

23. In the 2-8 km (tropospheric) layer the ozone-sondes suggest a significant 20% increase in ozone between 1967 and 1979 in North temperate latitudes. A similar increase in North polar latitudes makes it unlikely that this increase is due to local sources of urban photochemical pollution in the troposphere. Thus, the ozone-sonde data suggest the possibility that the near invariance in total ozone in the last decade has been associated with a partial balance between stratospheric ozone decrease and tropospheric ozone increase.

24. Total ozone measurements from the backscattered ultraviolet (BUV) Nimbus-4 satellite show a time-varying discrepancy with data from the Dobson network. It is presumed that there has been a drift in the satellite measurements. Without correcting this apparent drift, the satellite indicates about a 1% greater ozone decrease between 1970 and 1974 than does the Dobson network. The attempt to correct for the drift results in essentially no change in satellite-derived ozone amount between 1970 and 1974, in comparison with the Dobson decrease of nearly 2%.

25. Because of the excellent spatial coverage of a satellite system, proper calibration with the Dobson network should permit a considerable improvement in global total-ozone values. It is estimated that the mean monthly global total-ozone value so obtained should be in error by no more than 1%. However, even with this improved precision the problem remains of differentiating between natural ozone variability and man-induced ozone variability. For example, during the last decade there may have been a balance between the ozone increase resulting from stratospheric cooling and the decrease due to possible anthropogenic effects.

26. Trend detection : We are faced with two questions: How well can we measure total ozone? and: How well can we establish the effects of man-induced activity on any change in total ozone?

27. In answer to the first question it is considered that the standard error of estimate of mean monthly global total-ozone using the past Dobson network is estimated at about 2%. Recent improvements in Dobson inter-calibration, as well as a twofold increase in tropical Dobson stations, has reduced this value to about 1.5%. Further improvement in the Dobson network, involving mostly the location of the stations in the Southern Hemisphere presently devoid of observations, could reduce the standard error to nearly 1%. Because of the excellent spatial coverage provided by satellites, the standard error of estimate for a combined satellite-Dobson network would be less than 1%.

28. With regard to the second question it is recognized that, even though a reasonably accurate measurement of the global total ozone can be obtained, it does not mean that anthropogenic effects can be easily detected. The key issue is the relatively large natural variability in total ozone. With a data record of only twenty years it is not possible to specify with confidence this natural variability. Consequently, anthropogenic effects cannot easily be delineated even by sophisticated statistical techniques. As the data record becomes longer, such techniques will become more precise.

29. Recent developments in statistical methods show that at present a trend attributable to anthropogenic sources in the total ozone of the order of 3-6% is the smallest that could be detected by the Dobson monitoring network. As the data record becomes longer, this statistical analysis for the detection of trends will improve in precision. The introduction of a suitable validated global satellite vertical ozone sounding system may provide a measurement accuracy sufficient to detect a trend of the order of greater than 1.5%.

30. Sources and Sinks of CFCs: World production of CFCs 11 and 12 as reported by the Chemical Manufacturers Association (CMA) has fallen by 17 percent between 1974 and 1979 from 812.2 to 702.3 Tm (thousand metric tonnes) p.a. These figures are estimated to be accurate within  $\pm$  five percent and include an estimated eight percent contribution from countries not reporting to the CMA. The corresponding estimated release of these CFCs have fallen from 741.2 Tm to 610.0 Tm over the same period. There has been a reduction in the combined use for aerosols and open cell foam (giving immediate atmospheric release) from 608.8 Tm to 363.5 Tm over the period 1974 to 1979 but an increase in the amount used in refrigeration and closed cell foams (delayed release) from 203.8 Tm to 283.1 Tm over the same period. It is recognized that, in a few years time reduction of CFC use in aerosols could be offset by growth in non-aerosol uses.

31. Present model estimates of ozone depletion due to CFCs 11 and 12 allow only for their destruction in the stratosphere. Both 1D and 2D models give one hundred to two hundred years for CFC-11 and CFC-12 respectively, due to this mechanism. The presence of a loss mechanism in the troposphere would cause a reduction in their overall lifetimes and a commensurate reduction in the resulting estimate of ozone depletion at steady state assuming continued release of CFCs at current rates.

32. Atmospheric measurements of CFC-11 and CFC-12 have revealed a steady increase throughout the troposphere over the past decade. In principle, such measurements when taken with atmospheric release data, can be used to derive atmospheric lifetimes for CFC-11 and CFC-12 and hence determine whether there are significant tropospheric sinks. Several papers have been published giving the results of such investigations, which give rise to estimated lifetimes near the value calculated assuming only a stratospheric sink. However, the error limits on these estimates may be rather large, reflecting difficulties over siting sampling stations away from sources of CFCs and calibration errors. A network of five continuously monitoring stations has been set up in locations remote for significant CFC sources to acquire long-term data for CFC-11 and CFC-12 (together with some other halocarbons and nitrous oxide) using regular calibration with the specific objective of establishing atmospheric lifetimes.

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\* the figure for 1978 production of 709.1 Tm given in the Report of the Third Session of CCOL has later been revised to 735.3 Tm and the corresponding reduction between 1974 and 1978 becomes 14 percent instead of 17 percent. This amendment is within the  $\pm$  5% accuracy claimed for these data.

33. Direct evidence for specific tropospheric sinks continues to be sought. One mechanism for which there is some laboratory evidence, involves the photolysis of CFC-11 in the presence of dry sand, leading to the formation of CFC-21 ( $\text{CHCl}_2\text{F}$ ). This measurement of the amount of CFC-21 in the atmosphere should provide evidence for the extent to which this process occurs in nature. However, the experimental data is somewhat conflicting. Measurements taken at a distance from possible sink areas show CFC-21 concentrations of about 1 ppt which would indicate an insignificant loss of CFC-11 from the atmosphere by this mechanism, but some recent measurements (accepted for publication) demonstrate substantially higher concentrations downwind of a desert area. The overall significance of such measurements has yet to be resolved.

34. Production data and atmospheric measurements for other halocarbons which may also produce ozone depletion are less extensive than those for CFC-11 and CFC-12. Apart from methyl chloride, which is of non-industrial origin, the most significant of these other chlorine containing compounds are methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ) and CFC-113 ( $\text{CCl}_2\text{F CClF}_2$ ) but there are a number of others which need to be considered in a full treatment. On current estimates these substances would cause in the steady state an additional ozone depletion of about a third of that due to CFC-11 and CFC-12 if current releases continued indefinitely. However, the production of methyl chloroform and some others has grown substantially in the recent past and there has been a corresponding increase in atmospheric concentrations though these data are rather fragmentary. If this growth were to continue while the production of CFC-11 and CFC-12 remains constant or declines, then these other compounds could assume an importance equal to that of CFC-11 and CFC-12 at some time in the future. Thus there is a clear need to acquire relevant global release data and to extend corresponding atmospheric measurements.

#### VIII.

#### ATMOSPHERIC PHOTOCHEMISTRY

35. During the last few years considerable progress has been made in the laboratory measurement of rate coefficients, cross-sections, and primary quantum yields for use in atmospheric modelling. However, a number of problems remain, ranging from small differences in results for a given parameter obtained by different laboratories, to the possibility that major processes have not been incorporated into the photochemical model. The following discussion will emphasize the uncertainty in those processes which are not well defined, and for which the ozone perturbation calculations are sensitive, rather than discussing the large majority of processes for which the present data base is thought to be well established. Increased emphasis is currently being placed on understanding reaction mechanisms over the full range of atmospheric temperatures and pressures since the partial pressures of other gases such as water vapour, or oxygen, may occasionally affect reaction rates, and in addition, certain reactions may proceed via multiple reaction pathways.

36. The chemistry of the global troposphere is complex with both homogeneous and heterogeneous (for example rain-out) processes playing important roles. Significant progress has been made in understanding firstly, the coupling between the carbon/nitrogen/hydrogen/oxygen systems, and secondly, the details of the hydrocarbon oxidation mechanisms which play a vital role in controlling the tropospheric hydroxyl radical concentration. This is an important development insofar as the hydroxyl radical plays a central role in firstly, photochemically controlling ozone in the troposphere, and secondly, controlling the tropospheric concentrations of gases such as  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{CCl}_3$ . In the context of stratospheric chlorine photochemistry (i.e. a coupled oxygen/nitrogen/hydrogen/chlorine system) it should be stressed that the basic formulation remains unchanged from that originally forwarded by Rowland and Molina in 1974, namely that there are still no catalytic cycles involving chlorinated species which are thought to result in the production of odd oxygen. The only fundamentally novel idea which would alter the original Rowland and Molina formulation is the experimentally unproven hypothesis that  $\text{ClO}$  may complex with  $\text{O}_2$  to form  $\text{ClO O}_2$ , which might then react or photolyse in such a manner that there is a  $\text{ClO}_x$  catalytic cycle which results in the net production of odd oxygen. This would be most significant below 30 km. The numerous changes that have been made in estimates of certain rate coefficients have predominantly involved temporary reservoirs such as  $\text{HOCl}$ ,  $\text{HO}_2\text{NO}_2$  and  $\text{ClONO}_2$ . This has modified our understanding of the lower stratosphere where the temporary reservoirs such as  $\text{HOCl}$  and  $\text{ClONO}_2$  play a key role, i.e. below 30 km, but not our basic perception of the role of  $\text{ClO}_x$  in the photochemically-controlled region above 30 km where temporary reservoirs such as  $\text{HOCl}$  and  $\text{ClONO}_2$  play a far less significant role. Each chemical family in turn is discussed below, although it is recognized that there is strong coupling between each of them.

37. Odd-Oxygen Reactions ( $\text{O}_x$ ) : The key photochemical processes involving  $\text{O}_x$  species only, are now considered to be well understood. Minor uncertainties still exist in certain processes but these uncertainties do not cause significant problems for stratospheric modelling.

38. Odd Hydrogen Reactions ( $\text{HO}_x$ ) : The rate coefficients for reactions which control the abundance and partitioning between the odd hydrogen radicals ( $\text{OH}$  and  $\text{HO}_2$ ) are required with high accuracy due to the central role that the hydroxyl radical plays in controlling the catalytic efficiencies of both  $\text{NO}_x$  and  $\text{ClO}_x$ . Unfortunately some of the largest uncertainties, and most significant recent changes, in rate coefficients fall within this category of reactions. Most simple  $\text{OH}$  reactions were, until quite recently, thought to be well established, however, recent work on  $\text{OH}+\text{H}_2\text{O}_2$  and  $\text{OH}+\text{HNO}_3$  has shown this belief to be incorrect. Consequently, the more critical reactions need to be re-investigated, for example,  $\text{OH}+\text{HNO}_3$ ,  $\text{OH}+\text{HO}_2\text{NO}_2$ , and  $\text{OH}+\text{HO}_2$ . Understanding the reactivity of the  $\text{HO}_2$  radical still remains one of the major problem areas in atmospheric photochemistry. However, while it is essential to understand the effect of  $\text{H}_2\text{O}$  vapour or  $\text{HO}_2$  reactivity, it is important to recognize that such effects will be significantly more important for tropospheric than for stratospheric photochemistry due to the difference in the relative humidity of the two regions. Additionally, the question of pressure and temperature dependence of  $\text{OH}$  and  $\text{HO}_2$  reactions is highly pertinent considering the unusual pressure dependence observed in certain reactions ( $\text{OH}+\text{CO}$ ,  $\text{HO}_2+\text{HO}_2$ ), and the unusual temperature dependence observed in others ( $\text{HO}_2+\text{HO}_2$ ,  $\text{HO}_2+\text{ClO}$ ,  $\text{OH}+\text{HNO}_3$ ).

39. Odd-Nitrogen Reactions ( $\text{NO}_x$ ) : In general, the kinetic data base for  $\text{NO}_x$  reactions is relatively good. The major problem areas have already been outlined in the previous section (e.g. processes involving  $\text{HNO}_3$  and  $\text{HO}_2\text{NO}_2$ ). Additional studies of processes involving  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  are required but are unlikely to have a major impact on modelling results.

40. Odd Chlorine Reactions ( $\text{ClO}_x$ ) : The kinetic data base for  $\text{ClO}_x$  reactions has improved significantly in the last few years, but there are still several areas of concern. The problem of which isomers of  $\text{ClNO}_2$  are formed in the  $\text{ClO}+\text{NO}_2+\text{M}$  reactions, and what the photolysis products of these isomers could be has still not been resolved. The answer could affect the  $\text{NO}_x$ - $\text{ClO}_x$  coupling. Although recent results on the temperature dependence for  $\text{HOCl}$  formation and the absorption cross section of  $\text{HOCl}$  has improved our understanding of the rates of formation and destruction of  $\text{HOCl}$ , the exact role of  $\text{HOCl}$  in atmospheric photochemistry is still uncertain due to its dependence upon the  $\text{HO}_x$  budget.

41. Odd-Bromine Reactions ( $\text{BrO}_x$ ) : Due to the efficient coupling between  $\text{CO}_x$  and  $\text{ClO}_x$ , there has been renewed interest in the role of  $\text{BrO}_x$  in the lower stratosphere. The quality of the overall kinetics and photochemical data base for  $\text{BrO}_x$  is significantly poorer than it is for  $\text{ClO}_x$ . Several  $\text{BrO}_x$  rate coefficients were experimentally determined within the last year, and in each case the values were comparable to those previously estimated. An adequate laboratory-determined kinetics data base presently exists to perform ozone perturbation calculations with some realism.

## IX.

CURRENT STATUS OF MODEL PREDICTIONS

42. Most predictions of stratospheric ozone depletion from man-made causes continue to rely on one-dimensional (1-D) models. The principal focus remains with the impact of continued release of CFC-11 and CFC-12 although there are many other factors which may influence the stratospheric ozone amount over a similar time scale. Ignoring all other potential changes, current predictions of the impact of continued release of CFC-11 and CFC-12 at the 1977 rate is about 10 percent ozone depletion in steady state compared with the value of 15 percent given at the UNEP Co-ordinating Committee on the Ozone Layer held in November 1979. This downward revision has been caused by adjustments to the rate coefficients of some  $\text{HO}_x$  reactions and by a major revision to the rate coefficient of the  $\text{OH}+\text{HNO}_3$  reaction. The estimate of the present total ozone depletion due to CFC-11 and CFC-12 alone, has been similarly reduced and should be about 1 percent.

43. Two-dimensional model studies (without the above-mentioned major version) show that significant variations of the ozone depletion with latitude and season are to be anticipated. The qualitative aspects of such variations are, however, expected to be the same with the inclusion of the new rate coefficient although new calculations have not been carried out. The maximum reduction occurs in late winter/early spring with a minimum in late summer/early autumn. There is a greater reduction at high latitudes than in the

equatorial regions, with slightly more overall reduction in the northern hemisphere than in the southern hemisphere. Mean reductions in low latitudes may be about half such values in middle and high latitudes. A similar range occurs in the seasonal variations. These latitudinal and seasonal variations have implications for changes in the intensity of UV-B radiation at the earth's surface as compared to the global average results of 1-D models.

44. The ozone reduction shows significant variations with altitude with the greatest percentage depletion of about 40% predicted to occur at about 40 km in steady state. The estimated ozone reduction around 40 km is expected to be about 4% at the present day. The reinvestigation of the  $\text{OH}+\text{HNO}_3$  reaction has changed little the percentage ozone reduction prediction in this region. The main effect has been to reduce the ozone depletion prediction in the lower stratosphere where the bulk of the ozone column resides.

45. Whether the models realistically forecast what is likely to happen in the stratosphere depends on the correctness and completeness of their input data and their coverage of the simultaneous effects of other atmospheric pollutants. It is not realistic to consider global ozone reductions in terms of releases of CFC-11 and CFC-12 alone. Many other factors may increase or decrease the global amount and it is this combined effect which will determine what will actually happen to the ozone layer. A full study must take them all into account since they may interact together in a non-linear manner typical of a highly-coupled system. In addition to the natural perturbing effects such as lightning, volcanic eruptions, cosmic rays, solar proton events, global circulation changes and the variability of solar radiation, consideration should be given to:

- (i) Other man-made chlorine-containing compounds such as methyl chloroform, carbon tetrachloride and the other chlorofluorocarbons. (CFC-113, CFC-114 and CFC-22). The potential for future growth in their atmospheric releases are more difficult to assess but estimates indicate that if releases continue at present levels then they could increase the steady state ozone depletion by about one third.
- (ii) Increased emissions of  $\text{N}_2\text{O}$  from the soil due to fertilizer application and changes in land use. Previous work has shown that with a hypothetical scenario leading to a doubling of  $\text{N}_2\text{O}$  with continuing present CFC release would lead to ozone depletions almost half those anticipated with CFC release alone. This is due to the highly coupled nature of the perturbations. Since the recent reinvestigations of  $\text{HC}_x$  chemistry the joint  $\text{N}_2\text{O}$ -CFC perturbation experiments have not yet been carried out.

- (iii) Increased emissions of carbon dioxide ( $\text{CO}_2$ ) from combustion or following deforestation, increasing the stratospheric ozone amount through decreased stratospheric temperatures. Recent studies in both one-dimensional and two-dimensional models suggest that the effect of a hypothetical joint CFC- $\text{CO}_2$  scenario where the atmospheric burden of  $\text{CO}_2$  is doubled and with the continued release of CFC-11 and CFC-12 at 1977 production rate, is predicted to reduce the depletion by CFCs alone, by about a quarter. Stratospheric and tropospheric temperature changes may also affect the  $\text{H}_2\text{O}$  amount in the stratosphere which in turn will change the abundance of  $\text{HO}_x$ . However, the theoretical basis for this is too uncertain to make good quantitative estimates.
- (iv) Increased CO and  $\text{N}_x$  from combustion. Such emissions may not only increase tropospheric ozone but may also change tropospheric OH. Increased emissions from combustion may thereby influence the injection of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$  into the stratosphere. At present, detailed information on the tropospheric budgets is inadequate to form a quantitative view.
- (v) Increased use of man-made bromine compounds. Through the coupling of the  $\text{BrO}_x$  and  $\text{ClO}_x$  cycles, stratospheric  $\text{BrO}_x$  has the potential to increase the ozone depletion due to CFCs above the values it would have in the absence of  $\text{BrO}_x$ . However, quantitative data on the life cycles of bromine compounds is absent at present, and current release rates are believed to be small.
- (vi) Emissions from aircraft and aerospace operations. The recent reinvestigations of  $\text{HO}_x$  rate coefficient in acting to decrease the magnitude of CFC perturbations may, at the same time, alter current understanding of the impact of stratospheric  $\text{N}_x$  increases. More recently, it has been suggested that  $\text{N}_x$  emissions from subsonic aircraft, particularly in the middle and high latitudes, may have noticeably increased the ozone content of the upper troposphere. However, measurements of OH and  $\text{HO}_2$  are completely absent for this region and it is not possible to assess accurately the model calculations of these species in that region and the importance of recent changes in  $\text{H}_x$  chemistry.

46. At present, we are a long way from developing consistent and realistic strategies for studying all the perturbations to the ozone layer. This adds considerable additional uncertainty to the predicted ozone changes. Refinement of one-dimensional model structures is rapidly approaching its useful limit. Two-dimensional models overcome some of the difficulties and inadequacies of 1-D models and, as shown above, reveal information on the seasonal and latitudinal dependence of ozone changes. A start has been made on the inclusion of dynamical feedbacks and these may modify significantly, the magnitudes of predicted ozone changes. There have been a number of recent theoretical advances in two-dimensional modelling. As yet no new practical models have appeared based on these recent theoretical developments but the prospects for progress in this, so far insufficiently studied area, appear to be good.

X.

COMPARISON OF THEORETICAL MODELS AND MEASUREMENTS  
OF ATMOSPHERIC TRACE SPECIES

47. The first and so far the only general test of the validity of any photochemical model is the accuracy with which it reproduces the trace gas distributions in today's atmosphere. Unfortunately, a conclusive comparison between model predicted and measured trace gas distributions is limited by several factors:

- (i) Although much work has been done, the available data are still insufficient to fully characterize the spatial and temporal variations in the stratospheric distribution of the trace gases. Except for ozone only scattered vertical profiles are available for most trace constituents. Some important species have not been measured at all.
- (ii) Due to natural variability and sometimes to experimental uncertainties, the available measurements usually only define the atmospheric concentrations within a certain error range.
- (iii) Most of the measurements represent local and instantaneous concentrations whereas the models calculate concentrations which are averaged over considerable spatial and time scales.

48. Despite these limitations, the comparisons form a reasonable test at least for 1-D models, since, in their totality, the measurements place rather narrow constraints on the range of concentration values which can be assumed by the model for the various trace gas species. The models have been generally successful in describing the average vertical trace gas distributions in the stratosphere. This is especially true for the long-lived trace gases such as  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{H}_2$ , where the globally-averaged features are quite well described by 1-D models. With the recent availability of profiles of trace species from different latitudes, finer details may become apparent which will require multi-dimensional models for their interpretation. The existing data base is yet inadequate to provide a validation of multi-dimensional models.

49. For the short-lived species which are produced and destroyed within the stratosphere, qualifications have to be made. Some measured species such as odd oxygen,  $\text{O}$ ,  $\text{O}_3$ , and  $\text{HCl}$  show reasonable agreement between model and measurement over the altitude range of the latter. Some of the others show significant discrepancies at certain altitudes, for example  $\text{NO}_2$  in the lower stratosphere is underestimated,  $\text{NO}$  and  $\text{HNO}_3$  in the upper stratosphere are overestimated. Excluding the singularly high  $\text{ClO}$  measurement, the most notable discrepancy is that  $\text{ClO}$  in the lower stratosphere is predicted to be considerably higher than indicated by most of the measurements.

50. In summary, it appears that present models are fairly successful in reproducing most of the features of stratospheric photochemistry as represented by the limited observations. There are, however, some significant discrepancies such as for  $\text{ClO}$ , which indicate that the photochemistry or transport incorporated in the models may not be complete. This uncertainty which cannot at present be quantified may prove to be of importance for predictions of future changes of stratospheric ozone.

## XI.

INTERPRETATION AND EVALUATION

51. Since all models are approximations to reality, it is essential that the unquantified assumptions governing the adopted approximations should be considered along with other readily quantified parameters. Uncertainties in measured solar flux intensity, chemical kinetics reaction rate coefficients, model boundary conditions, transport coefficients, source distributions, and others can, in principle, be evaluated. Although all these parameters are not known to similar degrees of accuracy, recent progress in analysis, techniques and measurement programmes promise steady improvements in the years to come. Present analysis of the uncertainties inherent in the model predictions can only be considered as the best available information. The unquantified uncertainties, such as the possibility of missing chemistry, the adequacies of 1-D, 2-D or 3-D model transport formulations, diurnal, seasonal or spatial averaging procedures for the non-linear interactions and the adequacy of model validation procedures, by necessity, must be evaluated on a mostly subjective basis.

52. Existing views of the model's ability to describe the present day atmosphere and predict potential perturbation span the range from a high level of confidence based on the positive results discussed in previous sections to strong reservations based on the still unquantified uncertainties. The subjective components in the interpretation of model predictions will most likely persist.

53. The complementary relationship among 1-D, 2-D and 3-D models is widely accepted and current information strongly supports this view. Recent results from two-dimensional models on stratospheric ozone perturbation studies serve to elaborate on the seasonal and latitudinal variations of the ozone change but have not significantly altered global average predictions based on 1-D models. In addition, multi dimensional models have pointed to new coupling processes, most notably in the troposphere, that could not have been studied with 1-D models.

54. Difficulties in 1-D model validation persist in 2-D models. This has led to new interest in re-examining the question of whether the major chemical processes in the lower stratosphere have been included in the model. The development may affect the model predictions on CFCs effect quantitatively but not qualitatively, i.e. CFC increase leads to a decrease in total ozone. But for other perturbations, notably the  $\text{NO}_x$  perturbation, there remains considerable uncertainty as to the type of ozone changes that may result from an increase in the atmospheric burden of total odd nitrogen.

55. The two major aspects of model predictions, past or near term trend and steady state ozone change have different sensitivities to model input parameters. In the analysis of possible trends, a major uncertainty lies in the transport parameters. Whereas for steady state changes, one additional concern is with the uncertainty of the future state of the atmosphere. Recent research interest in coupled perturbations from multiple causes has contributed a wide appreciation of the degree of complexity of this problem.

## XII.

INCREASE OF UV-B IRRADIANCE

56. A decrease in atmospheric ozone results in increased penetration to the earth's surface of the damaging short wavelength UV-B radiation. The increase is non-linear and highly dependent on wavelength; it is the steepest for the shortest wavelengths in sunlight. The action spectra considered in biological effects of UV, such as the DNA or erythema or plant response action spectra, all show that 290 nm photons are about four orders of magnitude more effective than 320 nm photons. Therefore, it is important to consider the radiation flux over the entire UV-B spectrum.

57. Models have been developed which permit the quantitative weighting of increases in UV-B irradiance according to the various action spectra, taking into account variations in ozone column thickness, solar angle, aerosol thickness and surface albedo. The percentage change in the effective daily UV-B radiation dose produced by a one percent change in ozone column thickness is defined as the radiation amplification factor. Data shows that, in general, for biological action spectra commonly used by photobiologists, this radiation amplification factor varies from about 1.6 to about 3 for most latitudes and seasons, with the higher values existing near the polar regions.

## XIII.

BIOLOGICAL EFFECTS

58. Effects on human health : Considerable progress has been achieved in understanding the human health effects of increased ultraviolet radiation. Human health is influenced by UV radiation in many ways, such as the formation of vitamin D<sub>3</sub>, sunburn, eye diseases, and skin diseases including skin cancer. Among these effects, skin cancer stands out as the one problem to be significantly influenced by increased UV-B irradiance. The severity of health and other biological effects of radiation depend on its spectral composition, irradiance, and exposure time. The response may be modified by biological factors and environmental conditions. UV-B radiation has been demonstrated to be more biologically effective than UV-A radiation.

59. Epidemiologic studies have shown that the incidence of non-melanoma skin cancers correlates with exposure to sunlight; these data relate mainly to light-skinned people. Animal experiments have revealed that UV-B is the most effective wavelength region in carcinogenesis by UV radiation. These data indicate that an increased incidence of non-melanoma skin cancer is to be expected in the case of increased UV-B irradiance.

60. There are increasing indications that sunlight may also be one of the causative factors in the pathogenesis of malignant melanoma. These indications come from epidemiologic observations which, because they deal with exposure to total sunlight, do not point to any particular wavelength range in the solar spectrum. Animal experiments indicating the effective wavelength range are not available.

61. Should UV-B be involved, a decrease of stratospheric ozone might be expected to increase the incidence of melanoma. This is a possibility, but it cannot be substantiated on the basis of the presently available data.
62. In animal studies, UV-B radiation has been shown not only to be carcinogenic, but also to alter the response of the immunological system; this results in impeded recognition of a UV tumor as a foreign body.
63. Effects on terrestrial plants : Higher plants have obvious importance both in agriculture and as the basis of primary production in natural land ecosystems, such as forests. Unlike animals, which can reduce exposure of their living cells to sunlight through protective body coverings and behavioural responses, plants have evolved to expose much of their living tissue to sunlight in order to utilize its energy. Thus, an atmospheric ozone reduction, with its attendant increase in solar UV-B radiation, could be particularly significant for them.
64. Studies have been conducted in growth chambers and greenhouses, and in addition a few field studies, under conditions of enhanced UV-B radiation. In the experiments, damaging effects were seen to growth, composition and function, including photosynthesis, of a large variety of plant species, including many important crops such as soybeans. The enhanced UV-B exposure levels at which the harmful effects began to occur depended on the plant species and were in the range from 0 to 50 percent. Some plants exhibited increased growth when existing natural levels of UV-B were filtered out of the incident solar radiation.
65. Tests of more than 100 species or varieties of species in controlled environment growth chambers indicate that approximately 20 percent are sensitive to daily UV-B radiation doses of the order of those delivered by Florida sunshine 25-30°N at present ozone levels, while 20 percent were resistant to doses four times greater than this, and the remaining 60 percent showed some intermediate sensitivity.
66. Before any firm conclusion can be drawn about scaling such effects to agricultural productivity, further field studies are required.
67. Effects on aquatic organisms : Solar UV-B radiation at biologically effective levels have been measured to depths of more than twenty meters in clear waters and more than five meters in unclear water. Much marine life sensitive to these UV-radiation levels (fish, eggs and larvae etc.), live in the top 20 meters of ocean waters. Experimental studies with enhanced UV-B levels from zero up to fifty percent of natural levels have shown effects to fish, eggs, larvae and juveniles, shrimp, crabs, zooplankton and other aquatic animal organisms as well as to phytoplankton and other aquatic plants essential to the aquatic food web. Phytoplankton studies show that increased growth occurs when the UV-B radiation is filtered out of the incident solar radiation; indicating that existing levels of UV-B depress productivity.

68. Studies on over 60 aquatic micro-organisms, protozoa, algae and small invertebrates, that form the base of the food web of oceanic and estuarine ecosystems, indicate that most of these, too, are sensitive to current levels of UV-B radiation incident at the water surface. More recent and more quantitative studies indicate that at doses comparable to daily levels of existing natural UV-B radiation incident at the water surface, reduction of UV-B increases the growth of chain-forming diatoms is reduced, and similarly affects the biomass and specific diversity of attached marine algae and survival of coral reef epifauna. Similarly, a UV induced mortality of marine pelagic copepod and pelagic crab and shrimp larvae could occur at present UV-B radiation levels incident at the water surface.

69. Continued investigations will be required to assess the possible consequences for the many complex ecological interactions as well as for the productivity of fisheries.

## XIV.

INSTRUMENTATION

70. Further progress was made on radiation flux and spectral measurements in air and water by using high resolution spectroradiometers (e.g. double monochromator). Computer models are used to calculate the biological effectiveness of these UV-B fluxes with respect to ozone reduction for various latitudes and seasons, taking into account variations in ozone column thickness, solar angle, aerosol thickness and surface albedo.

## XV.

RECOMMENDATIONS

71. At its previous sessions the Co-ordinating Committee on the Ozone Layer has made a number of recommendations for improvement of activities relevant to the implementation of the World Plan of Action on the Ozone Layer. Although action has been taken on most of them, it is felt necessary to re-emphasize some of those issues again. The Co-ordinating Committee on the Ozone Layer noted that substantial progress in upgrading the international ozone monitoring network has taken place over the past few years. However, improvement is still not proceeding with the speed or sense of urgency commensurate with the potential seriousness of the ozone depletion problem. Greater commitment of effort and resources by both national and international agencies is urgently required if the ozone monitoring network is to adequately fulfil its role of providing a reliable data base for detection of ozone change.

72. The following specific actions are recommended:

1. to make the Global Ozone Observing System (GOOS) based on integration of satellite and ground-based systems fully operational;
2. to request UNEP to continue its support for strengthening and catalysing international activities through the WMO Global Ozone Research and Monitoring Project;

3. to intensify upgrading and intercomparisons of Dobson instruments;
4. to expand vertical ozone distribution measurements by continuing balloon-borne sondings and by widely implementing "short-Umkehr" measurements as well as by encouraging the development of reliable operational satellite sensor for accurate measurements over the complete altitude range of the stratosphere including the continued development of inflight calibrations;
5. to explore the feasibility of developing new, reliable and operationally inexpensive ozone sondes;
6. to continue efforts to establish the nature and importance of tropospheric sink mechanism for CFC's including the continued monitoring of CFC-11 and CFC-12 concentrations;
7. to request nations to give more attention to measurements of UV-B measurements, in principle in the vicinity of ozone measuring stations as it was noted that the UV-B measurements are so far only isolated national efforts which have not been internationally standardized and integrated.
8. to continue to develop higher dimensional models and compare the results;
9. to extend the measurements of rate constants over the pressure and temperature ranges found in the atmosphere, and identify the reaction products;
10. to search for and investigate any additional reactions which may affect stratospheric chemistry;
11. to continue efforts to increase understanding of tropospheric chemistry;
12. to undertake simultaneous in situ measurements of the relative concentrations of photochemically related compounds of the various families;
13. to extend measurements of Cl and ClO to the lower stratosphere using independent techniques;
14. to undertake measurements of hydroxyl concentrations in the troposphere and stratosphere;
15. to obtain 3-D fields of important trace constituents and meteorological variables in the stratosphere by satellites;
16. to continue to develop tropospheric monitoring to assess the lifetimes of stable species;

17. to monitor the solar flux variability in the spectral region 175-400 nm;
18. to improve knowledge relative to:
  - (i) the relationship of dose and dose-rate and response for the various biological effects of UV radiation;
  - (ii) the relationship between human exposure to solar ultraviolet radiation and the development of non-melanoma, and to better define the possible relationship between sunlight and melanoma skin cancer including social and environmental conditions; as a result of these studies, global base-line data on skin cancer incidence should be established;
  - (iii) the possible interaction of chemicals, including pollutants, and increased UV radiation;
19. to study biological action spectra and the spectral response using polychromatic radiations in order to include possible interactions of the various wavelength regions;
20. to determine the effects of existing and enhance UV-B radiation on:
  - (i) the sensitivity and activities of insects important to the biospheric balance (animal food chain, plant cross-fertilization, etc.);
  - (ii) micro-organisms, such as those causing plant diseases;
  - (iii) primary processes such as photosynthesis;
  - (iv) the photodegradation of herbicides, pesticides, fertilizers and similar agricultural chemicals;
  - (v) synergistic and secondary effects.
21. to determine the mechanisms by which UV-B radiation acts on biological species and systems;
22. to include photorepair, adaptation and protection mechanisms in the overall considerations of UV-B effects;
23. to extend aquatic effects studies to the natural water environments in order to gain knowledge of the resultant effect of enhanced solar UV-B radiation to aquatic food productivity;

24. to develop and publish a manual to provide guidelines for UV-B exposure studies to facilitate intercomparison of biological research results. The manual should include recommended radiation equipment and experimental methods for use in growth chambers, greenhouses and in the field, i.e. light sources, filter systems, irradiance measurements, spectroradiometer calibrations, etc.;
25. to develop individual and biological UV-B dosimeters.

XVI. DECISION 8/7B OF 29 APRIL 1980 OF THE  
GOVERNING COUNCIL OF UNEP REGARDING CHLOROFLUOROCARBONS

73. This item was discussed by the Committee and several suggestions were made as to how the Executive Director could accelerate international co-operation on the subject. The Committee welcomed and endorsed the decision and recommended the decision to policy makers for their consideration.

XVII. ANY OTHER BUSINESS

74. A press release was drafted by the Committee. The text of this ... document is reproduced as Annex 4.

XVII. CLOSURE OF THE MEETING

75. Mr. Engelmann thanked the Government of the Netherlands and the staff of the Institute for their splendid hospitality. He, in particular, singled out Dr. Schneider and his staff for their hard work and never-failing courtesy. He also thanked the Committee for its forbearance and spirit of co-operation which had helped to make the fourth session of the Co-ordinating Committee on the Ozone Layer so stimulating and successful. He expressed his gratitude to the Chairman and members of the Working Groups for so ably undertaking their difficult and onerous tasks. In closing the meeting he wished the participants a pleasant journey home and expressed his hopes of meeting with them next year.

The meeting closed at 4.30 p.m. on Friday, 14 November, 1980.

ANNEX 1

Co-ordinating Committee on the Ozone Layer  
Fourth Session, Bilthoven, 11-14 November 1980

List of Documents

UNEP/CCOL/4/1	-	Provisional agenda
UNEP/CCOL/4/2	-	Annotated provisional agenda
UNEP/CCOL/4/3	-	Ongoing and planned activities relevant to the World Plan of Action on the Ozone Layer - Contribution by the World Meteorological Organization
UNEP/CCOL/4/3/Add.1	-	- do - Contribution by Canada
UNEP/CCOL/4/3/Add.2	-	- do - Contribution by the Chemical Manufacturers Association
UNEP/CCOL/4/3/Add.3	-	- do - Contribution by the United Kingdom of Great Britain and Northern Ireland
UNEP/CCOL/4/3/Add.4	-	- do - Contribution by Australia
UNEP/CCOL/4/3/Add.5	-	- do - Additional contribution by the World Meteorological Organization
UNEP/CCOL/4/3/Add.6	-	- do - Contribution by the World Health Organization
UNEP/CCOL/4/3/Add.7	-	- do - Contribution by France
UNEP/CCOL/4/4	-	Summary of recent research results - Contribution by Chemical Manufacturers Association
UNEP/CCOL/4/4/Add.1	-	- do - Contribution by the United Kingdom of Great Britain and Northern Ireland
UNEP/CCOL/4/4/Add.2	-	- do - Contribution by the European Economic Community
UNEP/CCOL/4/4/Add.3	-	- do - Contribution by The Netherlands
UNEP/CCOL/4/4/Add.4	-	- do - Contribution by the Federal Republic of Germany (Parts I and II)
UNEP/CCOL/4/4/Add.5	-	- do - Additional contribution by the Chemical Manufacturers Association
UNEP/CCOL/4/4/Add.6	-	- do - Contribution by Italy
UNEP/CCOL/4/5	-	- do - Assessment of ozone layer depletion and its impacts

- UNEP/CCOL/4/6 - Decision 8/7B of the Governing Council of UNEP regarding chlorofluorocarbons
- UNEP/CCOL/4/Background 1 - World Plan of Action on the Ozone Layer as adopted by the UNEP meeting of experts designated by Governments, Intergovernmental and Non-governmental Organizations on the Ozone Layer, Washington, D.C. 1-9 March 1977
- UNEP/CCOL/4/background 2 - Report of the third session on the Co-ordinating Committee on the Ozone Layer
- UNEP/CCOL/4/Background 3 - Meeting on International Regulations of Emission of Chlorofluorocarbons, Oslo, 14-16 April, 1980 - Agreed Conclusion
- UNEP/CCOL/4/Background 4 - Decision concerning chlorofluorocarbons in the environment as adopted by the European Community Council on 26th March 1980
- UNEP/CCOL/4/Inf.1 - Documentation
- UNEP/CCOL/4/Inf.2 - List of participants

ANNEX 2

Co-ordinating Committee  
on the Ozone Layer  
Fourth Session

Bilthoven, 11-14 November 1980

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## ANNEX 3

### CONTRIBUTION BY MEMBERS ON RECENT RESEARCH RESULTS AND ONGOING AND PLANNED RESEARCH PROGRAMMES RELEVANT TO THE WORLD PLAN OF ACTION ON THE OZONE LAYER

#### Denmark

1. The Danish Government has concluded that a ban of CFC's could have the effect that substances substituting for CFC's might pose a health risk. Therefore the Danish Government intends to regulate aerosol propellants and solvents with a "positive list" of allowed substances. To make this list the first two of the following investigations are being carried out:

- (a) Ozone depletion effects of CFC's and possible alternatives for use in aerosols:

Several different substances, that could be possible propellants for aerosol use, are being compared. The comparison, mainly on the basis of the rate constant with respect to reaction with OH, should make it possible to select substances with tropospheric life-times short enough, that ozone depletion, to a great extent, would be avoided.

- (b) Health risks of CFC's and possible alternatives for use in aerosols:

A survey of the known health effects of possible propellants or solvents in aerosols is being carried out. This should make it possible to advise on what alternatives could be used without posing unacceptable health risks.

2. In addition determination of rate constants for selected reactions of importance to tropospheric and stratospheric chemistry is ongoing. This is a research project using pulsar radiolysis equipment. The rate constants found in this way will be compared with rate constants established by other methods.

#### France

##### Activities related to stratospheric research and monitoring

3. French activities related to stratospheric research and monitoring are shared by various laboratories in University, Industry (ONERA Aerospheric Research) and the Meteorological Office (Météorologie Nationale), under the joint sponsorship of two Agencies: DGRST (Delegation Générale à la Recherche Scientifique et Technique) for basic research and EERM (Etablissement de Recherches de la Météorologie Nationale) for monitoring. The CNES (Space Research) is also contributing to the research programmes. This report reviews the recent results obtained in stratospheric measurements (both ozone and other minor constituents), chemistry and modelling (including the assessment of ozone trends).

### Ozone measurements

4. DOBSON stations: continuous ozone measurements are currently carried out at the Biscarrosse SMS station on the coast of the Bay of Biscay (DOBSON spectrophotometer daily observations and BREWER-MAST ozone sonde weekly launchings some UMKEHR measurements) - and a new DOBSON station, located at MAGNY, in the vicinity of PARIS. (The CNRS ozone station at MONTLOUIS, in the Pyrenees, has been dismantled).

### Non-continuous measurements

5. Satellite measurements: The previous 1979 report mentioned the radiometric experiment on board the satellite OSO 8, based on a sun occultation technique on the terrestrial limb. From these data, the LPSP Laboratory has carried out a retrieval of ozone in the 50 km - 70 km altitude range, showing a high day-to-day variability (up to a factor of 2).

6. TIROS N and NOAA: Using the TOVS multispectral telemetry on board meteorological satellites (TIROS N and NOAA series), a new method for extracting the total ozone content (from the 9.6 micrometer band) is currently being checked at Lennion CMS. The method might be used for operational purposes in the near future.

7. Balloon measurements: A chemiluminescent ozone sonde prototype has been flown on a constant level balloon floating at 2.5 mb. A simplified version aimed at operational purposes is presently being tested by EERM.

8. Lidar measurements: First vertical profiles of  $O_3$  have been obtained by differential absorption of a backscattered laser signal, from a ground-based tunable laser (Observatoire de Haute Provence, CNRS/SA).

9. Aircraft measurements: A meridian flight ( $70^{\circ}W$ ) on board a Caravelle aircraft (the so-called STRATTOZ experiments), from North Greenland to the southern tip of South America, was organized by EERM in cooperation with ONERA, during springtime (May 1980) "symmetrical" to the previous Stratoz flight during the fall of 1978. It included spectrometric measurements of  $O_3$ , confirming an important asymetry between the two hemispheres.

### Measurements of other minor constituents

10. The STRATTOZ II experiment: In addition to the previous spectrometric devices which were involved in STRATTOZ 1 (ONERA grid spectrometer, IASB infrared radiometer) two air sampling experiments were performed by Professor Ehhalt, Federal Republic of Germany for  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $N_2O$ ,  $CH_3Cl$ ,  $CFC1_3$ ,  $CF_2Cl_2$  and the  $C_2H_2$  (in cooperation with Pr. Guiochon, Ecole Polytechnique) and Professor Rowland, for  $CH_3CCl_3$ ,  $CHCl-CCL_2$ ,  $CCl_4$ ,  $CH_4$ . The results already obtained on STRATTOZ 1 have been presented at the August 1980 Boulder Ozone Symposium, as concerns latitude variations of  $NO$  and  $N_2O$ ,  $CO$ ,  $HNO_3$  and  $HCl$ .

11. Methane and water vapour interaction: Four balloon flights have been performed by ONERA in order to evaluate the validity of the methane oxidation theory as an explanation of H<sub>2</sub>O increase in the stratosphere. Using an absorption spectrometry (sun occultation) technique with a grid spectrometer (0.08 cm<sup>-1</sup> resolution), it has been shown that above 28 km, 2 CH<sub>4</sub> + H<sub>2</sub>O is approximately constant (compatible with theory), while, below 28 km, the increase in stratospheric H<sub>2</sub>O cannot be satisfactorily explained by CH<sub>4</sub> oxidation.

#### Other measurements

12. Several balloon flights were carried out separately by Rigaud (laboratoire Val Joyeux) and Pommereau (CNRS/SA) for in situ NO<sub>2</sub> measurements. The former measurements were done at night-time.

#### Chemistry

13. New laboratory techniques have been developed for measurements of total chlorine (down to 3.5 ppbv) by the so-called PCUK chemiluminescence method; and CFMS concentration measurements (gas chromatography with electron capture: Guiochon Ecole Polytechnique). A new measurement (Combourieu-CROCCHP) of H<sub>2</sub>CO + O<sub>1</sub> reaction rate, has shown a slight difference with the previous one, quoted in the 1979 report (the new rate is higher).

#### Evaluation of ozone trends and modelling

##### Evaluation of ozone trends

14. Box and Jenkins method: Both varieties of the Box and Jenkins method (the so-called endogen and exogen varieties) have been used by EERM for global ozone trend evaluation for a set of 25 selected DOBSON ground stations, during the period 1957 - 1975. The sensitivity of the exogen variety, checked by a random simulation method, narrows down to 3% of the mean value, the threshold of trend detectability. No significant trend has been found in the considered ozone data set.

15. Proximity analysis: This new technique has been used for handling a full data set of 157 ozone stations, during 18 years. The "interdistances" (between ozone fields) matrix is projected into a two-dimensioned scheme, which allows a visualization of possible trends (no trend is equivalent to a "brownean" or "chaotic" distribution; a trend is detectable by some alignment of representative points). Numerical tests have been made available to support the purely visual evaluation. The high sensitivity of this statistical tool has been checked on a well-known meteorological field (geopotential). By simulating different values of trends, with gaussian noises, it has been shown that a trend of down to a few percent, on the largest samplings, was detectable. A technical document will be disseminated by EERM by December 1980.

## Modelling

16. The EERM 1D model, which has been described in the 1979 report, has been converted into a new version, taking into account the diurnal variations of constituents (the two versions give very close agreement for ozone content and ozone sensitivity to chlorine). The new version has been used for a specific study of sensitivity to an increase of nitrogen oxides. A doubling of  $N_2O$  flux, combined with CFC action, shows the sensitivity of ozone to chlorine decreasing, when nitrogen oxide concentrations increase. The current model will be soon completed with a radiative model, in order to study the photochemistry/temperature interaction and the "Climate impact" on ozone of a  $CO_2$  increase.

17. Planned activities include:

- Intercomparison of various in situ and ex situ techniques for measuring ozone and other stratospheric minor constituents at the Observatoire de Haute Provence (OHP) site.
- Investigation of trace species profiles by several techniques presently under development; lidar (Chanin - CNRS/SA), Fourier transformation spectrometer (Jouve), and microwave sounding (Bandy).
- Improvement of spectroscopic data, relevant to species of interest (CNRS/University).
- Use of new balloon techniques for long duration stratospheric flights (CNES) aimed at dynamical and chemical measurements.
- Ozone mapping from satellite telemetry at Lannion CMS (EERM).
- Evaluation of global ozone trends by "proximity" and "preference" analysis (EERM).
- Sensitivity studies on the 1-D EERM model.

## Germany (Federal Republic of)

### Sources and sinks of relevant compounds

18. Systematic investigations of  $N_2O$  - release rate from agricultural soils have been carried out since last summer. First results show a high variability of  $N_2O$ -release rates with respect to agricultural and meteorological parameters. For example, release rates (extrapolated for the whole year) were 290 g  $N-N_2O$ /acre per year for a wheat field and 55 kg  $N-N_2O$ / acre per year for green land. First measurements on non-agricultural soils under middle - European conditions show rather low  $N_2O$ -release rates. It was also observed, that such soils act as a source for chloroform. The destruction of CFC's adsorbed on surfaces has been

investigated using Auger-spectroscopy. On a surface of iron oxide, an exchange of chlorine (from  $\text{CFC1}_3$ ) and oxygen has been observed. It is in doubt, whether this effect might be relevant in the atmosphere, or at the surface of the earth, where concentration, surface and reaction-conditions are very different from those of laboratory experiments.

### Field measurements

19. A principal item of the German field measuring programme are balloonborne measurements of the vertical distribution of trace compounds involved in stratospheric chemistry. A set of data from ten balloon-flights is now available. Species measured include CFM 11 and 12,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$ . The vertical profiles of different flights for these long-lived compounds are in quite close agreement. The CFM profiles recorded at  $43^\circ\text{N}$  latitude show a considerable discrepancy from those calculated and measured at  $30^\circ\text{N}$ . This emphasizes the necessity for improved 2D-modelling, to take into account not only radiation distribution and transport, but also source inhomogenities. Balloonborne ozone soundings at the Hohenpeissenberg have been run since 1966, representing one of the world's longest surveys of this kind. Since about 1976 a significant decrease of ozone-concentrations at altitudes above 25km from the long-term average has been observed. This is, however, at variance with Umkehr observations; a thorough analysis of high altitude ozone trends appears highly important. New components being covered within the balloon-measurements programme are the hydrocarbons ethane ( $\text{C}_2\text{H}_6$ ) and propane ( $\text{C}_3\text{H}_8$ ). Whereas for  $\text{C}_3\text{H}_8$  the destruction is mainly due to reaction with OH radicals, for  $\text{C}_2\text{H}_6$  the destruction with Cl atoms is of similar importance. With the Cl-concentrations calculated in the models currently used, a much steeper slope would be expected with altitude than has been measured. This seems to indicate, that the Cl concentration in this region might be a factor of about five smaller than modelled. The electron paramagnetic resonance (EPR) method has been modified and improved for application for field measurements of free radicals. In the troposphere,  $\text{NO}_2$  values between 1 and 1.5 ppb and  $\text{NO}$  values of about 0.5 ppb have been observed at altitudes of up to 6 km. Stratospheric concentrations measured with this method were  $(12 \pm 4)$  ppb for  $\text{NO}_2$  and  $(0.8 \pm 0.3)$  ppb for  $\text{HO}_2$ .

### Reaction kinetics

20. The reaction rates of the two Chapman reactions:  $\text{O}(^3\text{P}) + \text{O}_3 \longrightarrow 2\text{O}_2$  ( $K_1$ ) and  $\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \longrightarrow \text{O}_3 + \text{M}$  ( $K_1$ ) have been determined. The direct measurements agree reasonably well with the data published so far. The measurements were made over a narrow temperature range such that the activation energies derived have relatively large errors. For the photolysis of  $\text{ClONO}_2$ , different channels are coming into consideration. The relative contribution of these channels is of great importance for the further chemistry of the species involved. Examination of reaction kinetics and investigation of the products formed under different conditions lead to the conclusion, that the channel leading to Cl and  $\text{NO}_3$  is the dominant one. Direct absorption of radiation by species like  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{HCHO}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{OHNO}$  is of particular importance, as this constitutes the primary step to the subsequent chain reactions. For most of these species, the photolysis rates have been determined actinometricly in the troposphere. In some cases, the branching ratios were investigated additionally. A smog chamber operating at stratospheric conditions has been constructed. The analysis of the species involved is carried out with Fourier transformation of infrared spectroscopy. First measurements were carried out on the decomposition of  $\text{HO}_2\text{NO}_2$  and on reactions of the  $\text{HO}_2$ -radicals formed at this process. Other measurements

concerned reaction rates of OH and Cl with hydrocarbons. Next to be investigated is the reaction of  $\text{HNO}_4$  and HO.

### Biological effects

21. Four plant species (barley, bean, corn, radish) were irradiated either continuously or in a natural light-dark rhythm in a growth chamber or in the field with enhanced UV-B intensities corresponding to ozone reduction rates between 3% and 50% when using plant weighting function as a basis of calculation. All plants show, depending on UV-B intensities, within the growing period, a reduction of fresh weight (up to 45%), leaf area (up to 60%), photosynthetic pigments and activity (both up to 65%). Biosynthetic capacity was reduced, especially in barley, with the exception of protein and flavonol formation which increased up to 40% compared to control plants. In field experiments six plant species (potatoes, beans, barley, cabbage, spinach, radish) were irradiated in addition to daylight with four different UV-B intensities corresponding to ozone reduction rates of 40%, 15%, 8% and 3%. Under these conditions the plants were maintained for several weeks until harvest. As in the growth chamber, compositions of plants and photosynthetic function of leaves decreased with increasing UV-B intensities. The yield of beans, potatoes, barley and cabbage were reduced at high UV-B intensities (=15% and 40% ozone reduction) but were somewhat enhanced at low UV-B intensities. As in the growth chamber, increasing amounts of proteins were found in several plants with increasing UV-B. Some experiments were carried out on the lethal and mutagenic effects of UV-radiation (254, 293, 303, 315 nm) in the yeast (*Saccharomyces cerevisiae*) as an eucariotic model. As a result, the mutagenic effect on the wild strain is more than two orders of magnitude less sensitive than on a strain with a lack of excision repair. The difference of mutagenic effect is smaller at shorter wave lengths than at larger ones.

### Italy

22. Several research activities connected with the possibility of stratospheric ozone depletion by chlorofluorocarbons (CFCs) are being continued in Italy under the sponsorship of the Government (Universities, National Research Council) and industry. The different fields of activity are presented as follows.

#### Ozone Monitoring

23. Four Dobson spectrophotometers are operating (Messina, instrument no. 46; Cagliari Elmas, no. 113; Sestola, no. 48; Vigna di Valle, no. 47) in connexion with the basic global ozone monitoring network. The Meteorological Service of the Air Force takes care of the instrumentation, the collection of data and connexions with the Toronto Data Center (Canada). In the Cagliari Elmas station, data are also collected weekly from two ozone-sondes MAST 730-5.

#### Stratospheric Constituents Measurements

24. A balloon experiment has been set up by IROE/University of Florence in collaboration with NPL/Teddington (UK), aimed at the evaluation of the vertical profile. The diurnal variability of some stratospheric constituents (HCl, HF, ClO,  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ) is still going on. The 1979 balloon flight has shown, for an upper limit for ClO of 1.5, 0.3, and 0.03 ppb at 35, 30 and 15 km of altitude respectively. The HCl/HF ratio has a value of 0.2-0.3, practically constant up to 40 km. A third balloon flight is

planned in 1980 from Sicily. A theoretical and experimental spectral study concerning  $\text{ClO}$ ,  $\text{HOCl}$ ,  $\text{ClONO}_2$ , etc. is being developed at the University of Florence and Bologna.

#### Methods for Halocarbons Concentration Measurements in the Atmosphere

25. Qualitative and quantitative analytical methods for the determination of chlorofluorocarbons (in particular  $\text{CHFCl}_2$ ) in the troposphere are being developed at the University of Urbino (Prof. Bruner). Systematic measurements have been carried out on samples from different areas of Italy, the Indian Ocean and the Red Sea. The project deals with the search for possible tropospheric sinks for chlorofluorocarbons.

#### Modelling

26. At the Physics Department of the University of L'Aquila, a numerical photochemical, radiative, convective one-dimensional model has been set up by Prof. Visconti. The model, which calculates the temperature profile and chemical composition of the atmosphere between 0 and 70 km, allows the study of two feedback processes connected with: firstly the tropospheric temperature-water content cycle; and secondly the stratospheric temperature-ozone content. Using this model, the effect on the ozone layer of doubling the atmospheric  $\text{CO}_2$  concentration has been studied; an increase in  $\text{CO}_2$  gives rise to stratospheric cooling and a consequent local increase of ozone. The same group of L'Aquila has developed a two-dimensional model for the study of tropospheric and stratospheric minor constituents and F11 distribution.

#### Chemical Kinetics

27. Prof. G. Fiocco and his collaborators at the University of Rome and at the Laboratorio Plasma Spazio (CNR) have been concerned with the influence of diffuse solar radiation on the stratosphere. The diffuse component of solar radiation has important effects on stratospheric structure and composition because of photodissociation and heating. The results of the analyses indicate that molecular scattering should always be included in photodissociation calculations, if an accuracy of the order of a few percent is desired. The variable part of the diffuse field due to surface albedo, clouds and aerosols could be responsible for large fluctuations in the thermal structure and composition of the stratosphere.

#### Effects

28. Research programmes are also being planned on the epidemiology of malignant melanoma, and the monitoring of erythemal ultraviolet radiation at the ground, by some researchers of the Istituto Superiore di Sanità in Rome.

JAPAN

29. Japanese research is mainly related to the measurement of atmospheric trace constituents. One experiment which has been done between 1977 and 1980 at the Meteorological Research Institute in Japan is the measurement of F 11, F 12 and N<sub>2</sub>O in the atmosphere. Air samples in the troposphere were collected on aircraft at altitudes up to 7 km over an area approximately 137° E to 142° E and 33° N to 35° N. Air samples in the stratosphere up to an altitude of 29 km were obtained in a balloon-borne stainless steel can. Vertical and horizontal distribution of F 11, F 12 and N<sub>2</sub>O were obtained. The other measurement is related to the lifetime of CFC's at the atmosphere. The purpose of this research is to clarify whether CFC's are decomposed in the stratosphere by investigating the change of concentrations during several years. In order to do this, the Meteorological Institute takes daily data of the concentration of CFC's at a place far from the possible emitting sites of CFC's, such as urban and industrial areas. By using an automatic analyser, F 11 and F 12 are measured every hour. By comparing the changing trend between CFC's at atmospheric concentrations and the consumption of CFC's, the lifetime of CFC's at the atmosphere will be determined. The necessary equipment will be installed this year and measurements will start soon.

Netherlands

Measurement and monitoring activities

30. Measurements of NO<sub>2</sub> and SO<sub>2</sub> using a modified correlation spectrometry technique. Although this programme was intended originally to measure the vertical gas burden in the troposphere, recently it appeared possible to measure also the concentration of NO<sub>2</sub> in the stratosphere at dawn and sunset using oblique incident sunlight. It is intended to extend the programme to measure ozone in the stratosphere. Measurement of the solar radiation in the U V. of selected wavelengths (315, 350 and 400 nm) as well as total intensity in the interval from 320-390 nm have been carried out. A network consisting of 5 stations has been set up in the Netherlands in connexion with the national air pollution network. Special emphasis is laid upon absolute intensity measurements. A calibration system has been assembled and tested. A research programme has been set up to investigate the possibility of measuring stratospheric freon and other chlorofluorocarbons from the ground using tunable diode lasers operating in the infrared.

Health aspects

31. A dose-response model, based on the results of animal experiments, is being developed for skin cancer induction in human population by chronic exposure to ultraviolet radiation. The model takes into account a variety of exposure habits and susceptibility of individuals in the population. The required input data for the dose-response relationship are the age specific incidences of the population in question. Calculations based on this model can be used as a step in the evaluation of the effect that a reduction of stratospheric ozone would have on non-melanoma skin cancer incidence. As an example an evaluation of the white population of the U.S.A. was presented.

It is estimated that, if the amount of stratospheric ozone were to have been continuously reduced by 1% over the last century, we would have had a 4% higher incidence of non-melanoma skin cancers in the U.S.A. (i.e. about 12,000 more non-melanoma skin cancer cases per year). This estimate agrees fairly well with earlier estimates based on combined climatological and epidemiological data.

#### Alternative aerosol propellants

32. In an investigation on the use of demethylether (DME) as an alternative propellant, very promising results have been obtained. DME is decomposed so quickly in the troposphere, that it is unlike to change the ozone layer to any significant extent. Using the current type of aerosol spray cans, no detectable amounts (< 1 ppm v) of peroxides are formed from DMA so that the possibility of explosions can be ignored. If DME is used together with current chlorine-containing types of disinfectants, no detectable amounts (< 0.1 - 1 ppv) of bis (chloromethyl) ether are formed. Chronic toxicological studies have not yet been completed, but no harmful effects of DME have been found so far.

#### Norway

##### Ozone Measurements

33. Observations of total ozone with Dobson spectrometers are done at three different locations of which Trömø at 70° N latitude is the northernmost location. These observations will in the near future be supplemented by Umkher observations in order to obtain information of the vertical distribution of ozone in the stratosphere over Norway.

##### Modelling

34. 1 - D and 2 - D modelling work on the trace gas distribution in the troposphere and stratosphere is performed at the University of Oslo. The 1 - D model is in particular used to investigate future depletion of stratospheric ozone due to halocarbons as a result of interaction with other chemical species influenced by human activities (CO<sub>2</sub>, N<sub>2</sub>O). 2 - D global modelling has first of all been concerned with tropospheric ozone generation due to the release of nitrogen oxides and hydrocarbons from ground level sources, and due to the release of NO<sub>x</sub> from subsonic aircraft. In the former case, the calculations indicate that the increase in tropospheric ozone is sufficient to lead to a noticeable increase in total ozone in the Northern Hemisphere (~ 1% at present). In the latter case future increases in air traffic (FAA high estimates) may also affect total ozone. The global 2 - D is also used to estimate fluxes of F 11, F 12, F 22 and CH<sub>2</sub>CCl<sub>3</sub> into the stratosphere, and their contribution to the stratospheric chlorine content. While F 11 and F 12 increase Cl<sub>x</sub> by 0.6 - 0.7 ppb in the upper and middle stratosphere (1980), methyl chloroform is estimated to add another ~ 0.2 ppb to Cl<sub>x</sub>. Release of methyl chloroform

have increased rapidly over the last years, and will probably continue to increase in the future. It is therefore likely that it will have increasing importance for the ozone depletion problem in the future.

#### UV-B radiation

35. Theoretical studies of changes in UV-B radiation as a result of ozone reduction are also performed at the University of Oslo. It has been shown that the change is dependent on the action spectra, on latitude and season. For a certain reduction in ozone, the change in UV-B radiation increases towards higher latitudes. This effect becomes more pronounced when the action spectra is shifted toward shorter wavelength (e.g. the DNA action spectra). At low and middle latitudes the ratio of UV-B increase to ozone depletion is  $\approx 2$ , while at high latitudes it is  $\approx 2$ .

#### Regulatory Measures

36. Norway has prohibited the manufacture and import of aerosol cans or the like where completely halogenated CFC's are employed as propellants. There is, however, a general exemption for medicinal products. The ban will come into effect 1 July 1981, and so far there seem to be only minor problems for industry related to the prohibition.

#### United Kingdom of Great Britain and Northern Ireland

37. A continuing programme of research is maintained in the UK including atmospheric measurements, chemical kinetic studies and numerical modelling. Overall assessment of the ozone depletion problem is also carried out.

#### Atmospheric Measurements

38. Ground-based measurements: Ground based equipment has been developed by the Meteorological Office for determination of total column  $\text{NO}_2$ , by measuring the differential attenuation of sunlight across the spectral range 435-350 nm. Values of the total  $\text{NO}_2$  in the vertical column observed at Bracknell have been in the range  $0.5$  to  $5.0 \times 10^{16}$  molecules  $\text{cm}^{-2}$ . Routine observations of total column ozone are being maintained by the Meteorological Office at Bracknell, Lerwick, Mahé and St. Helena, and the British Antarctic Survey continues to operate three Dobson instruments at high southern latitudes. UK scientists have taken part in the inter-comparisons of Dobson instruments organised by the WMO in 1978 and 1979. The results of a 3-year study of CFC 11 and  $\text{CCl}_4$  measurements made at Harwell showed a growth of CFC 11 of 1.1 ppt (parts per  $10^{12}$ ) per month over the period 1975-1977 consistent with a 50-yr atmospheric life-time (i.e. insignificant tropospheric sink). The  $\text{CCl}_4$  data showed no evidence for a natural source. Measurements have been made by Harwell of CFC 21 ( $\text{CHFCl}_2$ ), CFC 22 ( $\text{CHF}_2\text{Cl}$ ),  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_3\text{Br}$  and  $\text{C}_2\text{F}_5\text{Cl}$  by GC/MS techniques.

#### Aircraft-based measurements:

39. Aircraft-based measurements: The system formerly used by Harwell for collection of atmospheric samples from the troposphere and lower stratosphere using British Airways Concorde aircraft has now been replaced for operational convenience by one using a chartered Lear-jet 35 aircraft.

The final results obtained using Concorde included measurements of methyl bromide,  $\text{CH}_3\text{Br}$  of 10 ppt in the lower stratosphere compared with 20 ppt in clean tropospheric air. An airborne gas chromatograph has been flown on the C130 Hercules research aircraft of the Meteorological Research Flight (MRF) capable of detecting  $\text{CFC1}_3$ ,  $\text{CF}_2\text{C1}_2$ ,  $\text{CH}_3\text{CC1}_3$ ,  $\text{CC1}_4$ ,  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . The instrument has been flown in Saharan dust plumes, to detect possible  $\text{CFC1}_3$  destruction but with inconclusive results so far. Measurements of stratospheric water vapour content, up to 140 mbar pressure level, continue to be made by frost point hygrometry on the MRF Canberra aircraft. Investigations have been made to study the annual variation, and the meridional gradient from  $40^\circ\text{N}$  to  $70^\circ\text{N}$ .

40. Balloon-borne measurements: Harwell is cooperating with the stratospheric balloon programme carried out by the Max Planck Institute for Aeronomie, Lindau (FGR) in providing highly sensitive Gas Chromatograph-Mass Spectrometric (GC/MS) analysis of some samples. Main achievements to date have been the measurement of stratospheric profiles of  $\text{CH}_3\text{C1}$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{CF}_3\text{C1}$  up to an altitude of 32 km. The NPL took part in two successful launches of the joint UK/Italy submillimetre and Infra-red Experiment (SIBEX) have been made from the National Scientific Balloon Facility, Palestine, Texas, in November 1978 and April 1979. The two flights were planned to coincide closely with overpasses of the NIMBUS 7 satellite during the early and final stages of the LIMS (Limb Infrared Monitor of the Stratosphere) experiment. Profile concentrations have been obtained for  $\text{HNO}_3$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CF}_2\text{C1}_2$ ,  $\text{CFC1}_3$ ,  $\text{HF}$  and  $\text{HCl}$ , providing valuable 'ground truth' data in support of the satellite experiment. Further evaluation of the extensive amount of data gathered is proceeding. A third SIBEX flight by IROE/NPL will be made during the latter half of 1982. A further balloon-borne experiment NOBLE (Nitrogen Oxide Balloon Experiment) directed at simultaneous measurements of  $\text{NO}_x$  and the halocarbons is planned by NPL in collaboration with Department of Atmospheric Physics at Oxford University during the spring of 1981. It will record by infra-red techniques improved vertical profiles of  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{CF}_2\text{C1}_2$  and  $\text{CFC1}_3$  simultaneously and will be flown from NSBF, Palestine, Texas, together with a PMR (Pressure Modulated Radiometer) provided by Oxford University measuring  $\text{NO}$  and  $\text{NO}_2$  and possibly  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$ .

41. Rocket and Satellite Measurements: A rocket experiment to observe the diurnal variation of ozone in the height range 45-65 km was successfully carried out by the Meteorological Office in October 1979. The stratospheric and mesospheric sounder (SAMS) operated by Oxford University on Nimbus 7 is providing information on the concentrations  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{NO}$ , as well as temperature, in the stratosphere and mesosphere as a function of height.

#### Chemical Kinetics

42. At Harwell the technique of molecular modulation U.V. spectrometry has been employed to obtain kinetic and mechanistic information on the following reactions involving  $\text{ClO}_x$  and  $\text{HO}_x$  species.

The reaction  $\text{ClO} + \text{HO}_2 \longrightarrow$  products; the overall rate coefficient for this reaction has been determined at 298 K and 1 atm (760 Torr) pressure. The value is in agreement with other measurements obtained at low pressures (-5 Torr). The results imply a minor or negligible role for this reaction in converting active  $\text{ClO}_x$  species to  $\text{HCl}$  in the stratosphere.

The reaction  $C10+C10 \longrightarrow$  products; the temperature dependence of the overall reaction leading to the products  $C1_2 + O_2$  was determined. Kinetic complications due to the formation of the addition product,  $C1_2O_2$  were encountered, and the observed temperature dependence is incompatible with the kinetics and thermodynamics of the alternate channel in this reaction, leading to  $C1 + C100$  as products.

The reaction  $OH + HO_2 \longrightarrow H_2O + O_2$ ; This reaction is being studied by observing  $HO_2$  and  $OH$  radicals in the photolysis of  $O_3-O_2-H_2O$  mixtures at  $303^\circ K$  and 1 atm pressure. Work is continuing in an attempt to resolve the differences between previous studies of this reaction since it plays a major role in determining  $HO$  and  $HO_2$  densities in the stratosphere. At Cambridge University the study is continuing of the reactions of  $HO_2$  radicals relevant to atmospheric ozone chemistry. In addition to the continuing use of laser magnetic resonance spectroscopy a new technique is being developed involving diode laser spectroscopy and flash photolysis with which it should be possible to study reactions of  $HO_2$  over much wider pressure ranges than hitherto.

#### Numerical modelling

43. The Harwell 1D model has been updated with the recent CODATA set of rate constants together with the recently revised value for the  $OH + HO_2$  reaction published by De More. A steady-state ozone depletion of 15% is calculated for continuing CFC emissions at the 1976 rate, as given in Pollution Paper 5, and this estimate has recently decreased significantly to 10.7% due to a revision of the  $OH + HNO_3$  rate coefficient. The Harwell two-dimensional tropospheric model has been used to investigate the behaviour of those halocarbons emitted by man's activities which have significant sinks due to reaction with tropospheric hydroxyl ( $OH$ ) radicals. It appears that the tropospheric measurements, atmospheric release rates and  $OH$  reaction rates for methyl chloroform are consistent with present estimates of the tropospheric  $OH$  distribution and a methyl chloroform lifetime of about 5 years. The stratospheric ozone depletion estimated to result from the continued release of methyl chloroform at present rates is likely to be about 1 per cent in steady state. A radiative-photochemical column model has been used by the Meteorological Office to calculate the effects of CFC releases and  $CO_2$  emissions from fossil fuel burning on the ozone layer, separately, and in concert. Also, a two dimensional circulation model with photochemical reactions has been used by Oxford University to investigate the effect on the ozone layer of doubling the  $CO_2$  content of the atmosphere and of increasing chlorofluorocarbons. The effects are not linearly additive, because of the effect of temperature on the ozone concentrations. The upper atmosphere dynamical research group of the Meteorological Office is mainly involved at present in modelling and observational study of dynamical processes in the stratosphere and mesosphere. A three-dimensional primitive equation model is being developed for use in the theoretical studies, which are being carried out with the aid of data retrieved from the Meteorological Office's Stratosphere Sounding Units (SSU) currently on board the TIROS-N and NOAA-6 Satellites. Sudden warming events are the main topic of current effort, but later work will also be directed towards study of the transport and chemistry of minor constituents. Also at the Meteorological Office a diagnostic study has been made of the global distribution of ozone and water vapour in a general circulation model with 13 levels from 900 to 2 mbars. The fluxes of

water vapour across the tropopause have been examined, and trajectories calculated. A global OH distribution has been computed from the model fields of ozone, water vapour and  $\text{NO}_x$ . Longitudinal variations and their relative phases, were shown to be important. This three-dimensional model is to be used to interpret data from the HALOE instruments, planned for satellite use by NASA Langley Research Centre. Joint studies carried out by the University of Oxford in conjunction with Harwell have concentrated on the relationship between ozone depletion and the subsequent change in UV-B dose at the earth's surface. A factor of two is usually assumed in the relationship between ozone depletion and increased UV-B dose. Two-dimensional model studies of CFCs show that the ozone depletion is markedly seasonally and latitudinally dependent and that the simple factor of two no longer applies.

#### Assessment

44. A comparison of recent USA and UK reports on the impact of chlorofluorocarbons on stratospheric ozone is currently being carried out. This comparison includes the US National Academy of Sciences (NAS) and National Aeronautics and Space Administration (NASA) reports together with that of the UK Stratospheric Research Advisory Committee (STRAC). Although there are some minor differences there are no major discrepancies between the ozone depletions calculated from the various modelling studies. However, there are considerable differences of opinion over the degree of confidence which can be attached to the predicted future depletion deriving from the degree to which the models successfully simulate current atmospheric composition.

Contributions received from other countries too late for inclusion in Annex 3 will appear in an Addendum.

#### World Health Organization

45. The representative of WHO informed the Committee on WHO consultations on the monitoring of health effects of ultraviolet radiation held in Geneva, 16-20 June 1980. The recommendations adopted at the meeting, include proposals for coordinated studies to assess the relationship between human exposure to solar ultraviolet radiation and the development of non-melanoma and melanoma skin cancer, with particular emphasis on the establishment of dose-response relationships. Well planned and continuing surveys of non-melanoma skin cancer are needed, particularly in areas of high and low latitudes. Carefully recorded data on a large number of patients with malignant melanoma should be collected and analysed, with emphasis on patterns of sunlight exposure, histologic type, location of lesions, hereditary skin type and on effects of known or suspected associated factors other than UVR (i.e. chemical, occupational, residential, social, etc.). A plan of action for the study and list of participating institutions and experts has been prepared for submission to UNEP for possible financing of the project in 1981-1984. The published WHO/UNEP/IRPA Environmental Health Criteria document on ultraviolet radiation gives all available information for the evaluation of the health risks of ultraviolet radiation and could be updated in the future with UNEP assistance. Cooperation of national institutions in the development of appropriate international programmes are essential due to the limited resources available for such activities in WHO.

World Meteorological Organization

46. WMO continued its role of encouraging, promoting and facilitating observational and research activities of WMO members and summarizing and disseminating relevant results on various aspects of the World Plan of Action on the Ozone Layer. WMO aims at assisting in integrating and interacting between different measurement and other scientific groups.

Total Ozone

47. As called for in the World Plan, WMO has continued its work during 1980 in upgrading, re-activating and re-locating suitable Dobson spectrophotometers. These efforts, combined with appropriate intercomparisons, continuing over a period of years have resulted in a significant improvement in the global total ozone monitoring network, both in terms of data quality and coverage. A Meeting of Experts on the Assessment of Performance Characteristics of Various Ozone Observing Systems (Boulder, 29 July - 2 August 1980) was organized to discuss, inter alia, existing technical procedural criteria for standardization, validation and intercalibration of observing systems. A system for the integration of various observation techniques into a global ozone observing system (GOOS) was suggested, as a means of co-ordinating the various ozone measuring efforts obtained by a variety of measurement techniques. The proposal was prompted by the need for a continuous flow of reliable, total and vertical ozone data forming a coherent set to provide adequate answers to acute ozone study questions primarily for use in satellite reduction and detection of trends. The GOOS, as envisaged would be based on the existing network of ozone measuring stations. Members of WMO, operating Dobson spectrophotometers, are being urged to submit their data to the World Ozone Data Center in Toronto, Canada. It is suggested that it is important that they supply a list of all corrections applied, and the date(s) of application, for inclusion in the relevant WMO publication. A manual for operating Dobson spectrophotometers was prepared for the IGY (1956) which, in many aspects of modern calibration techniques, has become obsolete. With this in mind and as part of the activities within the WMO Ozone Project, Mr. W. Komhyr (NOAA, USA) has prepared a comprehensive operations handbook on ozone observations with Dobson instruments.

Vertical Ozone

48. Following the successful international rocket-borne ozonesonde, inter-comparison (September-November 1979, Wallops Island, USA) supported by FAA, NASA and NOAA, with the participation of Australia, Canada, India, Japan, and USA, WMO organized an expert meeting in May 1980 in Tokyo to assess the data from the comparison and initiate further studies to correct and revise historical rocket ozonesonde data as a coherent set. During the ozonesonde comparison organized by WMO in Hohenpeissenberg in April 1978, countries using various types of ozonesondes participated, with the exception of India. At a recent session of the International Ozone Commission of IAHAP (August 1980) it was strongly recommended that the Indian ozonesonde be compared with an instrument that took part in the Hohenpeissenberg comparison. In this connexion, WMO arranged for a series of comparisons between the Indian and Federal Republic of Germany ozonesondes in Hohenpeissenberg in early November 1980. Additional EEC comparisons are planned for Summer 1981 in Wyoming, USA. Scientists in the USA and Canada (J. DeLuigi and C. Mateer respectively) have developed

jointly a method of taking Umkehr observations which shortens the time necessary for the observation from more than three hours to about one hour. WMO has arranged for a comprehensive review on ozone measurements from satellites, including data availability. This will be available for distribution in 1981.

#### Rare species of importance to ozone layer

49. WMO organized an informal meeting of experts on rare atmospheric constituents of importance to the ozone layer in Washington, D.C. (March 1980). The nineteen experts from six countries reviewed advances in both theoretical studies and measurement needs in view of the anticipated and desired measurement capabilities, including satellites. The meeting stressed the need for co-ordination between groups as regards choice of observation time, location, type of measurements, accuracy and so on.

#### Ozone Models

50. At the meeting of experts on stratospheric circulation and analysis held in July 1979, it was strongly recommended that work should continue on 1-D, 2-D and 3-D ozone models as it had been demonstrated that each type had an essential role to play in stratospheric research. Consequently, an expert review meeting on 2-D ozone models was held in Toronto in January 1980. On this high priority subject, the meeting reviewed the state-of-the-art and identified critical deficiencies. The experts then discussed scientific objectives and foundations and the current understanding of the theoretical basis of the 2-D models as well as the need of data on atmospheric rare constituents. The report of the discussion will form the basis of a comprehensive survey on ozone modelling which will be available in 1981. In this field, it is felt necessary to continue encouraging comparative reviews of ozone models.

#### Impact on climate variability

51. Studies on this subject with respect to ozone have been encouraged within the WMO Ozone Project as a contribution to the WMO World Climate Research Programme (WCRP). A review paper on the possible impact of ozone variability and other rare species on climate is being prepared. The greater relevance to surface temperature changes of projected increase in tropospheric ozone concentrations is being revealed. The type of studies are long-term and advances would depend very much on the development of the global climate models which is one of the tasks of the WCRP. The work of the WMO Ozone Project in this field would continue in collaboration with the International Ozone Commission of IAMAP.

#### Organization of Economic Co-operation and Development

52. The OECD has prepared a report to serve as a basis for discussion on the chlorofluorocarbon/ozone reduction issue at the December 1980 meeting of the Environment Committee. The report was prepared in part by member nations and in part by the secretariat and is intended to be a summary of currently available information. The report covered, atmospheric chemistry and physics, health and environmental effects, trade and production data, technologies available for reducing use emission of CFCs and national and international activities and regulatory actions concerning CFCs. Future activities, if any, will be determined by the Environment Committee of the OECD in December 1980.

Commission of the European Community

53. The Commission is of the opinion that general critical comparisons between results of models and of the observations obtained in different countries are very useful for a further assessment of ozone layer depletion. The key question is to know whether there can be any appreciable difference between the calculated amount of ozone depletion and the actual response by the atmosphere to the effect of CFCs. The Brasseur report commissioned by the CEC gives such a reflection on the validation of the models and the method of formulating the problem. The Commission intends to continue in this sense its participation in the ongoing activities relevant to the World Plan of Action on the Ozone Layer by organizing in the Department of Environmental Research next January, a workshop on the impact of CFCs on the ozone layer. The purpose of this workshop will be to provide individual scientists an opportunity to compare their respective methods and results and to arrive at an objective assessment in the field of CFCs and ozone depletion on the international level. The results of this workshop will be provided to UNEP and the CCOL.

Chemical Manufacturers Association

54. Production and release data for F11 and F12 have again been collected from the world CFC manufacturers and the data submitted separately to UNEP. These figures show that world CFC production peaked in 1974, and that the 1979 production was 17.5 per cent below the 1974 level, continuing the decline observed since that year. Indeed, USA production capacity has been reduced since 1974, as some plants have been closed down and dismantled. When this factor is combined with the production capacity limitation in the EEC, high growth scenarios for CFC-11 and CFC-12 for the short or medium term appear extremely unlikely.

55. Progress in the CMA studies of the science are reviewed in the following sections:

Atmospheric Lifetime Experiment (ALE)

56. Preliminary results from one and a half years of data indicate a trend-method lifetime for F11 of roughly one half of the lifetime due to stratospheric removal processes alone (cited in the MAS report 1979, P.64, Table 5.1). The error bars are, however, very wide, namely seven years to infinity at this stage. Three years of data will provide a much firmer estimate. The error in the alternative overburden technique is such that no meaningful lifetimes can be obtained with this technique at this time. Present computer models, in contrast to this real world experiment assume no destruction method for F11 and F12 other than stratospheric processes. If lifetimes one half those now assumed are considered, the calculated steady state ozone depletion would be reduced by 50 per cent. The original four ALE monitoring stations have now been in operation for over 24 months, and performance continues at a high level. Calibration checks have been completed on the first 18 months data. A fifth station on the Oregon Coast (Northwest, USA)

has been in operation since March 1980. The data record at this station for F11 has been obtained from parallel equipment since 1979, augmenting the data in the important northern hemisphere-temperate zone. An interlaboratory comparison of F11 and F12 measurements at concentrations in the 50 to 300 ppt. range has been completed. The 19 laboratories who participated in analyzing the same samples obtained widely differing values for the CFC content. This work illustrates the difficulties of measurement at such low concentrations, and confirms the conclusion from theoretical studies that trend type techniques for determination of lifetimes, where absolute calibration is not necessary, should be preferred to overburden techniques. In order to improve knowledge of release of F11, a study of rigid foam manufacture and use was undertaken and completed. The release estimates produced include the new recognition that F11 is retained in these closed-cell foams for more than 80 years (Brandreth and Ingersoll, June 1980, SPI, Strasbourg) rather than being lost at the time of increase of thermal conductivity as previously assumed. The results of this study remove some of the uncertainties in the ALE programme. (Note the release data submitted separately is based on McCarthy, et al, Atmospheric Environment, II, 491, 1977).

#### Ozone Trend Analysis

57. Recent statistical analysis shows that no detectable depletion of the ozone layer has occurred, and that real-world data can provide an early warning system for small significant changes in ozone concentrations that might occur in the future. Regulatory action can now be based on actual ozone measurement rather than theoretical models without incurring the substantial risk of large depletion previously thought to be associated with this approach. The analysis of ground-based (Dobson) and satellite ozone data for trends by the two separate U.S. statistical groups, funded by CMA, continues. One of these studies, both of which are currently directed toward reducing the uncertainty in the detection of any long-term trend regardless of cause, indicates that the data from 36 Dobson stations are consistent with a slight increase in stratospheric ozone for the period 1970-78. Instrument drifts, station-to-station variance and white noise have been quantified to give  $\pm 1.4$  per cent error limit. This is to be compared with the  $\pm 3.6$  per cent error limit previously estimated at the Harpers Ferry NASA Workshop (NASA Ref. Publication 1049, December 1979). The difference between the current calculated depletion of ozone by CFC-11 and CFC-12, and the observed trend is statistically significant. Either the depletion

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errors, concluding that there is a 1 in 20 chance that the true steady state depletion will lie outside the range  $16.5 \pm 11.5$  per cent. The magnitude of the errors involves an assessment of the reliability of the existing rate data and model assumptions, and "educated guesses" (NAS 1979, p.189) about then unknown chemistry. Other qualified assessments of the science (NASA Ref. Publ. 1049 DOE pp.15) chose not to place uncertainty limits on the depletion estimates. On the contrary, DOE explicitly stated that it was unrealistic to make such estimates (DOE pp.15, p.194, paragraph 407). Investigations over the past year have shown that small changes in certain model inputs can indeed have a large effect on calculated ozone depletion. Specific findings include firstly the large reduction in calculated ozone depletion resulting from new developments in peroxy nitric acid chemistry. When the smaller photolysis cross section of Molina, and a reasonable estimate for the  $\text{OH} + \text{HO}_2\text{NO}_2$  reaction rate based in recent work at SRI are included in computer models, the calculated steady state depletion is reduced to about 12.5 per cent. A faster rate for  $\text{OH} + \text{HO}_2\text{NO}_2$  (a possibility indicated by the SRI study) reduces calculated depletion to 8.1 per cent. This new chemistry also indicates reduced OH in the lower stratosphere, and a much improved fit with measurements for ClO concentration profiles and the ratio of  $\text{HNO}_3/\text{NO}_2$ . Secondly the dramatic effect of branching in the  $\text{HO}_2 + \text{ClO}$  reaction to give  $\text{HCl} + \text{O}_3$  on calculated ozone depletion is considered. If there is 10 per cent branching to  $\text{HCl} + \text{O}_3$ , a reasonable possibility at stratospheric temperatures, the calculated ozone depletion would be halved. Similarly, the reaction  $\text{OH} + \text{ClO}$  may give  $\text{HCl} + \text{O}_2$  as alternative products.

60. In the real world, other perturbations to stratospheric chemistry occur. The importance of including these perturbations in calculating the possible CFC effect has recently been recognized. An investigation of the coupling of the effects due to increasing  $\text{CO}_2$ , resulting from greater use of fossil fuel, and those due to continued CFC emissions indicates that depletion estimates are reduced by subtracting approximately 4 per cent from those calculated from CFC emissions alone. The full 2-D model being developed in conjunction with the U.S. Air Force Geophysical Laboratory is now operational including pertinent chemistry of the major oxygen, hydrogen, nitrogen and chlorine species. This model will allow a more realistic comparison of theory with atmospheric measurements, as well as exploration of the latitudinal and seasonal distribution of calculated changes in ozone. Calculations made with the DuPont 2-D model, for instance, indicate discrepancies between theory and measurement for ClO and HCl concentrations which are similar to those from current 1-D calculations. The expectations by NAS that the discrepancies in the 1-D model would be largely corrected by 2-D modelling, have not been realized. (NAS 1979, P.161).

#### Atmospheric Chemistry

61. The industry programme to elucidate stratospheric chemistry centers on species and reactions likely to impact the fluorocarbon ozone depletion theory, e.g. Cl, ClO, higher chlorine oxides, OH and  $\text{HO}_2$ , and on reactions which might constitute ozone production cycles. The pressure and temperature dependencies and product distributions of important reactions have received increased emphasis recently. An unusual temperature dependence has been observed for  $\text{ClO} + \text{HO}_2$ , implying two separate mechanisms operate for the reaction. As mentioned in the modelling section, in addition to the expected products,  $\text{HCl} + \text{O}_3$  have been suggested as products. Similarly, the products of the reaction

HO + C10 are C1 + HO<sub>2</sub> and possibly HC1 + O<sub>2</sub>. Both reactions are under study. The rate constant of the very important reaction HO + HO<sub>2</sub> and its pressure dependence is under study. Low and high pressure values of the rate constant that have been reported previously differ by at least a factor of 10. The reaction directly affects ozone depletion estimates. The programme recently funded a critical analysis of stratospheric chemistry, with a special effort to define studies needed to improve the kinetic and photochemical data base used as input to the computer models. The analysis points out a large amount of important information does not exist or cannot be considered reliable without additional study. The Fluorocarbon Project Panel intends to use the analysis to guide future research. The study of the decomposition of F11 and F12, and selected chlorohydrocarbons on Tunisian sand show that under the conditions studied, the relative stabilities were as follows: CF<sub>2</sub>C1<sub>2</sub> > CFC1<sub>3</sub> > CC1<sub>4</sub> > CH<sub>3</sub>CC1<sub>3</sub>. Both light and dark decomposition reactions were identified. The rate of decomposition decreases with moisture concentration, and no decomposition of CFC-11 or CFC-12 is observed at 35 percent relative humidity and 20°C. Measurements of F21, a possible decomposition product of F-11, in air blowing from desert regions, is encouraging evidence for this decomposition process and will be followed up. The CMA programme of research in chemistry, modelling and measurements is continuing at an increased level of funding through 1980 and 1981.

ANNEX 3  
Addendum

REPORT OF CANADIAN OZONE LAYER RESEARCH ACTIVITIES  
TO UNEP CO-ORDINATING COMMITTEE ON THE OZONE LAYER  
OCTOBER 30, 1980

Stratoprobe balloon measurements indicate that ozone depletions will probably be about 10 percent rather than 20 percent if fluorocarbons continue to be used at current rate. This is based on low hydroxyl densities in lower stratosphere inferred from measurements of nitrogen constituents. As well, current ozone depletions appear to be less than 1 percent from Canadian ozone monitoring network. This also supports view that long-term depletions will be less than 10 percent, since current model projects estimate 1980 depletions of over 2 percent accompanying the long-term reductions of 20 percent. In ozone monitoring area, Canada has continued to operate ozone network of 5 stations with total ozone measurements daily and ozonesonde flights weekly. New Mark II Brewer ozone spectrophotometer has been developed and is now ready for commercial production. An interference of SO<sub>2</sub> on Dobson total ozone measurements has been discovered and measured on a daily basis at Toronto with Brewer spectrophotometer. Typical ozone interference amounts by SO<sub>2</sub> are 5 to 6 Dobson units at Toronto. Many of the Dobson network instruments in urban locations must be affected seriously by SO<sub>2</sub> interference and network should be evaluated for this problem. Large amounts of SO<sub>2</sub> from Mt. St. Helens eruption were observed at Toronto several days after the eruption in May. Effects of SO<sub>2</sub> from volcanic eruptions on Dobson network should also be evaluated particularly in reference to ozone trend analysis.

ANNEX 4

ASSESSMENT OF OZONE LAYER DEPLETION AND ITS IMPACTS,

NOVEMBER 1980

PRESS RELEASE

The UNEP Committee on the Ozone Layer met in Bilthoven 11-14 November 1980 for its fourth session. The Committee examined the substantial contributions presented to it by various countries and organizations and the research efforts in measuring and modelling necessary for the study of the stratosphere. On the basis of existing and new information available the Committee concluded as follows:

1. A risk of depletion of the ozone layer due to chlorofluorocarbon releases is still most likely, although in future other halogenated compounds which can reach the stratosphere, require increased consideration.
2. If chlorofluorocarbon releases continue at the existing rate, present model calculations estimate an ultimate ozone depletion of about 10 percent, compared with a figure of 15 percent estimated in last year's report. The change from the 1979 figure is due to new data on some chemical reaction rates. (Principally the reaction between hydroxyl radical and nitric acid).
3. No evidence of change in ozone attributable to human activity has been observed. According to the model calculation, a total ozone depletion of about 1% should have already occurred, but such an amount cannot be detected directly with present technology.
4. Significant progress has been made to perform more realistic model calculations which show latitudinal and seasonal variations that must be considered when evaluating the health and environmental effects of changes in the ozone layer.
5. Figures from the chemical industry show that world production of chlorofluorocarbons 11 and 12 has decreased between 1974 and 1979. Uses in aerosol has declined but other uses for example in refrigerators and foamed plastics have shown an increase. It is recognized that in a few years time, reduction of CFC use in aerosols could be ~~offset~~ by growth in non-aerosol uses. There are also indications of increased production of other chlorine containing compounds which could affect the ozone layer.
6. The relatively large natural variability of atmospheric ozone makes detection of long-term trends difficult. The Committee therefore recommended that existing satellite and well-kept ground based ozone observing systems should be integrated through a Global Ozone Observing System (GOOS).

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7. If stratospheric ozone decreases, more solar ultraviolet radiation, in the UV-B-range, will penetrate to the earth's surface. The health and biological effects to be expected from such an increase of ultraviolet radiation formed one of the main topics of discussion at the meeting. Most of the known effects of UV-B are damaging effects, so that there is concern for the consequences. There is broad agreement that an increase of solar ultraviolet radiation would lead to an increased incidence of non-melanoma skin cancer in light-skinned people. Recent research results indicate, that many terrestrial plants, including important crops, and many aquatic organisms, including shrimps and fish eggs, may also undergo damage by increased UV-B though further investigations are needed to establish the overall ecological effects.
3. The Committee emphasized the importance of Member countries and international organizations such as WMO, with the support of UNEP, continuing co-ordinated studies on the ozone depletion problem.