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on the Ozone Layer
Sixth session

Geneva, 5-8 April 1983

REPORT OF THE SIXTH SESSION

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I. OPENING OF THE SESSION

1. The sixth session of the Co-ordinating Committee on the Ozone Layer was opened at 10 a.m. on 5 April 1983 by Mr. Francesco Sella, Acting Director of the UNEP Environmental Assessment Service and Chairman of the Co-ordinating Committee on the Ozone Layer, in the Palais des Nations in Geneva.

2. Welcoming the participants, Mr. Sella noted that the sixth session was planned to be shorter than the fifth session as correspondence from members had indicated that no radical departure from the assessment agreed at the fifth session was expected. After introducing the agenda, he drew attention to the request made to the Committee by the Ad Hoc Working Group of Legal and Technical Experts for the Elaboration of a Global Framework Convention for the Protection of the Ozone Layer for recommendations or advice on scientific and technical matters. He suggested that the Committee might wish to comment on a special paper concerning the possible contents of annexes and/or protocols to a framework convention for the protection of the ozone layer, which was currently being elaborated by the Working Group. The Chairman pointed out the provisions of the World Plan of Action on the Ozone Layer, which required the Committee to consider the socio-economic implications of ozone layer protection measures. He said that that question could not be ignored, and proposed that it should be discussed at the seventh session.

II. DOCUMENTATION

3. A list of the documentation before the Committee appears in annex I.

III. AGENDA

4. The following agenda was adopted:

1. Opening of the meeting
2. Approval of the agenda
3. Presentation of recent research results and ongoing and planned research programmes and activities relevant to the World Plan of Action on the Ozone Layer
4. Assessment of ozone layer depletion and its impacts
5. Recommendations for future work relevant to the World Plan of Action on the Ozone Layer
6. Preparation of an executive summary of the assessment of ozone layer depletion and its impacts
7. Consideration of possible contents of annexes and/or protocals to a global framework convention for the protection of the ozone layer
8. Recommendations to the Ad Hoc Working Group of Legal and Technical Experts for the Elaboration of a Global Framework Convention for the Protection of the Ozone Layer
9. Press release
10. Any other business
11. Approval of the report
12. Closure of the meeting

IV. ATTENDANCE

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

Member States: Australia, Canada, Denmark, France, Germany Federal Republic of, Italy, Japan, Netherlands, Norway, Sweden, Switzerland, Union of Soviet Socialist Republics, United Kingdom of Great Britain and Northern Ireland, and 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

Organisation for Economic Co-operation and Development

Non-governmental organizations:

Chemical Manufacturers Association

International Council of Scientific Unions.

A full list of participants appears in annex II.

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

6. Presentations made by members under the above topic appears in annex III.

VI. ASSESSMENT OF OZONE LAYER DEPLETION AND ITS IMPACTS

7. The Committee formed three working groups which elected chairmen as follows:

Measurements and trends	R.D. Bojkov World Meteorological Organization
Chemistry and models	J. Chang United States of America
Effects	J.C. van der Leun Netherlands and M. Tevini Federal Republic of Germany

8. The working groups considered reports prepared by the working group chairmen of previous sessions on recent developments. On the basis of these reports, and the reports presented under agenda item 3, a draft assessment of ozone layer depletion and its impact was developed. The draft assessment prepared by the working groups was then considered by the Committee, and a consensus on a current assessment of the problem was obtained. The full text of the assessment appears below.

VII. ASSESSMENT OF OZONE LAYER DEPLETION AND ITS IMPACTS AS OF APRIL 1983

A. OZONE OBSERVATIONS

9. The ultimate test of the ozone depletion theory depends on the detection of long-term changes in global total ozone as well as vertical ozone distribution, which in turn requires a continuous and comprehensive flow of reliable data from the ozone observing system. Ground-based measurements form an important element of the system, both on their own account and by providing the ground truth for satellite-based systems, which can provide more comprehensive spatial information on both total and vertical ozone distribution. However, good ozone measurements are difficult to make, and their interpretation is subject to many uncertainties (e.g. long-term instrumental drift, as well as abrupt changes following the realignment and recalibration of instruments) and high natural variability (synoptic, seasonal, solar, etc.).

10. Total ozone. During the past decade, about half of the regularly operating Dobson ozone spectrophotometers have been upgraded and/or intercompared with either the world primary standard instrument located at NOAA in Boulder, Colorado, United States, or a regional (secondary) standard instrument. Most of the Dobson ozone data reported to the World Ozone Data Center (WODC) in Toronto are obtained from these instruments. The importance of these intercomparisons is reflected in the calibration errors discovered, which have exceeded 7 per cent in a few instances. Although shown by only a few instruments, these differences indicate the existence of stations at times generating data with large errors. The potential precision of a well-kept Dobson instrument network is estimated to be ± 1.5 per cent (95 per cent confidence level) for calculations of global annual means. The absolute accuracy of the network may be somewhat less than this, because of the uncertainty of the ozone absorption coefficients. However, this systematic error does not affect the calculation of trends. Drifting of instrument readings has been demonstrated, and frequent intercomparisons (once every three to four years) are therefore considered essential.

11. There is still room for improvement in the data obtained from the ground-based total ozone network - both in quantity and quality. There is spatially uneven distribution of the stations - about two thirds of the total number of stations are located between 30° and 60°N. More even distribution, more frequent instrument checks and increased regularity of observations (as described in the Ozone Observation Manual - WMO Ozone Project Report No. 6) could have a positive effect on the quality of the data.

12. Approximately a third of the existing ground-based stations do not report regularly to WODC, and therefore cannot be used in trend analyses. Of those which report regularly a significant fraction (approximately 20 per cent) provide data derived from lower-quality filter instruments. The International Ozone Commission has concluded that the performance characteristics of another instrument, the Brewer spectrophotometer, meet all observational requirements and will not distort the homogeneity of the network, and has therefore recommended its inclusion in the ozone measuring network, supplementing or possibly replacing some of the Dobson instruments.

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13. Over the past 15 years, several satellite-borne instruments have been developed to measure total column ozone. These instruments are based on measurements of the solar ultra-violet radiation back-scattered by the earth and the atmosphere (BUV, SBUV, TOMS) and nadir-emitted infra-red radiance in the 9.6 um band (IRIS, MFR, HIRS-2). The data which have been processed and validated are proving most valuable. Because of different laboratory absorption coefficient sets used by the satellite-borne ultra-violet instruments and the surface-based Dobson network, there is, for example, a systematic bias between nearly simultaneous Dobson and TOMS total ozone observations, with the Dobson data being 6.6 per cent higher on the average.

14. Because of their better spatial coverage and homogeneity of the observations, satellite systems are expected to play an increasingly important role in long-term observations of global total ozone content.

15. Because of absorption of solar ultra-violet radiation by sulphur dioxide, local pollution in urban areas and regional pollution in non-urban areas will produce Dobson total ozone measurements which are too high. Volcanic clouds also contain sulphur dioxide which will cause both BUV-type satellite and Dobson total ozone measurements to be too high. These effects require further study in order that the ozone and sulphur dioxide absorption effects may be separated and spurious results in total ozone trend determination thereby avoided.

16. Vertical ozone distribution. The model-predicted percentage depletion of the ozone concentration at upper stratospheric levels due to CFC releases alone is several times greater than the corresponding predicted percentage depletion of the total ozone amount. The increase of CO_2, predicted to cause cooling of the upper stratosphere, could augment ozone concentration there because of the temperature dependence of certain reactions, although to a lesser extent than would be necessary to compensate for the currently predicted depletion due to CFCs. Thus, data for these levels should provide the most sensitive information on ozone perturbations. Indications of continuously increasing tropospheric ozone with possible substantial climatic effects calls for more confirmative observations. These factors strongly support the argument for obtaining vertical ozone distribution data.

17. So far, ground-based Umkehr measurements represent the largest set of data for vertical ozone distribution. This set is especially useful for analysis of the 25-50 km region in the atmosphere. However, only about a dozen stations make these measurements regularly. A new "short" Umkehr multi-wavelength method, which saves considerable observer time, has recently been developed, and its use should be encouraged. Automation of a few Dobson stations, to facilitate Umkehr measurements, is being initiated during 1983. Further information of this type is also to be encouraged. LIDAR measurements in proximity to Umkehr stations are necessary for correcting for stratospheric aerosols from volcanic and other sources.

18. Direct measurements by balloon-borne sondes are needed for more detailed analyses of vertical ozone distribution, circulation studies, etc. The network of ozone sondes is known to be inadequate, as less than a dozen stations make weekly ozone soundings by balloon and only a few have continuous

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records for periods greater than 10 years. International intercomparisons of various types of operational ozone sondes have twice been conducted by WMO, in 1970 and in 1978-1980 at Hohenpeissenberg, Bavaria. Further comparisons are planned for June 1983 at Palestine, Texas. Efforts should be directed towards the continuation and improvement of balloon ozone sondes in parallel with the increase of indirect measurments of vertical ozone distribution by, for example, the Umkehr method, which are however inadequate below about 15 km.

19. Three solar ultra-violet satellite instruments (BUV, SBUV, SME) have been designed for obtaining information about the vertical ozone profile. In addition, two instruments (LRIR, LIMS) use limb scanning of emitted infra-red radiance in the 9.6 um ozone band for profile measurement, while another (SAGE) uses solar occultation in the visible regions. The data from these satellite instruments have been processed and validated, and are available from the United States National Space Science Data Center. Again, because of their good spatial coverage and homogeneity, these and other satellite systems may be expected to play an increasingly important role in observations of the ozone profile. Supported by Umkehr and other ground truth measurements, they provide the best means for the early detection of perturbations of the vertical ozone profile.

20. Rocket-borne measurements at present provide the only <u>in situ</u> data available for the upper stratosphere, and they are also necessary for comparison with satellite observations. About 60 recent intercomparative flights should enable an assessment to be made of data derived from previous rocket soundings, and this is expected to improve our knowledge, especially in the upper stratospheric ozone distribution.

21. New techniques using lasers (LIDAR and/or Heterodyne, etc.) with high-resolution or microwave soundings will contribute to the observing system of vertical ozone distribution. The microwave technique has the advantage of being unaffected by cloud interference. More precise laboratory measurements or spectroscopic parameters with both lasers and microwaves should be encouraged for reaching optimum design and implementation for ozone profile measurements.

22. <u>Global Ozone Observing System (GOOS)</u>. Careful assessment of the performance characteristics of the various ozone observing systems led to the conclusion that a continuous flow of reliable total and vertical ozone data forming a coherent set could be achieved by integrating the satellite-borne ozone observing systems and a set of well-maintained ground-based stations. This will offer the best basis for reliable trend determination, inasmuch as cross-checks between the two systems allow considerably higher precision in obtaining a valid global mean ozone value. In order to achieve full integration, there is a strong need for intercomparisons of routinely used ozone sondes with special high-accuracy instruments, in order to resolve certain remaining discrepancies in the 30-35 km region.

B. OZONE DATA ANALYSIS

23. The relatively large natural variability of atmospheric ozone complicates detection of trends. The ground-based Dobson network indicates that between 1958 and 1982, several periods of increases and decreases of ozone concentrations have occurred involving changes of one to several per cent,

each lasting several years. There are indications of a possible solar cycle variation which is as yet difficult to confirm with any statistical certainty. There is no evidence of an over-all change of more than 2 per cent in total ozone between 1958 and 1982. More refined statistical analyses of data from 36 Dobson stations show no evidence of a statistically significant trend from 1970 to 1981, when complete data records are tested against the hypothesis of no change before 1970.

24. Total ozone measurements from the Nimbus-4 satellite using the back-scattered ultra-violet (BUV) method show a time-varying discrepancy with data from the Dobson network. It is reasonably certain that an uncorrected drift remains in this satellite measurement. With this residual drift uncorrected, the satellite indicates an ozone decrease between 1970 and 1974 about 1 per cent larger than that shown by the Dobson network. Attempts to correct for the drift, by means of comparisons with the surface-based total ozone network, give results showing essentially no change in satellite-derived ozone amounts between 1970 and 1974, compared with the Dobson-indicated decrease of nearly 2 per cent. In future, because of the excellent spatial coverage of a satellite system, proper intercalibration with the Dobson network could permit a considerable improvement in estimates of the global total ozone amounts and trends. At least two studies have already used satellite and Dobson total ozone data to examine the representativeness of the Dobson network for calculating global means and existing trends. It is estimated that the error in the mean monthly global total ozone values so obtained should be no worse than 1 per cent.

25. Any potential influence on ozone amounts caused by chlorocarbons should be most apparent near 40 km, a height where photochemistry dominates transport effects. It is as yet uncertain to what extent the Umkehr-derived 10 per cent increase in the 32-48 km layer in north temperate latitudes between 1965 and 1970 is real (this may possibly be due to the tendency for a greater ozone amount to occur during periods of sunspot maximum), and to what extent it is artificial, resulting from the optical effects of aerosols injected into the stratosphere at the time of the eruption of Mt. Agung (1963) and their subsequent decrease.

26. In the same layer (32-48 km) there was an appreciable (about 4 per cent) decrease indicated immediately following the Mt. Fuego eruption in 1974. By 1979-1980 the ozone concentration in this layer had slowly reached about the same value as in 1973-1974, before the eruption. A study of the data for the 32-48 km layer from 13 Umkehr stations in the northern hemisphere indicates that no statistically significant change could be detected, when the data were tested against the hypothesis of no change before 1970. However, a study using the same data and making a statistical adjustment for aerosol effects indicated a downward trend of about -0.3 per cent per year in the Umkehr-derived ozone concentration in the 33-43 km layer. These results are preliminary and need to be treated cautiously because the aerosol adjustment was made assuming that atmospheric transmission data for this period from the only available station (Mauna Loa) could be applied to all Umkehr stations considered. Moreover, another statistical study using in part the same Umkehr data set reached the different conclusion that the globally averaged trend in

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the 33-48 km layer was 7.8 per cent per decade, with a 95 per cent confidence interval of ± 7.1 per cent. However, this particular statistical analysis failed to account for step changes in the record at four stations, and included unreliable data for some other stations.

27. Analysis of over 60 Umkehr measurements taken at Mauna Loa in the May-December 1982 period, after the eruption of the Mexican volcano El Chichón (April 1982), confirms that the optical effects of volcanic aerosols lead to underestimation of upper stratospheric ozone values in the Umkehr evaluation. It is essential to have LIDAR or other data on stratospheric aerosol distribution and to develop methodologies for correction of Umkehr evaluations. Satellite data from Nimbus 4 BUV show a marked downward trend for the same altitude layer between 1970 and 1977. However, a comparison of the ground-based data with the BUV data reveals a relative drift between the two data sets, because of the known BUV calibration drift problem mentioned earlier.

28. 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 indicate essentially no change in ozone amounts between 1970 and 1979, while the ozone sondes indicate an ozone decrease of a few per cent. Thus in this layer it is not possible to be sure of the actual ozone variation.

29. In the 2-8 km (tropospheric) layer, the ozone sondes indicate an increase of about 20 per cent in ozone between 1967 and 1981 in north temperate latitudes. The fact that a similar increase has been recorded 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 that the near invariance in total ozone in the last decade could have been associated with a partial balance between a possible stratopheric ozone decrease and the indicated tropospheric ozone increase. There is, however, a strong need for more detailed analysis and observations of tropospheric and stratospheric ozone data.

C. DETECTION OF OZONE TRENDS DUE TO HUMAN ACTIVITIES

30. With reference to the question of how well the effects of man-induced activity on any change in total ozone can be established, it is recognized that a reasonably accurate determination of trends in global total ozone can be obtained. However, since these sum all the effects in the individual layers, it does not necessarily follow that anthropogenic effects can be easily detected. The key problem is the relatively large natural variability in total ozone on all time scales. With a data record of only about 20 years, it is not possible to explain this natural variability with confidence. Consequently, anthropogenic influences, with the possibility of additional simultaneous positive and negative effects of different origin, cannot easily be delineated at present, even using sophisticated statistical techniques. However, the statistical estimation of trends in individual layers offers the possibility of a better diagnostic capability.

31. Three recent studies have estimated that ozone change for the decade 1970-1979, when the full data record is tested against the "no change before 1970" hypothesis, was a statistically non-significant increase of 1 per cent, with an uncertainty averaging ±1.5 per cent. The error limits (95 per cent confidence limits) reflect the natural, spatial and instrumental uncertainties that are revealed in the analysed data.

32. Recent developments in statistical methods show that at present, a trend of 2 per cent change since 1970 attributable to combined anthropogenic sources in the total ozone is the smallest that could be detected by the Dobson observing network. However, on meteorological considerations, taking into account possible influences and effects unrevealed by the statistical analyses, the threshold may be as high as 4 per cent. As the data record becomes longer, this statistical analysis for the detection of trends may improve in precision.

D. SOURCES AND SINKS OF TRACE GASES

33. Over the past few years we have become aware of a growing number of atmospheric trace gas species whose concentration has been increasing, at least in part as a result of man's activities, and many of which are expected to affect ozone by virtue of their involvement in tropospheric and stratospheric chemistry. The list of such species includes CFCs, other halocarbons, nitrous oxide, other nitrogen oxides, carbon monoxide, carbon dioxide and, as reported most recently, atmospheric methane. Of these, most information is available concerning the sources of CFCs 11 and 12 and CO_2.

34. The production of CFCs 11 and 12 by the companies participating in the CMA data collection programme was 637 kt in 1981, which represents a 21 per cent reduction from the 1974 level, with the bulk of the reduction occurring betweeen 1974 and 1977, and with a levelling off between 1980 and 1981. It is estimated that CMA production represents between 86 and 92 per cent of the total world production.

35. The CMA has, as in previous years, assessed world production by estimating production in countries and companies which do not participate in the CMA exercise. This is based on published data for 1968-1975 for one non-CMA producer, adjusted to try to take into account other non-CMA producers. A growth rate of 3 per cent from 1975 onwards had been assumed in previous estimates, but it was subsequently considered to be unrealistic. For the 1981 data set, therefore, a growth rate of 18 per cent, derived from the data for 1968-1975, was adopted. The latest data set, covering the years up to 1981, includes this correction applied retrospectively. The effect on the world production data published at the last meeting of CCOL is to leave the 1974 world production estimate at 851 kt a year, but to increase the 1980 figure from 696 to a 743 kt a year. Total world production for 1981 was estimated to be 760 kt a year. The change could be significant for F-12, especially when attempting to equate release rates and atmospheric burden. This emphasizes the desirability of finding an acceptable means of replacing the estimates for non-CMA producers by actual data in order to improve the estimates of global production and releases.

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36. The corresponding estimated global releases of CFCs, which have also been updated to include improved understanding of release patterns, fell 12 per cent from 770 kt in 1976 to 676 kt in 1981. Estimated releases have increased since 1980, and may continue to do so.

37. Atmospheric measurements of CFCs 11 and 12 have revealed a steady increase throughout the troposphere over the past decade. Such measurements are important in determining the accurancy of global release estimates, and can also be used to derive atmospheric lifetimes for CFCs 11 and 12. A network of five observing stations has been set up in locations remote from significant CFC sources, to acquire long-term data for CFC 11 and CFC 12 (together with carbon tetrachloride, methyl chloroform and nitrous oxide), with the specific objective of establishing atmospheric lifetimes. Analysis of the first three years' data from these stations by the trend technique has shown the atmospheric lifetime of CFC 11 to lie between 56 and 156 years (one sigma limits), with a central value of 83 years. For CFC 12 the lifetime lies between 81 and infinity years, with a central value of 769 years. Further atmospheric measurements, and particularly more accurate estimates of production and release, would help narrow the uncertainty limits. Nevertheless, the general agreement between observed and calculated lifetimes for CFC 11 indicates that a tropospheric sink is relatively unimportant. Preliminary analysis of an additional year's data for CFC 12 suggests some reduction in the central value, but not sufficient to indicate a significant tropospheric sink. There will be a continuing need to maintain a global measurement network of high quality for CFCs 11 and 12 together with other chlorocarbons, for a much longer period, to provide an independent check on release data.

38. No organization currently collects global production data for halocarbons, other than CFCs 11 and 12, that may affect the ozone layer. Extensive atmospheric measurement data are now available for methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4), but there are a number of other halocarbons that need to be considered in a full treatment. Approximate estimates of current production indicate that these substances increase the calculated steady-state ozone depletion by about a third of the depletion calculated for CFCs 11 and 12. Industry estimates suggest that the production of methyl chloroform was essentially constant for the years 1979 to 1981 inclusive, and the high growth in production observed in the 1970s has now ceased. There continues to be a clear need to acquire relevant global release data and to extend corresponding atmospheric measurements.

39. Recent studies indicate that the present atmospheric N_2O concentration is about 3 to 5 per cent above its pre-industrial value, and is increasing at a rate of about 0.2 per cent per year. It could increase by a further 5 to 7 per cent by the year 2000, depending on the level of agricultural production and increased fertilizer use. Emissions of NO_x from aircraft increased substantially up to 1975, and since then at a less certain rate.

40. Carbon dioxide is increasing as a result of combustion and deforestation at a rate of 1.5 ppm per year, and is expected to reach double the pre-industrial level by about 2030. Recently, some evidence of increasing

levels of atmospheric methane has been published. The present rate of increase would lead to a doubling of present concentrations by about 2010. However, the cause of the increase is unknown at present, and so is the likelihood of a continuing increase.

E. OZONE EFFECTS ON CLIMATE

41. Ozone, together with CO_2 and H_2O, is mainly responsible for the long-wave opacity of the atmosphere. Absorption of ultra-violet radiation by ozone is the main energy source for the stratosphere. The expected displacement of the ozone distribution to lower altitudes by chemical perturbations due to N_2O, NO_x and CFCs will lead to lower temperatures in the middle and upper stratosphere, and higher ones in the lower stratosphere, enhancing the effects of CO_2. If tropopause temperatures increase there may well be an increase in the stratospheric water vapour content, which in turn will feed back on stratospheric chemistry.

42. The increase in ozone concentrations in the lower stratosphere and upper troposphere may contribute significantly to the greenhouse effect. This may in future be enhanced by increases in tropospheric ozone production, which may result from increasing concentrations of CH_4, CO and NO_x due to anthropogenic activities. The reactions involved are difficult to model, but there is some observational evidence of tropospheric ozone increases over the past 15 years. A doubling of the tropospheric ozone content could lead to a surface temperature increase of almost 1°C, compared to 2-3°C for a doubling of CO_2.

43. The changes in energy depositions discussed above significantly alter the dynamics of the stratosphere. In turn, this may influence the stratospheric ozone and trace gas distribution. The magnitude of the latter effect cannot yet be quantified - hence the necessity to develop sophisticated, fully interactive 3D models. For this it will be critical to reach a better understanding of stratosphere-troposphere exchange processes.

44. Several of the trace gases which effect stratospheric ozone photochemically, especially N_2O, CH_4 and the CFCs, have strong absorption bands in the 7-13 um spectral wavelength region, the so-called atmospheric window. These gases enhance the greenhouse effect, and may lead to surface warming. The sum of the combined future effects from changes in the atmospheric content of these gases (including ozone) may add up to a surface temperature increase of about 1°C by the latter half of the next century.

45. Increased research efforts should concentrate on radiative-chemical and radiative-dynamical interactions between different trace gases which, in certain cases, could result in additive, and in other cases compensating radiative effects. These require, along with continuing stratospheric research, further studies of tropospheric chemistry and strato-tropospheric interaction, and clarification of the very complex role of ozone and other trace gases in the climate system.

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F. ATMOSPHERIC CHEMISTRY

46. During the last few years considerable progress has been made in the laboratory measurement of rate coefficients, cross-sections, primary quantum yields and product distributions for use in atmospheric modelling. There is now a better data base for reactions exhibiting unexpected temperature and pressure dependence of rate coefficients, but our understanding of the mechanisms is still inadequate. 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. Since the fifth session of CCOL, progress has been steady if less spectacular than during the preceding period. Perhaps the most significant changes have been in our improved understanding of the kinetic behaviour of OH, HO_2 and $ClONO_2$ species and the revision of the penetration to lower altitudes of stratospheric solar UV flux in the wavelengths between 195 and 220 nm. It is believed that the flux penetration was previously underestimated as a result of the use of erroneously high values for the molecular oxygen absorption cross-sections in this region of the spectrum. It should be noted that the correct values of the oxygen cross-sections are still not well defined.

47. 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 analysis of reaction products rather than relying solely on measuring the disappearance of reactants. This is particularly important for those reactions which may proceed via multiple reaction pathways. Investigations of reaction mechanisms over the full range of atmospheric temperatures and pressures are important, since extrapolation of results from outside this range is sometimes unreliable. The partial pressures of other gases such as water vapour or oxygen may occasionally affect reaction rates.

48. A systematic study of the processes which control the trace gas composition of the troposphere is necessary for investigation of many problems in stratospheric chemistry. The troposphere serves as a source region for a large number of gases that play important roles in the photochemistry of the stratosphere. Furthermore, tropospheric ozone contributes to the total ozone column and plays a significant role in the energy balance of the atmosphere. Since the concentrations of several of these gases are controlled by chemical sources and sinks in the troposphere, global changes in the chemical composition of the troposphere may alter the fluxes of these species to the stratosphere. The most important sink for many of these species is reaction with OH. Any large-scale changes in tropospheric OH densities may therefore affect fluxes of some source gases to the stratosphere. Significant progress has been made in understanding the couplings between the carbon/nitrogen/hydrogen/oxygen systems, as well as the details of the hydrocarbon oxidation mechanisms which play a vital role in controlling tropospheric hydroxyl radical and ozone concentrations. Since the fifth session of CCOL there have been several reports of an increase in atmospheric methane concentration in recent years. There is some evidence that a substantial increase in methane

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may have occurred over a much longer period. There is currently no satisfactory explanation for this increase. Consequently, there is an urgent need to improve our understanding of hydrocarbon cycles in the troposphere, and the way in which they affect the tropospheric hydroxyl radical and ozone concentrations.

49. Extensive chemical kinetics research has emphasized the importance of temporary reservoir species such as $HOCl$, HO_2NO_2, N_2O_5 and $ClONO_2$, which in the lower stratosphere act to lessen the efficiency of NO_x and ClO species in destroying ozone. The successive changes in calculating ozone depletion resulting from improved measurements of key coefficients remain a feature of the models and serve to emphasize the uncertainties in calculating ozone depletion. However, the period since the last CCOL session has seen smaller changes in calculated ozone depletion values than the preceding period. The current state of measurements for individual chemical "families" is discussed separately below, though it should be recognized that there is a strong coupling between them.

I. Odd-oxygen reactions (O_x)

50. The chemistry of the basic O, O_2 and O_3 system is well established, and there have been no recent changes in recommended rate coefficients. There is some experimental interest in the roles of excited states of O_3 or O_2, especially $O_2(^1\ )$, but at present there is no evidence that these states have any important effects on the over-all chemistry of the stratosphere. The data base for $O(^1D)$ reaction chemistry is considered reasonably sound. There remains a need for studies of the products of some radical-producing O(D) reactions, and work has been carried out on reactions with CFCs and N O.

51. UV radiation at wavelengths above 100 nm is absorbed by molecular oxygen between 100 and 240 nm and by ozone between 200 and 320 nm. O_2 and O_3 control the penetration of solar radiation into the atmosphere and therefore determine atmospheric transmissivity. In the O_2 Hersbergy continuum (180-220 nm) the data used for atmospheric studies are based on laboratory measurements made at high pressures and extrapolated to low pressures for stratospheric applications. Conventionally adopted values are inconsistent with recent observations of solar radiation flux in the stratosphere, however. O_2 cross-sections in this region, which are about a factor of 2 lower, would appear to offer a solution to this problem. If calculated solar fluxes in the lower stratosphere have indeed been underestimated, this would be important for other molecules such as N_2O, CCl_4, CF_2Cl_2 and $CFCl_3$, which are photodissociated in the 200 ± 20 nm region. Accurate values for ozone cross-sections at 200 ± 20 nm are required for solar flux calculations, because penetration also depends strongly on ozone transmissivity.

2. Odd-hydrogen reactions (HO_x)

52. The rate coefficients for reactions which control the abundance of and partitioning between the odd-hydrogen radicals (OH and HO_2) are required with high accuracy because of the central role that they play in controlling

the catalytic efficiencies of both NO_x and ClO_x cycles. Changes in the recommended rate coefficients for the reactions of OH with HNO_3 and HO NO were previously responsible for significant revisions of calculated ozone changes. Earlier work indicated unexpected pressure and temperature dependence of reactions involving the HO_x radicals. New results have been reported for the reactions of HO_2 with H, O, OH and HO_2 which lead to better characterization of the reactive channels and the pressure, temperature and water vapour dependencies of the rate coefficients. Although there are some outstanding problems in relating the new data base to chemical kinetics theory, the new data have been incorporated in the latest rate coefficent recommendations.

3. Odd-nitrogen chemistry (NO_x)

53. The kinetics data base for this class of reactions has also been significantly improved with new data for the reactions OH + HNO_3, OH + HO_2NO_2 and HO_2 + NO_2 + M. The negative temperature dependence for the OH + HNO_3 reaction is well established, but conflicting results have been reported for the temperature dependence of OH + HO_2NO_2, and the products of this reaction have not been identified. Moreover, the temperature dependence and products of the photodissociation of peroxynitric acid are not established. These gaps in the data base lead to some uncertainty in the description of HO_2NO_2 behaviour in the lower stratosphere.

54. Studies of the processes involving NO_3 and N_2O_5 mentioned in the last report are now under way. Data have been reported for the temperature dependent absorption cross-sections for N_2O_5, but new and much-needed kinetics data for NO_3 reactions have not yet appeared.

4. Odd-chloride reactions (ClO_x)

55. The overall kinetic data-base for ClO_x reactions has improved significantly in recent years. There has been a significant revision in our understanding of HOCl, $ClONO_2$ and other ClO_x radical-radical reactions. The important rate coefficients for reactions such as Cl + O_3, NO + ClO, O + ClO, Cl + CH_4 and OH + HCl have not changed substantially since 1977. In the reaction of Cl with HO_2, HCl is the major product but the channel producing ClO + OH is now known to be more significant than previously thought, while of little atmospheric importance. Recent kinetic studies of the HO + ClO and HO_2 + ClO reactions suggest that formulation of HCl is negligible, thus diminishing their potential importance in the stratosphere as chain terminators. The possible role of HOCl as a chlorine reservoir in the stratosphere is now thought to be minor in the light of recent improved knowledge of HO_x chemistry.

56. A major uncertainty at the time of the previous report was the problem of which isomers of $ClNO_3$ are formed in the ClO + NO_2 + M reactions, and how $ClONO_2$ photolyses. It has now been shown that the only isomer of significance is $ClONO_2$, and that "fast" rather than "slow" rate coefficients should be used for its formation.

One rate coefficient recommendation which has changed substantially is that relating to the Cl + $ClNO_3$ reaction, which is now known to be almost two orders of magnitude faster than previously believed. This change has little impact on modelling stratospheric chemistry, but is of significance with regard to the interpretation of laboratory experimental data on the photolysis of chlorine nitrate. The reinterpretation of earlier laboratory data for $ClONO_2$ photolysis is consistent with recent results from some direct studies which show that production of Cl and NO_3 is the dominant process at both 266 nm and 355 nm.

5. Hydrocarbon chemistry

57. The observed increase in atmospheric methane concentrations underlines the need to understand its chemistry in the atmosphere. In the stratosphere, the reaction $Cl + CH_4 \longrightarrow HCl + CH_3$ constitutes the main loss process for active chlorine. The dominant sink of methane is, however, its reaction with OH, leading to water vapour formation. The main intermediate product is CH_3O_2. The subsequent reactions in the methane oxidation cycle are less well known, and better information is needed about the reaction $CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$ and about reactions of CH_3O, especially with O_2, at stratospheic temperatures. Uncertainties in reaction kinetics and mechanisms exist for other hydrocarbons such as C_2H_6, C_3H_8 and C_2H_2, which are useful as tracers to test the transport and chemistry used in models. Ethane and propane oxidation leads to the formation of peroxyacetylnitrate (PAN), which is a sink for active odd nitrogen in the troposphere and lower stratosphere.

G. ATMOSPHERIC OBSERVATIONS

58. At present, and probably for the foreseeable future, heavy reliance must be placed on theoretical models in order to understand the atmosphere. However, these models must be checked against observations at all accessible points. A variety of in situ and remote sensing techniques are now being used to determine the atmospheric concentrations of a large number of chemical species either from the ground or from aircraft, balloon and rocket platforms. This type of data is required to test the radiative-chemical aspects of the models. A capability to measure several species globally from satellites has now been demonstrated, and such a data base will be required to test the chemical, radiative and dynamical aspects of multidimensional models. In the longer term, these field and satellite programmes will overcome our greatest problem, i.e. the shortage of data.

59. Before comparing theoretical descriptions of the present atmosphere with observations, it is vital to have an understanding of the accuracy and precision of observations. At present it is not always obvious whether differences between measurements of the same species, at different times, are due to measurement inaccuracy or to atmospheric variability. Consequently, a major effort is currently being made to intercompare numerous different instruments, using similar and dissimilar experimental techniques, which simultaneously measure a wide range of key atmospheric constituents in the same air mass. To date, there have been intercomparisons of:

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(a) Balloon-borne and rocket-borne ozone instruments;

(b) *In-situ* balloon-borne water vapour instruments; and

(c) 13 remote sensing balloon-borne instruments, using 8 different techniques including grating spectrometers, radiometers and Fourier transform interferometers, to measure some key atmospheric constituents including HNO_3, NO_2, NO, HCl, HF, O_3, N_2O, H_2O, CH_4, etc. These sensors utilized the visible, infra-red, far-infra-red and microwave regions of the electromagnetic spectrum in both the absorption and emission mode.

60. The data from these intercomparisons are currently being evaluated. Several additional intercomparisons of ballon-borne instruments are planned, including:

(a) *In situ* grab sampling techniques for source gases;

(b) *In situ* water vapour sensors,

(c) *In situ* and remote techniques for O_3;

(d) 18 remote sensing instruments, supported by ground-based and aircraft-borne instruments, for a large number of atmospheric constituents.

61. It is now well recognized that the simultaneous measurement of photochemically coupled species in the same air mass will allow a more critical test of photochemical theory than is provided by isolated measurements of single species. To date, there have been only a limited number of such simultaneous measurements with which to test theory. Once the quality of the data is understood from the various intercomparison campaigns it should be possible to make the type of measurements required to do so.

62. Within the next year, several newly developed *in situ* and remote sensing techniques should be available to augment existing instrumentation to measure nearly all key atmospheric species over a significant altitude range with the required accuracy and precision. An exception to this may be in the area of the temporary reservoirs, where there are no reliable measurements to date. However, for some of these species there is hope of utilizing the newly developed remote sensing instruments.

63. The only two parameters for which there are long-term extensive satellite and ground-based global data sets are ozone and temperature. However, the seven months' LIMS data (HNO_3, NO_2, O_3, H_2O, temperature), the first year's SAMS data (H_2O, N_2O, CH_4, temperature), the first two years' SBUV/TOMS data [O_3 (column and vertical distribution) and solar flux] and the first two years' SAGE data (O_3, NO_2, aerosols) have now been processed and the data are now archived at the National Space Science Data Center in Washington, United States. In addition, data from SME satellites (O_3, NO_2, aerosols and solar flux) are now becoming available. Significant scientific findings have already been derived from stratospheric satellite data: for example, the altitude dependence of the relative roles of transport and photochemistry; correlations between solar flux temperature and O_3; and the structure of planetary wave disturbances. To date, satellite data have not been fully utilized in studying physical and chemical processes. However, a large number of theoretical studies are currently in progress which should more fully exploit the potential of the satellite data.

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H. COMPARISON OF MEASUREMENTS AND MODEL CALCULATIONS

1. Odd-oxygen family

64. The oxygen species of interest in the stratosphere are ground state atomic oxygen $O(^3P)$, excited-state atomic oxygen $O(^1D)$, singlet molecular oxygen $O_2(^1\Delta)$ and ozone O_3. There exist only six profiles of $O(^3P)$ and one of O_2 $(^1\Delta)$ in the stratosphere. $O(^1D)$ cannot be measured in the stratosphere because of its low concentration. The relevant comparison for $O(^3P)$ measurements is the ratio $O(^3P)/O_3$. Comparisons of the measured ratios with those predicted by models show good agreement.

65. The data base of global ozone measurements is sufficiently large so that both seasonal and latitudinal changes such as the equatorial minima and high-latitude spring maxima in total column ozone are well known. An important feature is the different latitudinal behaviour of ozone in the southern hemisphere compared with the northern hemisphere. 2-D models have adquately simulated the altitude/latitude/seasonal distribution of ozone derived from ground-based observations and ozone sondes, mostly in the northern hemisphere. However, this data base is somewhat limited, and to date the newly available satellite data base has not been noted that this kind of agreement is often achieved after considerable numerical experimentation.

2. Odd-hydrogen family

66. Although the HO_x species play a central role in stratospheric photochemistry, knowledge of atmospheric concentrations of OH, HO_2 and H_2O_2 is inadequate. The available observations for both OH and HO_2 can do little more than demonstrate the existence of these radicals in the stratosphere and provide a crude picture of the altitude dependence of absolute concentration above 30 km. For lower altitudes, there are no data at present, and this is a serious gap in our knowledge. However, several techniques under development provide good prospects for improvement of this data base in the near future. The situation for hydrogen peroxide is even less satisfactory, since there are no positive observations of this species in the stratosphere and prospects for its detection in the near future are marginal. In the absence of detailed knowledge of OH, HO_2 and H_2O_2 there is no adequate test for the validity of HO_x chemistry in the models. Recent ground-based measurements of the total column of OH do reflect some constraint on this key species, and are indeed consistant with model predictions.

3. Odd-nitrogen family

67. The odd-nitrogen species considered important in the chemistry of the stratosphere are N, NO, NO_2, NO_3, N_2O_5, HNO_3, HO_2NO_2 and $ClONO_2$. Measurements have been made of stratospheric NO, NO_2, HNO_3 and NO_3. Tentative identification has been made of N_2O_5 and $ClONO_2$, and an upper limit of the abundance of HO_2NO_2 has been reported. Several measurement techniques have been used for each of NO, NO_2, and HNO_3. The data exhibit considerable scatter, and it is not possible to determine changes

in the vertical distributions of NO, NO_2 and HNO_3 with either season or latitude. It is not clear whether the scatter is instrumental or due to atmospheric variability. Diurnal variations of NO and NO_2 are well established. Column density measurements show seasonal and latitudinal variations for NO, NO_2 and HNO_3.

68. Model-predicted profiles of NO and NO_2 in the middle latitudes lie within the range of measurement. However, the variations in reported atmospheric concentrations are sufficiently large that comparison between observation and theory is not a critical test of model performance. In the middle latitudes the model predictions and observed concentrations of HNO_3 are still in disagreement, especially above 30 km. Significant variations of NO_2 and HNO_3 occur in the polar winter régime, and these variations are at present not quantitatively reproduced by any model calculations. The upper limit reported for HO_2NO_2 at approximately 30 km is significantly lower than model predictions. Generally, it appears that available measurements of NO_x species have yet to provide a critical test of model performance. However, the measurements of HNO_3 and the measured upper limit of HO_2NO_2 suggest inadequacies in model descriptions of the behaviour of these species.

4. Odd-chlorine family

69. Knowledge of atmospheric ClO has been improved recently by new ground-based microwave measurements. These largely confirm previous balloon-based vertical profile measurements, but both sets of measurements exhibit significant variability at all altitudes. There is no current explanation of this observed variability. The closest agreement between calculated and observed ClO occurs between 25 and 35 km, although the mean of observations falls nearly a factor of two below the model values at 25 km. Above 35 km, the calculated ClO abundance decreases rapidly with altitude, while observations show no evidence of a decrease, so that at 40 km the calculations are approximately a factor of 2 below the observed ClO. This is particularly disturbing since ClO_x catalytic destruction of ozone occurs principally in this region. Measurements of concentrations of atomic chlorine and the ratio Cl/ClO are limited but are broadly consistent with the expected photochemical partitioning between the active species.

70. Measurements of HCl consist of vertical profiles from 14 to 40 km supported by ground and airborne total column measurements. Observations show a variability within approximately a factor of three and the altitude of the maximum HCl abundance and any seasonal variations cannot be clearly established. Calculated HCl profiles fall towards the middle to high end of the observations up to about 30 km, but the data at 35 to 40 km possibly indicate an HCl mixing ratio (-2 ppbv) somewhat higher than calculated values. Recent observed latitudinal variations in the HCl column are modelled fairly successfully except near the equator. Calculated concentrations of the important temporary reservoir species, chlorine nitrate ($ClONO_2$) and hypochlorous acid (HOCl), remain below the detection limits for the observational techniques so far employed.

71. Total chlorine measurements indicate the presence of approximately 3 ppbv of Cl_x in the late 1970s, which is consistent with the measured in-situ concentrations of HCl and ClO at about 40 km. By comparison, model calculations, involving all major Cl precursor molecules, predict approx. 2.2 ppbv total Cl_x in the upper stratosphere.

5. Source gases

72. Except for H_2O, the behaviour of all the major source gases in the stratosphere is reasonably well understood. Vertical profiles at several latitudes have been obtained for H_2, N_2O, CH_4, CF_2Cl_2 and $CFCl_3$. While their individual rates of decrease in the vertical direction are different, they all exhibit the same general zonal and vertical distribution. In the tropics, the profiles show less vertical changes in the 10-35 km region than in the higher latitudes. There is significantly more scatter in individual data sets in the altitude range where transport and chemical lifetimes become comparable. Theoretical models seem to be able to represent the qualitative features of each source gas distribution, but not in all aspects of the available quantitative details. The most notable discrepancy is the underestimation of vertical fall-off. These differences have little impact on the over-all budgets of the trace species families NO_x, ClO_x and HO_x in the region of greatest interest. There are only a few mid-latitude CH_3Cl and CO vertical profiles available, and they are in general agreement with theoretical estimates. The lack of an extensive data base for these species prevents more refined analysis.

73. The distribution of H_2O in the stratosphere remains the most difficult to understand. Current theory fails to account for the fluctuation and distributions of stratospheric water vapour. The source of the difficulty appears to lie both in the data quality and in lack of theoretical understanding. It is expected that current efforts in H_2O instrument intercomparison will lead to an improved data base, which may lead to better understanding of this important source gas in the stratosphere.

6. Solar flux variability

74. Changes in atmospheric chemistry could be induced by solar flux variations between 100 nm and 240 nm where molecular oxygen absorbs; special attention must be given to the spectral region near 200 $\pm$ 20 nm (atmospheric window), where various molecules such as N_2O, CCl_4, CF_3Cl and CF_2Cl_2 are photodissociated. Although the total solar irradiance (solar constant) and its variations with solar activity can be measured with great accuracy from satellites, this is not the case for spectral irradiances in the ultra-violet regime above 100 nm. While the best calibrations give a precision of better than $\pm$ 10 per cent, examination of different sets of observations that are often regarded individually as satisfactory reveals consistent differences of $\pm$ 20 per cent and in certain cases as much as factor of 2. The most recent values obtained using rockets have mean values for 1 nm which generally differ by about 10 per cent. Data acquired over a period of time using satellites are inevitably influenced by changes in the sensitivity of the instruments, which must be determined in order to deduce variations

due to solar activity during a complete cycle. Without such information it is not possible to deduce the way in which solar activities varies at different wavelengths. However, the 27-day cyclic changes in solar activity can be clearly seen, ranging from about 1 per cent near 240 nm to 20 per cent near 180 nm. Longer-term cycles are not detectable in view of the uncertainty in the data base at present.

I. CURRENT STATUS OF MODEL PREDICTIONS

75. In the past two years there has been increasing realization that consideration of possible changes in ozone must include simultaneously the effects of several potential perturbing influences because of the strong chemical coupling between the various species involved. Because such complex calculations must include both radiative and chemical effecs, so far only one-dimensional (1-D) models have been applied to this task. Joint scenarious now include the effects of halocarbons and NO_x emissions from aircraft, and increasing atmospheric CH_4 concentrations have also been considered.

76. Nevertheless, for the purposes of understanding the role of a given species in such a complicated system, there is still some value in considering individual perturbations singly or in pais, especially as there is considerable uncertainty about future scenarious. Such calculations also permit simple investigation of changes brought about by revised rate coefficients or other model inputs. Many calculations of this type have been performed using both 1-D and 2-D models, and have shown that the global average results from 2-D models generally agree well with 1-D calculations. Thus such comparisons indicate the continuing value of making the more simple 1-D assessments.

77. When 2-D calculations are made, variations with latitude are seen in many trace gas concentrations at altitudes below 40 km. Latitude changes above that altitude are smaller because of the reduced importance of transport in that region. Consequently, variations in calculated ozone depletion are expected for most perturbations. For example, 2-D calculations considering only CFCs 11 and 12 give ozone decreases both in total column and locally at high altitudes which are greater at higher latitudes. Seasonal effects are also important, with most appreciable effects in winter in most models. For other perturbations considered alone or together, latitude variations have not yet been considered.

78. The most recent calculations for single perturbations show a smaller ozone reduction for chlorine perturbations and a slightly greater ozone reduction for odd-nitrogen perturbations. For example, the continued release of CFCs 11 and 12 in the absence of other perturbations gives a calculated ozone depletion in the range 3 to 5 per cent at steady state. The corresponding estimate at the fifth session of CCOL was 5 to 10 per cent. The verticale ozone column shows a reduction in the upper stratosphere of approximately 40 per cent peaking near 40 km as in previous results, and an increase in the lower stratosphere.

79. The "doubling N_2O only" scenario has not been recalculated recently, but is expected to give slightly greater calculated steady-state depletion than the range of 8 to 16 per cent quoted in the last report. The reduction occurs mostly in the middle and upper stratosphere.

80. It must be stressed that the ranges quoted above are indicative only of variations in the predictions from several models, and do not reflect the full range of uncertainty arising from limitations in our understanding of chemical reaction rates, absorption cross-sections, transport parameterization or other model inputs. Furthermore, uncertainty estimates cannot include such unquantifiable factors as unknown chemistry or factors at present difficult to quantify such as subtleties of transport descriptions and feedback mechanisms.

81. This revision in estimates from earlier reports results from many small changes in the chemical rate coefficients, of which changes in HO_x chemistry and adoption of the "fast" rate or formation of chlorine nitrate, $ClONO_2$, are most significant. The use of decreased values for the absorption cross-section of oxygen in the Herzberg continuum region also plays a role.

82. In addition to the above, attention must also be given to man-made perturbations by:

(a) Chlorine-containing compounds such as methyl chloroform, carbon tetrachloride and chlorofluorocarbons (e.g. CFC-113, CFC-114, CFC-115 and CFC-22). The calculated ozone depletion to date due to the combined effects of these compounds should be about equal to or larger than that due to CFC 11 and 12 alone. This reflects the substantial contribution from past emissions of CCl_4. The potential future growth in atmospheric releases of these compounds is difficult to assess, but estimates indicate that if releases continue at present levels they could increase steady-state ozone depletion over that from CFC 11 and 12 alone by about a third. Most of this enhancement is derived from the release of CCl_4, CFC-113 and methyl chloroform, with minor contributions from CFCs 114, 115 and 22. Methyl chloroform is of particular interest for ozone perturbations in the near future, as its atmospheric concentrations have increased markedly over the last few years.

(b) Oncreased atmospheric concentrations of CO_2 from fossil fuel combustion and deforestation. The potential effect of CO_2 increase arises from consequential cooling of the upper stratosphere and the effect this has on the rate coefficients of chemical reactions. Recent model calculations considering only the effect of a doubling of CO_2 in the atmosphere indicate a resulting increase in total ozone of approximately 3-6 per cent.

(c) Emissions of nitrogen oxides (NO_x) from aircraft. Emissions of NO_x from subsonic aircraft may already have increased the ozone content of the upper troposphere in the northern hemisphere. The direction of the ozone change depends on the altitude at which aircraft NO_x is injected. Calculations based on published release rates give increases in total ozone in the northern hemisphere of 0.2 to 0.3 per cent in 1980. Calculations for various postulated mixed subsonic and supersonic aircraft fleets operating between altitudes of 6 and 19 km all show increases of ozone in the period 1980 to 1990, with the largest increases located in the 8 to 10 km region. Total column increases at 30°N are estimated to be 1 to 2 per cent, and about an order of magnitude larger for the region between 8 and 10 km. It should be stressed that these last estimates are based on rather large increases in NO_x release rates between 1980 and 1990, and may therefore not be realistic.

(d) Increased atmospheric methane. Since the fifth session of CCOL several authors have reported a rise in atmospheric methane concentration of nearly 2 per cent per year during 1979 and 1980. The extrapolation of this change is highly uncertain. It is nevertheless of interest to estimate the impact of a possible doubling of methane on ozone. Such calculations have been performed, and the impact, particularly on tropospheric ozone, is pronounced. Given a doubling in CH_4 alone, 1-D model calculations give increases in tropospheric ozone of the order of 15 per cent and in total ozone of the order of 4 per cent.

83. Effects due to natural phenomena such as lightning, volcanic eruptions, cosmic rays, solar proton events and the variability of solar radiation, have been studied mostly in different contexts.

84. Considerable progress has been made since the last CCOL session towards including all perturbations simultaneously within newly developed combined photochemical and radiative-convective models. However, we have some way to go towards developing consistent and reliable strategies for studying all the possible perturbations to the ozone layer. The problem of specifying future scenarios as well as accurate historical records for diverse perturbations adds further uncertainty to the calculated ozone changes. Nevertheless it remains appropriate to consider the best available information in order to attempt a more realistic assessment of past and future changes.

85. Figure 1 presents a typical result in the calculated vertical profile changes of ozone between 1940 and 1981 using multiple scenarios including CFCs, N_2O, aircraft NO_x emissions, CO_2 and CH_4. There are other changes that have not been included in these particular calculations. The solid line indicates the ozone change in molecules/cm^3 calculated to have occurred during the period from 1941 to 1981, while the dashed line indicates that part of the total occurring during the last 10 years of that period. The maximum local changes from 1971 through 1981 are a decrease of approximately 5 per cent at ~ 40 km and an increase of approximately 6 per cent at ~ 10 km. The integrated change over the 40-year period is calculated to be an increase in total ozone of 0.8 per cent, of which 0.3 per cent occurred between 1971 and 1981. Individual calculations show that the decrease at high altitudes is brought about primarily by CFCs, moderated by CO_2 and CH_4. Near the ozone maximum at 25 km, the increase is due mainly to CH_4, with a contribution from CO_2 and CFCs, offset by a small decrease from aircraft NO_x. In the lower stratosphere and upper troposphere, the increases arise from CH_4 and aircraft NO_x. N_2O contributes only a very small decrease throughout the stratosphere as a result of its very slow rate of growth. Each of these calculated qualitative effects is, however, modified to some extent through chemical coupling with the other perturbations.

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86. Figure 2 shows the time dependent change in ozone calculated for similar perturbations in various combinations, where CLC refers to all chlorocarbons currently considered in stratospheric modelling calculations. Changes in ozone are given relative to calculated ozone for the year 1911. A comparison of the "CLC + NO_x + N_2O" curve with that for "CLC only" demonstrates that the early increase arising from NO_x is more than offset in subsequent years by decreases due to the slow growth in N_2O. Inclusion of CH_4 increases in such calculations is expected to lead to further calculated increases in ozone. Time-dependent calculations demonstrate not only the qualitative features of the various contributions, but also the very different time dependencies of the effects.

87. The complexities evident in recent multiple perturbation calculations present new interpretative challenges to modellers. The model calculations based on the "best guess" scenarios indicate little change in total ozone over the next few decades, although there is significant redistribution of stratospheric ozone. Should such predicted changes occur with sufficient magnitude, changes in climate could occur.

INTERPRETATION AND EVALUATION

88. Many types of numerical models can play and have played important roles in stratospheric research. The 1-D models of stratospheric chemistry provide a means of exploring photochemical theory without detailed representation of the complexity in atmospheric transport processes. Similarly, the 1-D radiation energy balance models remain the most commonly used model for studying trace species-climate interactions. Although 2-D models of stratopheric chemistry have seen increased use in recent years, there does not appear to be a 2-D coupled climate-chemistry model. In principle, 3-D models can be made more internally consistent and can include more interactive physical processes than the more parameterized models. Unfortunately, because of limitations in both physical and human resources, fully coupled radiative-dynamic-chemical 3-D models are still in the early stages of development. Because of the expected high cost involved in using such models, they will most likely be used in limited studies, oriented more towards research than applications. It is apparent that the study of atmospheric photochemistry and dynamics requires a wide spectrum of different models of varying degrees of complexity, each of which has a contribution to make and none of which is pre-eminent.

89. 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. Although the ability of models to simulate the present-day atmosphere correctly is a necessary first test of the models, it is not sufficient to establish the predictive reliability of model calculations. In addition, it is necessary to demonstrate the ability of the models to simulate an observed change in the atmosphere and its time dependence. Attempts to do so with recent multiple perturbation scenario calculations appear to produce results consistent with those from ozone trend analysis. This by itself has not accomplished the desired goal, because comparison of a calculated zero effect is more comforting than persuasive. A conclusive comparison between model-predicted and measured trace gas distributions and ozone variations is limited by several factors:

(a) Although much work continues to be done, the available data are still insufficient to permit full characterization of the spatial and temporal variations in the stratospheric distributions of these gases. Except for ozone, only scattered vertical profiles are available for most trace constituents. Some important species have not been measured at all.

(b) As a result of natural variability and experimental uncertainties, the available measurements usually define the atmospheric concentrations only within a certain error range.

(c) Most of the measurements are of local and instantaneous concentrations, whereas the present models calculate concentrations which are averaged over considerable spatial and time scales.

90. With the increasing concern over chemistry and climate coupling, needs for better data (both theoretical and observational) relevant to the lower stratosphere and upper troposphere have been established. Because of natural fluctuations driven by dynamic processes, extensive spatial and temporal coverage in measurements of trace species concentrations for this region would be required. Furthermore, a better description of the budget of reservoir species such as HNO_3, HO_2NO_2, H_2O_2, etc. would also be required.

91. Current understanding indicates that photochemistry predominates over all other physical processes in determining ozone distributions in the upper stratosphere. Consequently, viewing 1-D or 2-D models as pure local photochemical models is quite reasonable, and there are no serious problems in accepting these predictions of changes at these altitudes as globally representative. The principal concern about the quality of theoretical models in this region is with representation of physical processes such as solar heating due to ozone, H_2O changes and possible solar UV variability. Upper stratospheric ozone is more sensitive to these uncertainties, and hence there is difficulty in modelling the "real" trend during the past decade in this region.

92. In addition to these technical considerations, there is a subjective element involved in considering the model predictions. 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 be considered only as the best available information. The unquantified uncertainties, such as the possibility of missing chemistry, the inadequacies of 1-D, 2-D or 3-D model transport formulations, diurnal, seasonal or spatial averaging procedures for the non-linear interactions, and the admitted inadequacies in model validation procedures, must of necessity be evaluated on a most subjective basis. The subjective components in the interpretation of model predictions will probably persist.

93. 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 description of variables governing the temporal evolution of the system, such

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as transport parameters and solar flux variations. For long-term changes, an 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. Single isolated scenarios are inadequate in describing reality, either past, present or future. Increased efforts must be devoted to assessing the most probable coupled scenarios based on evolution in world economic and cultural patterns.

BIOLOGICAL EFFECTS

94. If a depletion of total atmospheric ozone occurs, solar UV-B irradiance will increase. This may have impacts on plants, animals and man. It is therefore necessary to identify the biological effects to be expected and to make quantitative assessments of these effects, especially with regard to agricultural production, fisheries and human health, and to determine the mechanisms by which UV-B radiation acts on biological molecules, cells, species and ecosystems. Most of the known biological effects of UV-B are damaging effects, so that the possibility of increased UV-B irradiance gives particular reason for concern. It is also recognized that climatic changes may occur which may have biological consequences.

95. Computer calculations of solar UV-B radiation reaching the earth's surface have been determined for a variety of combinations of UV-B radiation wavelengths, latitude, season and time of the day for normal and depleted total ozone amounts. These data are useful for biologists in properly simulating enhanced UV-B radiation conditions, both in the laboratory and in the field. New experiments using properly simulated natural and enhanced UV-B radiation will provide data for the evaluation of the UV-B effects on agricultural productivity.

1. Effects of increased UV-B irradiance on terrestrial plants

96. Higher plants have obvious importance, both in agriculture and in natural terrestrial ecosystems such as forests. Plants have evolved to expose much of their living tissue to sunlight in order to utilize its energy, Thus a reduction of total ozone, with its attendant increase in solar UV-B radiation, could be significant for them.

97. Studies have been conducted in growth chambers adjusted to the natural daylight rhythm, in greenhouses and in the field under natural conditions and with enhanced UV-B radiation. The researchers noted damaging effects to the growth parameters, leaf surface structure, composition, physiological function, germination and productivity of a large variety of plant species, including many important crops, such as wheat, rice, soya beans, barley, potatoes and beans. The enhanced UV-B exposure levels at which the harmful effects began to occur depended on the sensitivity of the plant species, and ranged from natural sunlight levels to 50 per cent enhancement of UV-B radiation. Tests on more than 100 plant species and varieties in controlled environment growth chambers indicate that approximately 20 per cent are already sensitive to present daily UV-B doses at latitudes of about 30°N; 60 per cent showed intermediate sensitivity, while 20 per cent were resistant

even to UV-B doses four times greater than normal. Although earlier work primarily simulated high UV-B radiation levels with low white light, recent studies in growth chambers have showed that high levels of white light with enhanced UV-B radiation simulating ozone depletion of 10-12 per cent also have deleterious effects in sensitive plants. These experiments have indicated that plants are particularly sensitive during the early stages of seedling growth and development. Furthermore, it has been shown that the effect on growth and photosynthesis of UV-B in combination with other commonly experienced stresse, such as water and mineral deficiency, is greater than the sum of the effects produced by the stresses independently. It has also been observed over several growing seasons that under enhanced UV-B, the competitive behaviour of plant species is changed, depending on the composition of the plant communities.

98. The action spectra for most of the effects of UV radiation on plants are similar to the DNA and erythemal action spectra. The action spectrum for damage to photosynthetic activity, however, differs markedly from these. The photosynthetic action spectrum shows a decrease of effectiveness by only a factor of three over the wavelength region from 280 to 340 nm, whereas the DNA action spectrum varies at least by a factor of 1000 over an even narrower wavelength range. Accordingly, the damaging effects may be related more to the DNA or similar action spectra than to the effects on photosynthetic activity only.

99. Non-damaging but highly sensitive and specific UV-B effects on formations of secondary plant substances which may act as natural protective agents were found in many plants. Studies continue to determine the capacity for acclimation to enhanced UV-B radiation, adaptive mechanisms and the physiological basis for different cultivar sensitivities.

2. Effects on aquatic organisms

100. Solar UV-B radiation inducing biological effects has been measured to depths of more than 20 m in clear water and more than 5 m in unclear water. Much marine life sensitive to these UV radiation levels (fish eggs, larvae, etc.), lives in the top 20 m of ocean waters. Experimental studies with enhanced UV-B levels have shown damaging effects on fish (eggs, larvae and juveniles), shrimps, crabs, zooplankton and plants essential to the aquatic food web. These damaging effects include decreases in growth, survival and other functions of these organisms. Furthermore, experiments with marine diatoms have shown high reductions in biomass, protein and pigment at UV-B irradiances equivalent to less than 10 per cent ozone reduction. In addition, studies on chain-forming diatoms and other phytoplankton in the laboratory 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.

101. In laboratory studies of the relative sensitivities of species within a selected aquatic ecosystem, enhanced UV-B resulted in shifts of community composition of marine phytoplankton and zooplankton. These results were corroborated by a study in a natural marine ecosystem. 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 dose-response curves and action spectra for a variety of aquatic organisms are being determined.

102. Continued investigations concerning the range of natural ecological uncertainties, which are much larger than the uncertainties in the particular photobiological effects, will be required to permit assessment of the possible consequences for the many complex ecological interactions as well as for the productivity of fisheries.

3. Effects on human health

103. Human health is influenced by UV radiation in many ways for example by the formation of vitamin D_3, sunburn, eye diseases, photo-allergic reactions and skin diseases including skin cancer. Among these effects the first-mentioned is considered to be positive and all the others negative. Skin cancer stands out as one problem to be influenced by increased UV-B irradiance. The severity of the 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.

104. Epidemiological studies have shown that the incidence of non-melanoma skin cancer correlates with exposure to sunlight; the 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 increased incidence of non-melanoma skin cancer is to be expected to result from increased UV-B irradiance.

105. Non-melanoma skin cancer is exceptional among the biological effects under discussion, in that statistics are available. This has made it possible to make comparatively developed quantitative extrapolations, which are still being refined and improved. Studies indicate that, apart from the radiation amplification, biological amplifications exist for the particular biological effects. Specifically, for every 1 per cent increase in effective UV-B irradiance, the incidence of basal cell carcinomas will increase by 1 to 2.5 per cent and the incidence of squamous cell carcinomas by 2 to 5 per cent.

106. There are several indications that sunlight may also be one of the causative factors in the pathogenesis of malignant melanoma, which affects people of all skin types. These indications come from epidemiological 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. Should UV-B be involved, a decrease in 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 data available at present.

107. UV-B radiation has been shown to alter several responses of the immunological system. UV radiation has been reported to depress delayed hypersensitivity responses in human and mouse skin; it causes depletion of Langerhans cells in both human and mouse skin, and induces alterations in the distribution and function of subpopulations of circulating lymphocytes in man and mice. UV-B irradiation effects on the immunological system diminish the ability of a mouse to reject a transplanted tumour induced by UV-B radiation in another mouse. Recent observations confirm that UV-B radiation also impedes the ability of a mouse to reject tumours initiated by UV radiation in its own skin. The doses of UV-B causing these immunological changes are much smaller than the doses which induce tumours.

108. Increased UV-B irradiance might also increase the positive effects of UV-B. Increased formation of vitamin D_3 in the skin of people living in countries with dark winters might help to alleviate vitamin D deficiencies. Increased UV-B during dark winters might also help the human skin to maintain some of its tolerance to UV-B. This would reduce the problems some people have in regaining their adaptation in spring; this would tend to reduce the number of photodermatoses. These positive effects of increased UV-B are of limited significance, and are certainly less important than the increased negative effects.

4. Socio-economic effects

109. In view of the limited amount of work on socio-economic aspects of this problem so far carried out on an international basis, the Committee felt it inappropriate to include a reference to them in the present assessment. However, it noted the importance of the subject, and referred to the World Plan of Action on the Ozone Layer, which states that the assessment of a potential environmental hazard should contain an evaluation not only of its costs and benefits to society but also of the costs and benefits that would result from a reduction of that hazard. Its two recommendations, that production and emission data should be collected and that a methodology for comprehensive assessment should be developed, have been fulfilled to a significant extent.

110. The Committee considered that the conduct of a comprehensive international assessment of the socio-economic effects of measures taken to reduce impacts on the ozone layer will require more data than are generally available. For the analysis of costs, data on uses, industry structures and predicted growth rates are needed. While these data often exist and serve as the basis for national analyses, national laws on confidentiality often preclude their release for use by those studying the problem on an international scale. The conduct of quantitative analyses of benefits requires reduced uncertainties concerning the magnitude of health and environmental effects of both UV radiation and climate changes. At present, benefits can best be described in terms of existing knowledge of health and environmental effects discussed in the previous sections of the report.

111. The Committee recommended that more data should be generated, and agreed to keep the Ad Hoc Working Group apprised of the current situation and the need for intensified research.

VIII. RECOMMENDATIONS FOR FUTURE WORK RELEVANT TO THE WORLD PLAN OF ACTION ON THE OZONE LAYER

112. The Co-ordinating Committee made the following specific recommendations for future activities to promote the implementation of the World Plan of Action on the Ozone Layer:

1. Countries and institutions operating ozone measurements should continuously contribute to the Global Ozone Observing System (GOOS) based on integration of satellite and ground-based systems, and should help to make the system fully operational;

2. Upgrading and intercomparisons of Dobson instruments should be intensified and testing of new instruments and techniques (i.e. use of lasers, microwaves, etc.) should be encouraged;

3. Vertical ozone distribution measurements should be expanded by:

   - Extending Umkehr observations;

   - Continuing balloon-borne soundings, especially at locations which already have long records;

   - Encouraging further development of reliable operational satellite sensors for accurate measurements over the complete altitude range of the stratosphere, including the continued development of in-flight calibrations;

   - Arranging for comparisons between balloon-borne sondes and other methods for ascertaining vertical ozone distribution;

4. The determination of new ozone absorption coefficients should be completed, and recalculations of all previous vertical ozone distributions taken by Umkehr and satellite arranged to ensure homogenity of records;

5. Further intercomparisons of methods and continuous cross-checks between data should be encouraged in order to make new techniques useful for trend analyses;

6. A systematic review (using original calibration records) should be promoted to achieve homogeneity of long ozone records, and to give particular emphasis to their interpretation;

7. The World Ozone Data Centre should be requested to collect all calibration and other relevant information needed for ozone data analyses, and the collaboration of the operating stations should be sought;

8. Studies aimed at clarifying physical processes and phenomena having an impact on error detection of ozone records (i.e. volcanic eruptions, solar events, etc.) should be promoted;

9. The attention of all countries and economic organizations not yet reporting production figures for CFCs 11 and 12, as well as other chlorocarbons, should be drawn to the need for reporting pertinent chemical production, release and usage data, including the more detailed data on production and uses needed for socio-economic analyses;

10. A call should be made for continued support to the five-station Atmospheric Lifetime Experiment, which has provided a five-year record of CFCs, chlorocarbons and nitrous oxide;

11. Steps should be taken to promote studies of the radiative effect of ozone and other minor species relevant to ozone photochemistry and tropospheric/stratospheric dynamics and chemical/dynamic interactions for the purpose of detecting possible climatic impact;

12. The determination of rate coefficients over the pressure and temperature ranges found in the atmosphere should be extended, and the products identified;

13. Any additional reactions which may affect stratospheric chemistry should be searched for and investigated;

14. Measurements of trace species of importance to the ozone question should be encouraged;

15. The intercomparison of different sensors for the measurement of trace species concentrations in the stratosphere should be encouraged;

16. Simultaneous in situ measurements of the relative concentrations of photochemically related compounds of the various families should be undertaken;

17. Measurements of the radical species should be extended to the lower stratosphere and upper troposphere using independent techniques;

18. 3-D fields of important trace constituents and meteorological variables in the stratosphere should be obtained using satellites;

19. On going research on the representation of transport processes for chemical models should be intensified;

20. Studies of the radiative effect of ozone and other minor species relevant to ozone photochemistry and stratospheric dynamics should be promoted for the purpose of detecting possible climatic impact;

21. Development of multidimensional models and coupled radiation-chemistry models should be continued;

22. Study of the simultaneous effects on the various species which may perturb atmospheric ozone should be continued;

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23. Efforts should be made to provide a well-documented and realistic set of scenarios of changing chemical compositions of the atmosphere;

24. Steps should be taken to promote studies aimed at clarifying physical processes and phenomena having an impact on error detection in ozone records;

25. Research should be conducted on the development of methods for quantifying the diagnostic capability of stratospheric chemistry models;

26. Efforts should be intensified to increase understanding of tropospheric chemistry;

27. Efforts should be made to improve knowledge pertaining to:

(a) The relationship of dose, dose rate and response for the various biological effects of UV radiation;

(b) The relationship between human exposure to solar ultra-violet radiation and melanoma skin cancer, including social and environmental conditions; global base-line data on skin cancer incidence should be established;

(c) The identification of high-risk groups among the populations;

(d) The possible interaction of wavelength regions, mainly UV-B and UV-A, and the possible role of photoprotection, photo-augmentation and photorecovery in carcinogenesis by UV radiation;

(e) The possible interaction of chemicals, pharmaceuticals and pollutants with UV radiation;

28. The biological effects of UV-B on agricultural crops in different geographical locations and under local growing conditions should be studied;

29. Aquatic effects studies should be extended to the natural water environment in order to gain knowledge of the effect of solar UV-B radiation on aquatic food productivity;

30. Studies should be continued on biological action spectra and the spectral response using polychromatic radiation in order to include possible interactions of the various wavelength regions;

31. Photorepair, adaptation and protection mechanisms should be included in the over-all consideration of UV-B effects;

32. Steps should be taken to determine the influence of changes in UV-B radiation on:

(a) The sensitivity and activities of insects important to the biospheric balance (animal food chain, plant cross-fertilization, etc.);

(b) Micro-organisms, such as those causing plant and animal diseases;

(c) Primary processes such as photosynthesis, biosynthesis, etc.;

(d) The photodegradation of herbicides, pesticides, fertilizers and similar agricultural chemicals;

(e) The effects of other stress situations;

33. The mechanisms by which UV-B radiation acts on biological molecules, cells, species and ecosystems should be determined;

34. Improved individual and biological UV-B dosimeters should be developed;

35. The UNEP secretariat should urge FAO and member States to take an active role in studying the biological effects of UV-B radiation and climatic changes on food production;

36. The UNEP secretariat should urge WHO and member States to take an active role in studying the effects of UV-B radiation and climatic change on human health.

IX. EXECUTIVE SUMMARY/PRESS RELEASE

113. An executive summary of the conclusions of the Co-ordinating Committee was prepared. The text appears in annex IV. The Committee decided not to issue a separate press release, as it felt that the executive summary would be adequate for that purpose also.

X. CONSIDERATION OF POSSIBLE CONTENTS OF ANNEXES AND/OR PROTOCOLS TO A GLOBAL FRAMEWORK CONVENTION FOR THE PROTECTION OF THE OZONE LAYER

114. The Committee considered documents UNEP/CCOL/6/4 and UNEP/CCOL/6/4/Add.2 prepared by the Government of the United States, and UNEP/CCOL/6/4/Add.3 prepared by the Government of Norway. It considered that document UNEP/CCOL/6/4/Add.1, prepared by the Government of Sweden, was not of a technical nature, and therefore did not consider it. The special papers had been prepared at the request of the Ad Hoc Working Group of Legal and Technical Experts for consideration at the second part of its second session. However, it was felt that in view of the technical nature of the papers, the opinion of CCOL on the papers should be sought before their consideration by the Working Group.

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XI. RECOMMENDATIONS TO THE AD HOC WORKING GROUP OF LEGAL AND TECHNICAL EXPERTS

115. A general discussion was held to decide what recommendations the Committee might wish to make to the Ad Hoc Working Group on scientific and technical matters. A report was prepared on this topic for transmission to the Working Group, which also contained the Committee's views on the possible content of annexes and/or protocols to the global framework convention. The report appears in annex V.

XII. APPROVAL OF THE REPORT

116. The draft report of the session and its five annexes was approved unanimously by the members of the Committee.

XIII. CLOSURE OF THE SESSION

117. Following the customary exchange of courtesies, the session was closed by the Assistant Executive Director, Office of the Environment Programme.

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ANNEX I

List of documents

UNEP/CCOL/6/1	Provisional agenda
UNEP/CCOL/6/2	Annotated provisional agenda
UNEP/CCOL/6/3	Recent research results and planned and ongoing activities relevant to the World Plan of Action on the Ozone Layer - submitted by WMO
UNEP/CCOL/6/3/Add.1	Report submitted by the Chemical Manufacturers Association
UNEP/CCOL/6/3/Add.2	Report submitted by the United Kingdom of Great Britain and Northern Ireland
UNEP/CCOL/6/3/Add.3	Report submitted by Austria
UNEP/CCOL/6/3/Add.4	Report submitted by Canada
UNEP/CCOL/6/3/Add.5	Report submitted by Denmark
UNEP/CCOL/6/3/Add.6	Report submitted by France
UNEP/CCOL/6/3/Add.7	Report submitted by the Federal Republic of Germany
UNEP/CCOL/6/3/Add.8	Report submitted by Italy
UNEP/CCOL/6/3/Add.9	Report submitted by Japan
UNEP/CCOL/6/3/Add.10	Report submitted by the Netherlands
UNEP/CCOL/6/3/Add.11	Report submitted by Norway
UNEP/CCOL/6/3/Add.12	Report submitted by Sweden
UNEP/CCOL/6/3/Add.13	Report submitted by Switzerland
UNEP/CCOL/6/3/Add.14	Report submitted by the Union of Soviet Socialist Republics
UNEP/CCOL/6/3/Add.15	Report submitted by the United States of America
UNEP/CCOL/6/3/Add.16	Report submitted by the World Health Organization
UNEP/CCOL/6/3/Add.17	Report submitted by the Commission of European Communities

UNEP/CCOL/6/3/Add.18	Report submitted by the International Council of Scientific Unions
UNEP/CCOL/6/3/Add.19	Report submitted by the Organisation for Economic Co-operation and Development
UNEP/CCOL/6/4	Special paper on the possible contents of annexes and/or protocols to the draft convention for the protection of the ozone layer - report submitted by the United States of America
UNEP/CCOL/6/4/Add.1	Report submitted by the Swedish Embassy, Nairobi
UNEP/CCOL/6/4/Add.2	Report submitted by the United States of America
UNEP/CCOL/6/4/Add.3	Report submitted by Norway
UNEP/CCOL/6/5	Assessment of ozone depletion and its impact: draft revised text for "Observations and trends" - submitted by R. Bojkov
UNEP/CCOL/6/5/Add.1	Assessment of ozone depletion and its impact: revised text for "Effects" - submitted by the Chemical Manufacturers Association
UNEP/CCOL/6/5/Add.2	Draft revision of Working Group contribution to the final report of the sixth session of CCOL, submitted by Mr. A.E.J. Eggleton
UNEP/CCOL/6/Inf.1	List of documents
UNEP/CCOL/6/Inf.2	List of participants
UNEP/CCOL/6/Background 1	Report of the fifth session of the Co-ordinating Committee on the Ozone Layer
UNEP/CCOL/6/Background 2	The current status of knowledge of stratospheric ozone - submitted by the Chemical Manufacturers Association
UNEP/CCOL/6/Background 3	Environmental, health and economic implications of the Use of chlorofluorocarbons as aerosol propellants and possible substitutes - submitted by Australia
UNEP/CCOL/6/Background 4	1981 world production and sales of fluorocarbons FC 11 and FC 12 - submitted by Chemical Manufacturers Association

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ANNEX II

List of participants

Australia	Mr. Ian Galbally Ms. Jane Cowcher
Canada	Mr. Carl Mateer
Denmark	Mr. Henri Heron
France	Mr. Maurice Muller Mr. Francis Nouyrigat
Germany, Federal Republic of	Mr. Wolf Dieter Garber Mr. Helmuth Bauer Mr. Jurgen Russow Mr. Manfred Tevini Mr. Paul Crutzen
Italy	Mr. Maurizio Cignitti Mr. Dante Cadorin
Japan	Mr. Taka Hiraishi
Netherlands	Mr. Jacob Swager Mr. Jan C. van der Leun Mr. Joop van Ham
Norway	Mr. Ivar S. Angell Isarksen Mr. Per M. Bakken
Sweden	Ms. Ingrid Jedvall
Switzerland	Mr. Hans U. Dütsch
Union of Soviet Socialist Republics	Mr. Vladimir Zakharov Ms. Lyubov Rubinina
United Kingdom of Great Britain and Northern Ireland	Mr. Alan E.J. Eggleton Mr. Richard Anthony Cox
United States of America	Mr. Herbert L. Wiser Mr. Julius Chang Mr. Robert T. Watson
World Health Organization (WHO)	Mr. Eugene Komarov
World Meteorological Organization (WMO)	Mr. Rumen Bojkov

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<u>United Nations Environment Programme</u> (UNEP)	Mr. F. Sella Mr. G. Golubev Mr. P. Usher
<u>European Economic Community</u> (EEC)	Mr. George Strongylis Mr. Anver Ghazi
<u>Organisation for Economic Co-operation and Development</u> (OECD)	Mr. Stephen R. Weil
<u>Chemical Manufacturers Association</u> (CMA)	Mr. Gordon Diprose Mr. Joseph Steed
<u>Internation Council of Scientific Unions</u>	Mr. Marcel Nicolet

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ANNEX III

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

AUSTRALIA

The Bureau of Meteorology in the Department of Science and Technology operates a network of six Dobson ozone stations located between 14°S and 54 S, and an ozone sonde station at 38°S.

The Department of Science and Technology conducts halocarbon and nitrous oxide monitoring in clean air at the Baseline Air Pollution Monitoring Station at Cape Grim, Tasmania.

The Division of Atmospheric Physics of the Commonwealth Scientific and Industrial Research Organisation has current research in the following areas:

1. Theoretical studies of the dynamics of the stratosphere.

2. Measurements of stratospheric constituents over Australia and comparison with modelling studies.

3. Tropospheric ozone, including removal processes.

4. 2-D modelling of atmospheric halocarbon distributions.

The Australian Environment Council, with the National Health and Medical Research Council, is responsible for developing national policies for the protection of the ozone layer. A report on "Environmental, Health and Economic Implications of the Use of Chlorofluorocarbons as Aerosol Propellants and Possible Substitutes" is in the process of publication.

CANADA

1. Ozone Monitoring

(a) Canadian ozone monitoring network

Canada continues to operate a network of five Dobson spectrophotometers at Resolute Bay, Churchill, Edmonton, Goose Bay and Toronto taking daily total ozone measurements and Umkehr observations whenever possible. A Brewer spectrophotometer will be installed at Edmonton beginning in fall 1983. Weekly ozone sonde flights are undertaken at four of the five stations (Toronto excluded) to measure the ozone profile with ECC ozone sondes.

(b) Brewer spectrophotometer

Two Mark I Brewer ozone spectrophotometers have been actively engaged in field measurement programs as well as in the ongoing ozone and sulphur dioxide monitoring program at Atmospheric Environment Service headquarters, Toronto.

The new Mark II Brewer ozone spectrophotometer is in operation at Toronto. It is also utilized to measure sulphur dioxide amounts for possible future correction of local Dobson values.

Four new Brewer spectrophotometers have been delivered for installation in the Canadian ozone monitoring network. A method for the evaluation of zenith observations has been developed, and a preliminary Umkehr evaluation programme has been developed. A modification to the Brewer spectrophotometer to permit measurement of UV-B radiation and Sunburn Index has also been made.

(c) World Ozone Data Centre

Canada continues to operate the World Ozone Data Centre on behalf of the World Meteorological Organization. Data are published monthly in "Ozone Data for the World", along with an annual catalogue of ozone data available at the Centre. Magnetic tapes of total ozone, Umkehr and balloon ozone sonde data are provided to scientists and research institutes at nominal cost.

(d) SBUV/TOMS

Active participation in the SBUV/TOMS experiment team has continued.

2. Recent research results and planned programmes relevant to the World Plan of Action on the Ozone Layer

(a) STRATOPROBE balloon flights

The analysis of further STRATOPROBE balloon flights supports the previous conclusion of low hydroxyl densities in the middle stratosphere. Model simulations of these flights with the new reaction rate set reproduce the balloon measurements well.

AES participated in phase I of the NASA balloon intercomparison experiment in September 1982 at NSBF in Palestine, Texas.

(b) Aircraft survey missions on the El Chichón cloud - Several latitude survey missions have been conducted on the volcanic cloud. Ozone, sulphur dioxide and aerosols have been measured from 10°S to 70°N. Ground measurements have been conducted at Mauna Loa and Toronto with similar instrumentation. The results indicate that ozone measurements are being contaminated by the presence of the volcanic cloud.

(c) Ground truthing

Participation and ground truthing for the LIMS experiment science team activities has continued as well. Ground truthing measurements in support of the SME satellite have been carried out.

(d) One-dimensional modelling

The York University one-dimensional photochemical model is currently being used to simulate balloon flight results and to conduct scenario calculations.

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(e) Two-dimensional modelling

The AES 2-D model, incorporating feedback effects between chemistry, radiation and transports, has been run to simulate the effects of the volcanic cloud on the stratosphere.

DENMARK

At the Risoe Laboratory the rate constant of the F-12 and OH reaction is being reassessed to be ready for publication in the near future.

At the University of Aarhus the Dobson station is continuing the measurements of total column ozone, reporting regularly to the World Ozone Data Centre.

FEDERAL REPUBLIC OF GERMANY

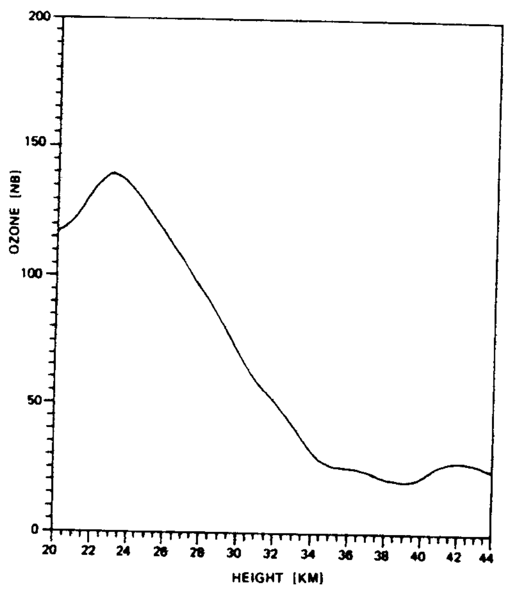
1. Field measurements

A laser radar (LIDAR) system for monitoring vertical ozone distribution has been installed on country's highest mountain, Zugspitze (2964 m) by the Max-Planck-Gesellschaft, the Deutsche Forschungsgemeinschaft and the University of Munich.

The system is based on a 100 mJ XeCl-Excimer laser operating at repetition rates of up to 100 Hz. The laser radiation with a wavelength of 308 nm is strongly absorbed by ozone. A second line at 338 nm, generated by stimulated Raman scattering, is not absorbed by ozone and is therefore used as reference. Both lines are emitted at the same time, improving the precision of the measurement.

The measuring signal for the ozone concentration is obtained by the differential absorption technique using the time interval between emission of a light pulse and detection of the back-scattered radiation as a measure for the altitude. Initial measurements have been successfully performed.

An example for a recorded ozone distribution is given in the following figure:



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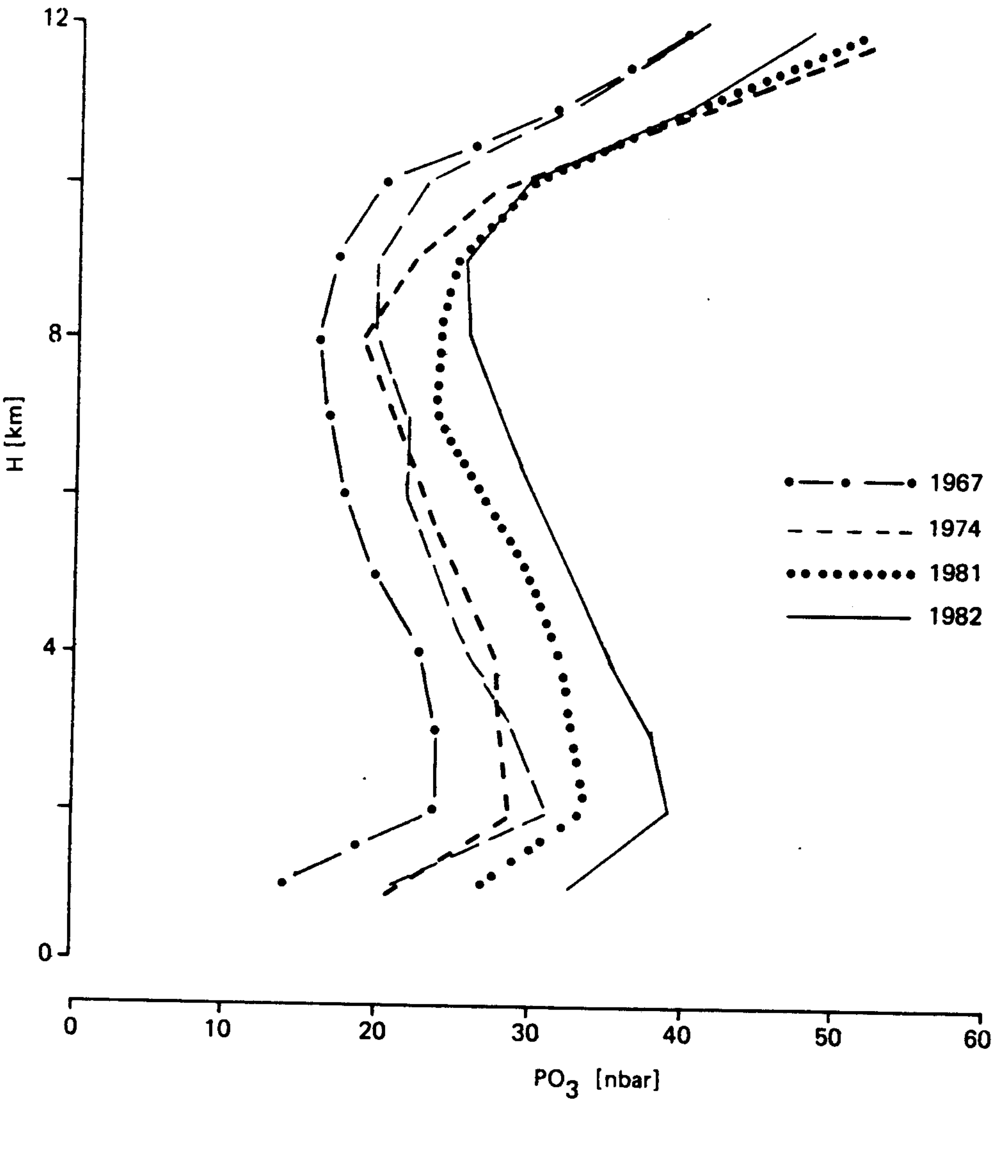
The future aim is to test the long-term stability of this ozone measuring device.

In addition to the ozone distribution, the stratospheric aerosol concentration is also monitored. Therefore the measurments also give information on the temporal behaviour of the aerosol cloud from the El Chichon volcano eruption in the spring of 1982.

The results of the ground-based measurements of the ozone distribution are compared to balloon-borne ozone soundings carried out at the German Weather Service observatory at Hohenpeissenberg. Experts believe that the LIDAR technique might overcome the low precision of Umkehr measurements and constitute a valuable connexion between ground based and satellite ozone monitoring.

The ozone measurements of the Meteorological Observatory in Hohenpeissenberg are the of highest importance, as they represent the only available monitoring series in the Federal Republic of Germany, covering an approximate 15 year period for both the vertical ozone distribution and tropospheric ozone.

The results of these measurements indicate an ozone decrease mainly in the lower stratosphere and a distinct increase of tropospheric ozone, as shown in figures 2 and 3.



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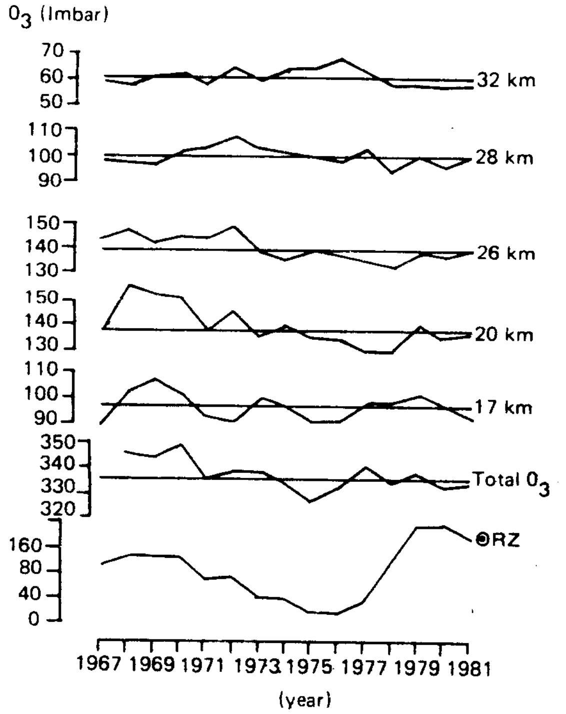


Annual mean values: O_3 (km steps), total O_3. rel. sun-spot-numbers Hp 1967–1981

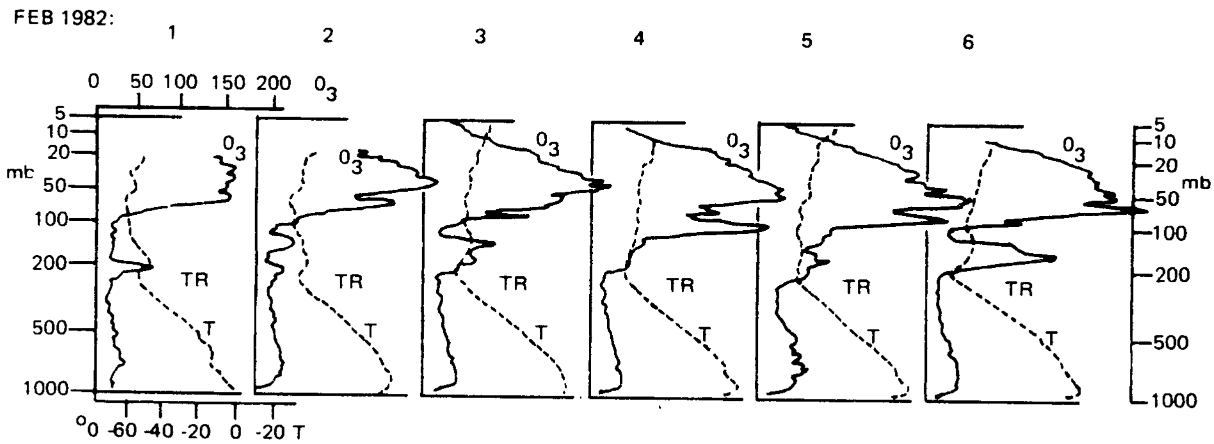
It must be said, however, that Hohenpeissenberg is not representative for the whole northern hemisphere, and, particularly with respect to stratosopheric ozone, trends reported so far are inconsistent.

To improve the basis for both long-term monitoring of the atmospheric ozone concentration and comparability, ozone-measuring devices using different methods are used in parallel at the Hohenpeissenberg station. This includes measurements of total ozone and of the vertical ozone distribution.

With a view to long-term trend analysis, this intercomparison is carried out continuously. In addition, scientists from the Hohenpeissenberg observatory will take part in the planned NASA intercomparison flights this year in Palestine, Texas. In the course of the MAP/GLOBUS campaign planned for September 1983 in France, different methods for ozone profile determination will be compared. The Hohenpeissenberg observatory will take part in this activity.

The Fraunhofer Institute for Atmospheric Environmental Research in Garmisch-Partenhirchen has continued its investigation into the variability of the ozone layer and its influencing factors. For this purpose, balloon borne ozone soundings have been recorded on about 300 consecutive days since 1980.

The results show the high degree of variability which is often associated with superposition of ozone-rich stratospheric and ozone-lean tropospheric air, leading to a kind of "puff-paste" structure (see fig. 4).



These changes in middle Europe are frequently caused by sudden formation of deep pressure troughs over the eastern Atlantic, shifting the zonal flow to meridional directions. The passage of these troughs over Europe is connected with the occurrence of strong jet streams and changes in tropopause heights, wind velocity and direction. Thus the wind régime alone is able to cause large variations in ozone distribution. Previous findings, that sudden upheavals of the ozone profiles frequently occur after acute solar disturbance, mainly H_x-flares, could be confirmed.

To investigate the latitudinal distribution of different trace gases in the northern hemisphere, the Max Planck Institute at Lindau (Harz) carried out a measurement campaign ("SIMOC") in May 1981, using an aeroplane (Falcon E of the DFVLR). The measurements ranged from the north cape to the equator.

Simultaneous measurements were carried out using microwave measurement techniques for O_2 and O_3, optical methods for O_3 and NO_2 and chemical methods (GC and IR-absorption) for CO, CO_2, CH_4, N_2O, C_2H_6, C_3H_8, CH_3Cl, $CFCl_3$ and CF_2Cl_2.

The data have not yet been processed completely. However, as expected, the microwave measurements show an increase with latitude for total ozone. A decrease in high altitudes, however, could not be observed. The mean of all ozone profiles recorded during the SIMOC campaign is distinctly lower than the United States standard ozone profile and shows the opposite latitude dependence at altitudes above 30 km. The representativeness of these measurements remains open to question.

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For the optical measurements, fig. 5 gives the observed O_3 and NO_2 distribution (abundance above aircraft).

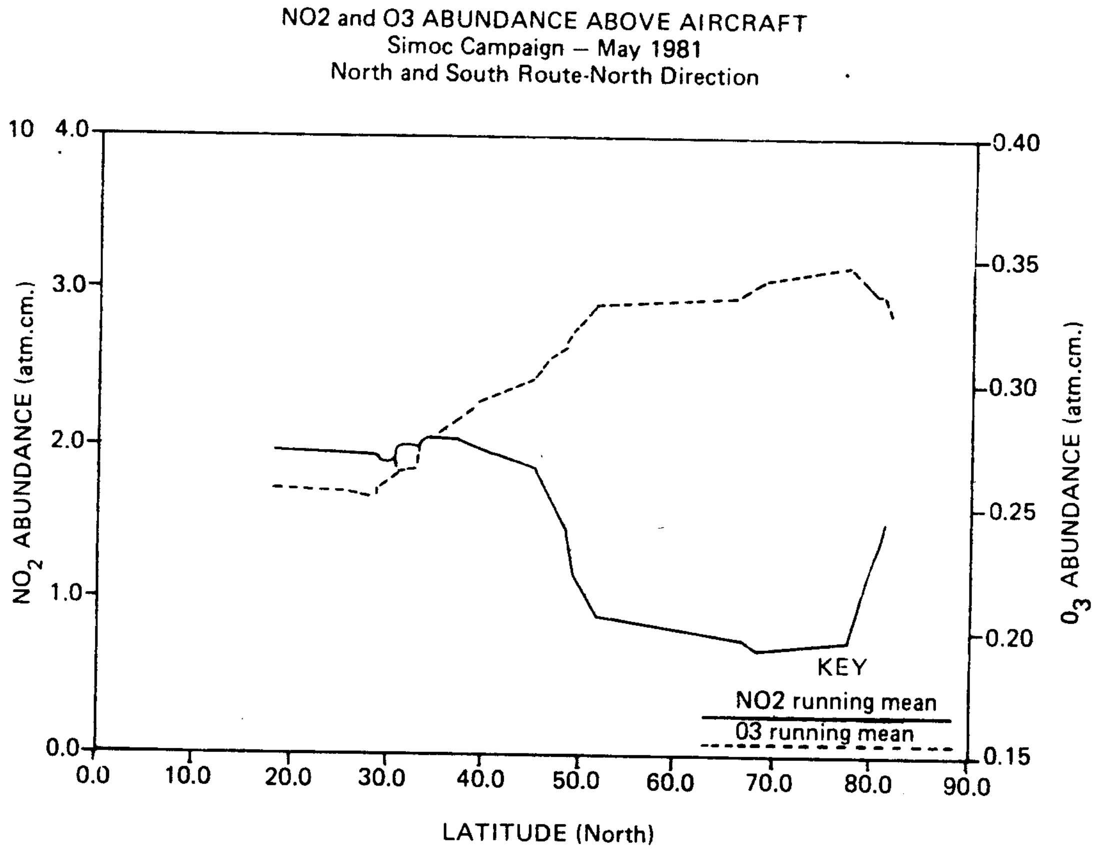
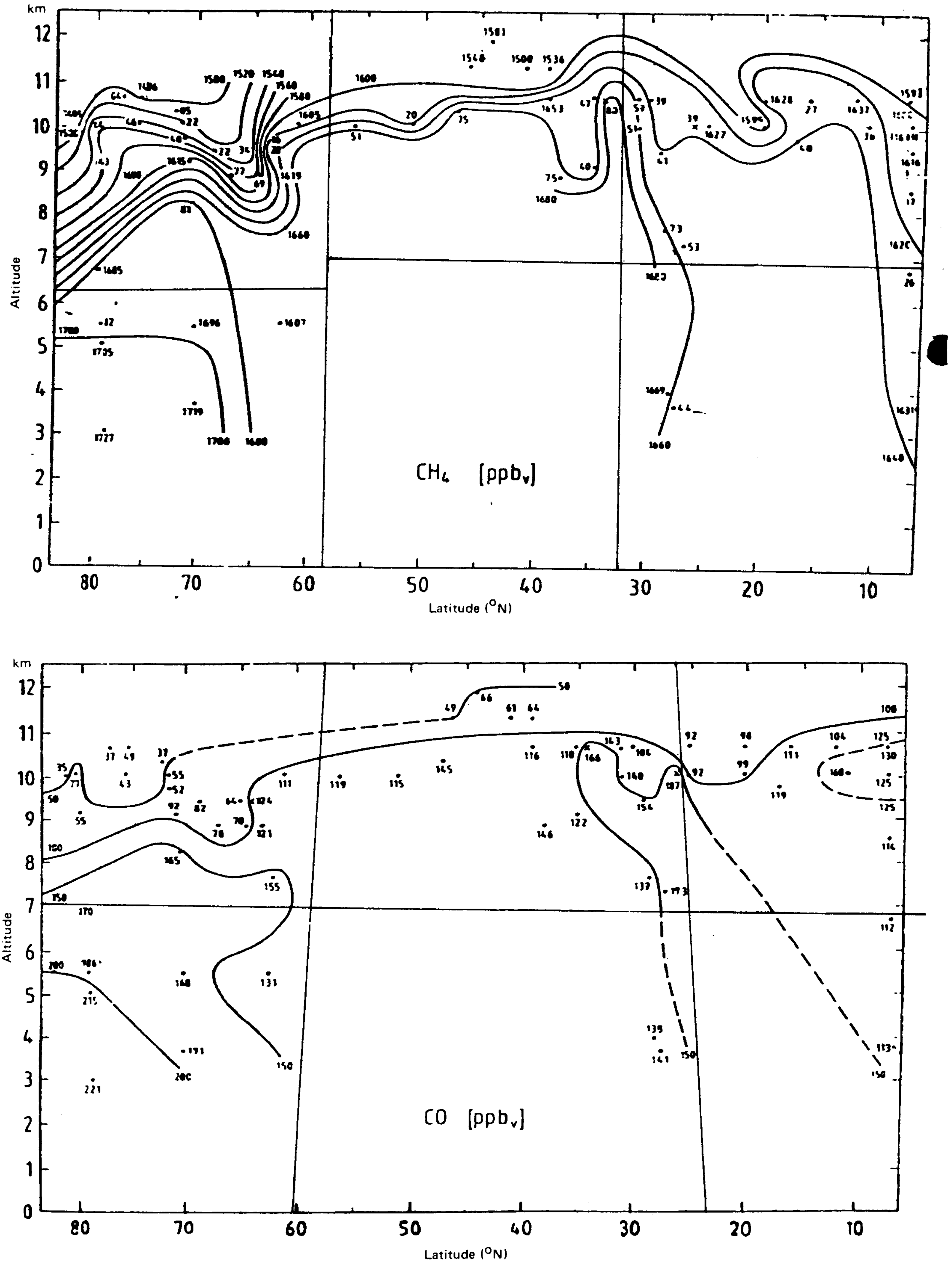


Figure 6 shows the distribution of CH_4 and CO mixing ratios measured by GC.



In our contribution to the fifth session of the Committee it was mentioned that acetonitrile was observed to be ubiquitous in the troposphere and could be observed in the stratosphere as well. Acetonitrile measurements have been continued. The concentrations in several rural areas ranged between 2 and 6 ppbv; measurements in the city centre of Wuppertal showed a mean value (7 measurements) of 7,4 $\pm$ 2,4 ppbv. During the burning of bush and grass in a rural area of Germany, a concentration increase to a value of 35 ppbv was recorded (from 4 ppbv before the fire), indicating combustion as a possible source for acetonitrile.

A joint analysis of data on tropospheric methane mixing ratios was carried out by KFA Jülich, the University of Liège and the Naval Research Laboratory in Washington D.C. Analysis of IR measurements of atmospheric CH_4 column density showed that there was little or no increase between 1948 and 1965. Between 1965 and 1975 a small increase in tropospheric CH_4 appears at an average rate of about 0.5 per cent a year, as suggested by independent sets of CH_4 measurements. Between 1978 and 1980 a CH_4 increase of 1 to 2 per cent a year was observed by several laboratories. The over-all trend for the past 30 years is subject to a fair amount of uncertainty.

In a previous project, the vertical profiles of different source gases were investigated. In a newly planned balloon-launching programme, the seasonal and latitudinal variations will be additionally investigated. Different devices, e.g. cryo samplers, IR emission spectrometers and mass spectrometers, will be used.

Some of these launchings are part of the "Comparative and Complementory Stratospheric Study" (CCSS) of MAP-GLOBUS planned for September 1983. In addition, two cryosamplers from the Federal Republic of Germany will take part in the planned NASA intercomparison flights in August 1983 in Palestine, Texas.

2. Reaction kinetics

The important reaction

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad (K_1)$$

has been investigated and the rate constant calculated to be

$$K_1 = 1,1 \cdot 10^{-10}\ cm^3\ s^{-1}$$

at a pressure of about 1 atm (University of Bochum).

Vacuum UV flash photolysis of H_2O was used to generate equal concentrations of H and OH radicals, the H radicals further reacting to HO_2 in the presence of O_2. The disappearence of OH radicals was investigated in the presence and absence of O_2 by OH resenance absorption.

The rate constant K_1 found here is relatively high, especially as compared with those usually recommended for modelling based on different evaluations (e.g. NASA, 1977, 1979; Hampson, 1975, 1980). An increase within K_1 is accompanied by a decrease in the calculated ozone depletion due to the destruction of odd hydrogen.

The ubiquitous abundance of acetonitrile has already been mentioned. This observation is supported by the rate constant for the reaction

$$CH_3\ CN + OH \qquad (K_2)$$

which was found to be

$$K_2 = 2{,}5\ .10^{-14}\ cm^3 molec.^{-1}\ s^{-1}$$

This low rate constant would be consistent with an atmospheric lifetime of more than a year with respect to this sink.

The chemistry of phosgene is of some interest, as phosgene and its fluorinated homologues are apparently formed during the photochemical decomposition of chlorocarbons and chlorofluorocarbons in the stratosphere.

The reactions of $CO\ Cl_2$ with OH and $O^{(3p)}$ were consequently investigated by the Dechema Institute. The reaction rates found are

$$K_{CO\ Cl_2/OH} = 1{,}5\ .10^{12}\ exp - \frac{1206}{}\ [cm^3 molec^{-1} s^{-1}]$$
(p 1,1 mbar, T = 300 - 421 K)

and

$$K_{CO\ Cl_2/O(^3P)} = 7{,}4\ .\ 10^{-11}\ exp - \frac{1431}{}\ [cm^3\ molec^{-1}\ sec^{-1}]$$
(p = 1,2 mbar, T = 300 - 608 K)

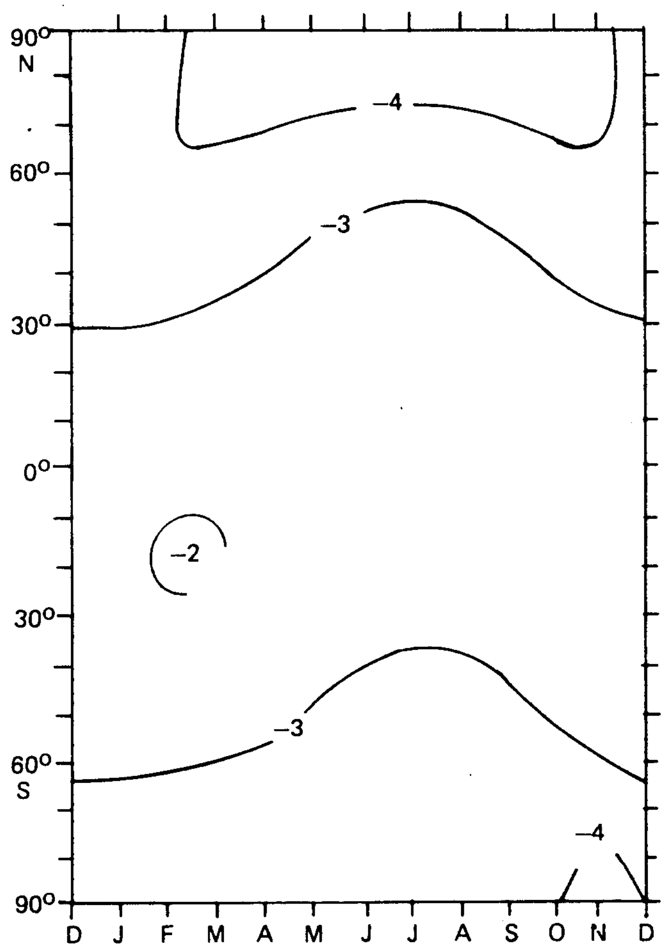
Identified reaction products were: CO Cl, HO Cl, Cl, HCl, CO H Cl, CO, Cl O and CO_2.

In order to develop suitable tests for the approval of new chemical within the licencing procedure, the abiotic degradability of chemical compounds is investigated using different methods. The research is mainly aimed at OH reactions, which often determine the atmospheric lifetime and whether or not a chemical compound is reaching the stratosphere.

3. <u>Modelling</u>

Photochemical models of the stratosphere and available measurements of ozone concentrations have been compared in a review prepared by the Air Chemistry Division of the Max-Planck Institute for Chemistry in Mainz. An important finding is that there are significant discrepancies between the models and the available measurements. In particular, differences occur in the region between a height of 25 and 35 km. The review concludes that photochemical processes and the chemical composition of the stratosphere are at present only incompletely known, which leads to an insufficient understanding of the ozone distribution.

The Air Chemistry Division of the Max-Planck Institute in Mainz, in collaboration with the University of Miami and the NASA Langley Research Center, has developed a two-dimensional photochemical model of the atmosphere in an effort to examine changes of the ozone layer due to dichlorocarbon emissions. The importance of tropospheric ozone contributions to total ozone is pointed out. In the model, C Cl_4 and CH_3 C Cl_3 are included in addition to CF Cl_3 and CF_2Cl_2. The calculated stratospheric ozone decrease is approximately 3 per cent by 1980 as compared to the pre-industrial state (fig. 7). 1/ This result is somewhat higher than the figures given by similar models. 2/ In this connection it is important to note that the historical emission rate of C Cl_4 to the atmosphere is incompletely known.



1/ About half of this occurred prior to 1970.

2/ Mainly as a result of the inclusion of past CCl_4 emissions.

/...

The influence of other trace gases has also been investigated. The influence of a possible long-term increase in tropospheric CH_4 of up to 2 per cent per year was found to be small, although this increase helps to mask decreases in stratospheric ozone caused by the chlorocarbons.

Increasing NO_x emissions due to industrialization also tend to mask decreases in ozone.

The model study concludes that significant disagreements remain between theoretically calculated and observed concentrations.

4. Biological effects of enhanced UV-B radiation

Studies were continued on the biological effects of enhanced UV-B radiation in growth chambers, greenhouses and in the field with various crop species and cultivars. Additionally, experiments were initiated with marine diatoms and with the slime mould Dictyostelium. The results up to May 1982 were presented during a Federal Republic of Germany - United States workshop on the biological effects of UV-B radiation held in Munich-Neuherberg from 25 to 27 May.

Experiments in growth chambers examined the effects of UV-B radiation alone and in combination with additional stresses on plant growth, development, composition and structure. Cucumber and radish were grown under two UV-B irradiances and three levels of water stress. On a weighted daily dose basis (weighted according to the generalized plant action spectrum) the UV-B treatments were equivalent to ambient levels (controls) and those predicted for 12 per cent ozone depletion during the summer solstice at 49° N latitude. Seedling growth, estimated from fresh weight, height and leaf area, was reduced by enhanced UV-B. Leaf structure, chemical composition and leaf surface waxes were significantly changed. Photosynthesis was also reduced despite a large increase in leaf diffusive resistance. Water stress enhanced the deleterious UV-B effects on the growth and function of seedlings, and cucumber was much more sensitive than radish. These results indicate that cucumber is one of the most UV-B-sensitive crop species so far identified. This higher sensitivity might be due to a reduced capacity to synthesize sufficient amounts of protective flavonoid compounds.

In another experiment the interaction between UV radiation and mineral nutrition was examined in lettuce and in a native herbaceous plant (Rumex alpinus). The greatest dry weight reductions in UV irradiated plants were found in plants grown with the lowest mineral nutrition. Moreover, these differences diminished as more optimal nutrient concentrations were used.

To determine the effectiveness of different wavelengths on whole plant photosynthesis, intact plants were irradiated in quartz (UV transmitting) and plexiglas (UV absorbing) cuvettes. Radiation of wavelengths shorter than 305 nm reduced net photosynthesis in lettuce and Rumex. Wavelengths longer than 305 nm had no apparent effect on plant photosynthesis.

Action spectra have been developed for protective flavonoid biosynthesis showing that wavelengths near 298 nm were most effective in protecting maize coleoptiles.

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Greenhouse experiments were conducted with additional white light and filtered (Schott WG 305) UV-B radiation (equivalent to 25 per cent ozone reductions with the plant weighting function). 22 cultivars belonging to seven crop species (wheat, barley, spinach, bean, radish, lettuce and cabbage) were used in this screening experiment. After seven weeks of treatment, cultivars showed different sensitivities to UV-B, which is consistent with previous results on many other cultivars found by United States investigators. Plant height was significantly reduced in over 40 per cent of the cultivars, whereas total dry weight was reduced in only 3 cultivars. In over 50 per cent of the cultivars, the flavonoid concentration was increased.

In field experiments where 10 per cent and 25 per cent ozone reductions (plant basis) were simulated, 7 cultivars and three species (lettuce, cabbage, grape) were investigated. Dry weight was reduced in only 2 cultivars at both ozone simulation rates, and again protective compounds accumulated depending on incident UV-B levels in most but not all cultivars. Experiments with five species of marine diatoms (Thalassiosira rotula, Bellerochea yucatanensis, Biddulphia sinensis, Ditylum brightwellii and Lauderia annulata) show high sensitivity at low UV-B irradiances (equivalent to less than 10 per cent ozone reduction with plant weighting function). Biomass production, protein and pigment concentration were reduced as a function of incident UV-B radiation. Amino acid composition was also altered during UV-B treatment, and a consistent relationship between these changes and species sensitivity seems to exist.

Action spectra on the mobility of the slime mould Dictyostelium show that mobility is reduced with shorter wavelengths and increasing doses in short-term experiments.

FRANCE

Since the fifth meeting of CCOL, France has continued its programme of research on the ozone layer, including atmospheric measurements, laboratory chemical kinetic studies and stratospheric numerical modelling. A meeting of French and Belgian scientists working in these fields was held in Palaiseau on 4 and 5 October 1982, in order to take stock of research on stratospheric physico-chemistry in France and Belgium, and to make appropriate recommendations for future work needed for a better knowledge of the ozone layer. A detailed report is to be published in June 1983.

The geophysical observatory set up at the Observatoire de Haute-Provence (OHP) has been selected by WMO to become one of the seven stations in the world which are to observe the ozone layer with automated Dobson spectroplatometers; the aim is to establish continuous Umkehr records for further ozone studies and satellite calibration.

1. Atmospheric measurements

(a) Ground-based measurements

Continuous measurements

(i) Dobson and LIDAR stations:

- Continuous ozone measurements are being carried out at the Biscarrossee SMS station. Observations include daily measurements of total ozone using Dobson spectrophotometers No. 11 and No. 49, weekly launching of Brewer Mast ozone sondes and Umkehr measurements during summer-time in clear sky conditions. The results of these measurements are regularly sent to Toronto (WODC), Bracknell (Meteorological Office) and Zurich (Institut Suisse de Météorologie).

- As already mentioned, routine measurements of the ozone total content and vertical distribution will be performed at the OHP (Reims University) using the Dobson No. 85, which has been automated to perform Umkehr measurements as part of the global network of seven automated stations. It will be operated every clear day, which means to a total of about 200 measurements per year taking into account the meteorological conditions on the site. This programme will also include comparative routine measurements of the ozone vertical distribution and total content using Brewer Mast ozone sondes launched at the Observatory, routine measurements of the tropospheric and stratospheric aerosol content using a ruby LIDAR system and complementary high-quality measurements of the ozone vertical distribution and total content using UV LIDAR soundings between 0 and 40 km (see below) and high resolution IR spectrometers (0 - 35 km).

- In 1982 the laser sounding systems of CNRS/SA were permanently installed at the OHP, thus allowing regular measurements of the ozone vertical distribution by the differential absorption method (Dial). The main results obtained so far include: determination of the ozone vertical profile from ground level to 40 km in one hour integration time by use of a new couple of laser wavelengths (305 - 310 nm), simultaneous measurement of the ozone total content (comparison with the Dobson results); and determination of repetitive ozone vertical profiles between 5 and 15 km in 3 minutes' integration time with a vertical resolution higher than 300 m (study of stratosphere - troposphere exchanges). Another important result is that for the first time, NO_2 was measured at night between 15 and 45 km by the Dial method (NO_2 absorption bands at 440nm).

(ii) CO_2 survey stations:

- An automated station has been operating since December 1982 at the Pic du Midi (EERM). It observes the diurnal and seasonal cycles of CO_2 (BAPMON network of WMO).

- Atmospheric CO_2 is also regularly measured at the station of Amsterdam, Ise and in the south of the Indian Ocean (CFR/CNRS).

<u>Non-continuous measurements</u>

Microwave heterodyne spectrometry at the Bordeaux Observatory, followed by appropriate modelling calculations (Lille University), allows the vertical ozone profile to be determined between 0 and 70 km. The column densities of O_3 above 40 km and of CO above 70 km have been estimated:

$$N_{O3} = (2,20 \pm 0,2).10^{17} mol./cm^2$$
$$N_{CO} = (7,4 \pm 2,3).10^{15} mol./cm^2$$

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(b) Balloon-borne measurements

- Simultaneous measurements of NO_3 and O_3 were performed at different periods of the night from stratospheric balloons launched from the CNES balloon station at Aire-sur-l'Adour in September 1980 and September 1981 (Station Scientifique du Val Joyeux/Université Paris VI, and the Observatoire de Genève). The experimental NO_3 vertical profiles compare favourably with those predicted by photochemical theory. Differences can be explained by the dependence of the recombination rate of NO_2 and O_3 upon altitude. The O_3 concentrations above 30 km measured by spectrosphotometry around λ = 660 nm show remarkable stability. Measurements obtained by means of this technique could be used as a reference for the detection of long-term variations in O_3.

- In addition to the stratospheric open balloons already used by several European teams for comparison of simultaneous measurements by different methods, CNES is developing new types of balloons (pressurized stratospheric balloons and Montgolfières infra-red) for vertical and long-duration flights to allow study of the variability of ozone and other minor constituents with space and time.

- The Service d'Aéronomie du CNRS was one of the participants in the International Balloon Intercomparison Campaign (BIC) which took place in autumn 1982 at Palestine, Texas. The French experimental group made measurements on atmospheric species of the NO_x family.

(c) Intercomparison of measurement techniques

- The results of the international campaign which was held during June 1981, mainly at OHP for ground-based measurements and at Gap for balloon flights (see Ozone Layer Bulletin No. 7, p.20), have been published recently. They provide valuable information on the accuracy of the measurements made by the various techniques used in ozone determination: Dobson-Umkehr, Dial, high resolution IR and UV spectrometers, microwave spectrometry and different types of ozone sondes. It has also been shown that there is a good correlation between the ozone and temperature vertical profiles, and that there is no variability in the ozone profile between 22 and 32 km during a diurnal cycle.

- Intercomparison of balloon-borne measurements will be made during the MAP-GLOBUS international campaign at Aire sur l'Adour in September 1983.

(d) Aircraft measurements

- The results from the Stratoz II experiment have been published (see Ozone Layer Bulletin No. 7, p.20).

- A Similar experiment, Stratoz III, is scheduled by EERM for June 1984, the aim being to serve better knowledge of the seasonal variations of O_3 NO, NO_2, HNO_3, HCl, HF, N_2O, CH_4, H_2O and CO, and to study the air flows through the tropopause. Several French and European groups are expected to participate in the experiment.

(e) Satellites measurements

The new method developed by EERM for extracting the total ozone content using data from TOVS multispectral telemetry has given very promising results: in the middle latitudes, the total ozone is retrieved with an error of less than 5 per cent compared with the measurements of the Dobson stations. Similar retrievals could be achieved from other satellite data sets (Firos N/NOAA and Meteosat).

(f) Evaluation of ozone trends

The statistical frequency analysis of vertical ozone profiles over the Berlin station shows that after 1970 the ozone layer between 150 mb and 300 mb increased at the expense of the layer above 100 mb. This work will be extended to other ozone stations.

2. Laboratory measurements

(a) Spectroscopy

The widths of the high-resolution IR absorption bands of the ozone molecule have been studied (LPMOA Orsay). These spectroscopy data are useful for the analysis of LIMS radiometer measurements. Other high-quality IR spectroscopic data have been obtained on several molecules relevant to ozone chemistry (Laboratoire d'Infrarouge, Orsay).

(b) Chemical kinetics

- CRCCHT/CNRS in Orléans has studied the following reactions in flow reactors coupled with an EPR spectrometer or with a mass spectrometer and a cell for laser-induced fluorescence analysis:

(i) $OH + HNO_3 \longrightarrow H_2O + NO_3$

Rate constant (7, 3 $\pm$ 2) 10 ^{5} exp [(867$\pm$85)/T] $cm^3\ mol^{-1}s^{-1}$ between 251°K and 403°K. This value implies a decrease of the estimated ozone depletion by chlorofluorocarbons.

(ii) $OH + Br_2 \longrightarrow HOBr + Br$

This reaction is an interesting source of HOBr in view of spectroscopic studies.

(iii) $Br + HO_2 \longrightarrow HBr + O_2$

This reaction is a possible sink for the Br atoms in the stratosphere.

- The Laboratoire de Chimie Générale (Université Paris VI) has studied the reaction $HO_2 + HO_2$ which produces H_2O_2 and H_2. The formation of molecular hydrogen could be an explanation for the "drying" of the strotosphere.

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3. Modelling

- The EERM 1D model has been updated with the recent JPL 1982 set of rate constants. This set includes only minor revisions compared to the NASA/CODATA 1981 compilation. For instance, the previous estimate of the steady-state ozone depletion of 7 per cent calculated for continuing emission of F11 and F12 at their 1976 rates has been reduced to 5.8 per cent. A series of coupled perturbations were also performed with the 1D model. It was found that ozone behaviour in coming decades will be highly dependent on the rates of increase of various trace gases like CO_2, N_2O, CH_4 and NO_x.

The EERM 2D model was also used to evaluate the ozone reduction due to the increase in chlorofluorocarbons. Using the NASA/CODATA 1981 set of reaction rates, the steady-state ozone depletion due to the release of F11 and F12 at their 1976 rates reaches 5 per cent. This percentage is significantly smaller than that derived from 1D calculations. It can mostly be attributed to shorter lifetimes for the CFCs when latitudinal variations of the dissociation rates are taken into account.

A three-dimensional dynamic model is also under development at EERM. It is a spectral model in primitive equations with 28 vertical levels from ground to 0.01 mb (about 80 km). Physical parametrizations include a diurnal radiative cycle and a hydrological cycle in the troposphere, whereas UV absorption by ozone and infra-red cooling due to CO_2 and O are introduced for the stratospheric levels using a "Newtonian cooling" approximation.

The model was successfully integrated from rest over a 110-day period, with isolation and sea surface temperatures fixed for January conditions. Analysis of model statistics will be made with emphasis on the relative role of transient and stationary components of the mean flow.

- Modelling of the radon decay and its decay products can be applied to the study of troposphere - stratosphere exchanges (CFR/CNRS).

ITALY

The following research and monitoring programmes connected with the "ozone probem" are under way in Italy.

Modelling

A photochemical transport 1-D model which takes into account the radiative contribution of CO_2, CH_4, N_2O, O_3 and O_2, is being used to evaluate the variation of the atmospheric ozone equilibrium due to all identified man-made perturbations.

Comparison of the calculated vertical profiles of the most important atmospheric species in 1981 with the relevant experimental data ensures acceptable validation of the model.

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An evaluation of some multiple perturbation scenarios based on changes in atmospheric levels of NO_x, N_2O, CH_4, CFCs, CCl_4 and CH_3-CCl_3 up to the year 2020 is being carried out.

Atmospheric measurement

At the University of Florence the programme of measurements of stratospheric species through a high-resolution interferometer operating in the submillimetre spectral region (SIBEX) is still continuing. This programme, which began in 1979, is supported by the Italian National Research Council and Chemical Manufacturers Association.

The 1979 campaign furnished very high-quality data, but a lack of detailed spectroscopic information made it necessary to analyse the results with laboratory measurements. This special activity has been performed in collaboration with Institute of Spectroscopy and Physical Chemistry of the University of Bologna.

The most important result of the 1979 campaign has been the first identification in the submillimetre region of the OH and NO species; moreover, evaluations of simultaneous vertical profiles, between 20 and 40 km, of HF, HCl, OH, CO, HCN, H_2O and O_3 have been obtained.

The high-resolution interferometer of the University of Florence, equipped with the He3 detector manufactured by the University of Oregon, has been included among the 16 experiments (5 from Europe) of the Balloon Intercomparison Campaign (BIC) funded by NASA, EEC and CMA.

The first phase of this campaign (September and October 1982) has been completed with the launch of four balloons from Palestine, Texas. The collected data appear to be of good quality and are being examined. A second phase is foreseen, with a simultaneous launch of balloons, during April 1983, also from Palestine, Texas.

A team from the University of Urbino is continuing the effort to evaluate a possible tropospheric sink of CFC 11 through the measurement of CFC 21. A campaign of few weeks has been carried out in the Egyptian desert in order to evaluate a possible desert destruction effect for CFC 11.

A group operating at the University of Rome Physics Department, in collaboration with the Institute of Atmospheric is carrying out detailed observations of the stratospheric aerosol layers following the 1982 volcanic eruptions. The LIDAR instrument at Franscati has the advantage of providing high-resolution profiles without the need to integrate successive pulses. This group is also considering the possibility of establishing a network of LIDAR stations in Africa.

Ozone monitoring

The Dobson spectrophotometers of the national ozone monitoring network, after calibration carried out in collaboration with Canadian experts, have been relocated in Vigna di Valle (Roma), Sestola (Modena), Cagliari Elmas and

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Brindisi, and are now operating regularly. Since relocation, the instruments have once again been intercompared by the use of a travelling standard lamp of the World Ozone Data Center.

Weekly measurements of vertical ozone distribution are carried out at the Cagliari Elmas station using the Vaisala ozone sondes (these sondes will soon be replaced by Mast cells).

In line with the need for knowledge of ozone concentration near the ground, measurements by electrochemical cells are made daily at the Cagliari Elmas station.

Epidemiological studies

An investigation of the incidence of malignant melanoma in the population of Rome for the period 1970 - 1979 will soon be completed. Data have not yet been made available by the authors.

JAPAN

A. Study of CFC effects on stratopsheric ozone depletion

1. A study was carried out by the Mitsubishi Research Institute, Inc. for the Ministry of International Trade and Industry (MITI) and was completed in March 1982. The study consists of:

(a) Review of available results of research activities by OECD, NAS, United Kingdom Department of the Environment and some other organizations.

(b) Statistical analysis of O_3 monitoring results obtained through the World Ozone Data Centre.

(c) Review of structures, methodologies, coefficients and other factors used in various model studies.

(d) A one-dimensional model study.

2. O_3 monitoring data from nine chosen stations were statistically analysed. Major conclusions were;

(a) The higher annual averages and the higher seasonal variations were observed at the higher-latitude stations. Seasonal peaks and minimums were observed in March and October in the northern hemisphere.

(b) Using the fast Fourier transform method, the periodicity of ozone monitoring data was analysed. It was found for all the nine stations that there is the prominence of the component having a one-year cycle.

(c) A separation of seasonal component, irregular component and trend component was undertaken. O_3 levels observed in the northern temperate zone showed a maximum around 1970 and a gradual decrease or level-off tendency later, which was also the case for tropical areas. However, an increasing trend from the mid-1970s was observed in the case of the southern temperate zone.

3. A one-dimensional model study was undertaken which showed an ozone decrease (equilibrium level) of 5.3 9.8 per cent. Further, 5 scenarios, chosen from OECD scenarios, were applied to the model and ozone layer trends were calculated until the year 2100 for each scenario.

B. Gas-chromatographic measurements of N_2O in the troposphere

4. The Meteorology Agency carried out a sampling and measurement of N_2O at an altitude of 7km. from autumn 1978 to spring 1979. The samples were analysed by GC-ECD and a mean value of 0.31 ppm was identified.

C. Development of improved UV radiation equipment and procedure

5. In 1980 the Meteorology Agency undertook a statistical analysis of data on UV radiation, effective cloud amount, horizontal visibility and total O_3.

6. In April 1982 the Meteorology Agency initiated a research project on the trend prediction of the straspheric ozone layer. The Agency will initially examine the accuracy and limitation of one-dimensional models. In connexion with this project, the Agency will develop improved UV (280-320nm) measuring equipment.

D. Research into soil chemistry relevant to NO_x and S compounds

7. The Agriculture Ministry runs research activities in the fields of soil chemistry, i.e. the generation of COS, H_2S, CH_3SH and other sulphur compounds as well as N_2O from soil.

NETHERLANDS

A. In the human-health section, the fact that UV-B can induce skin cancer is still the main issue. Recent research results obtained in the Netherlands with respect to non-melanoma skin cancer include:

1. An improved determination of the dose-response relations for UV-tumorigenesis in mice. The study confirmed that every mouse exposed to a sufficient dose of UV-B developed skin tumour; these tumours were of the squamous cell carcinoma type. The more UV-B was administered, the faster the tumours developed.

The response of a group of animals may be expressed as the median tumour induction time; this is the time required for 50 per cent of the animals to develop skin tumours. The median tumour induction time proved to be composed of a dose-dependent initiation interval and a dose-independent growth interval. This is a correction to the old conception, that the tumour development time consisted of one stage of continuously accelerating growth.

The new data allow refined quantitative predictions of the increase of skin cancer incidence in case of increased UV-B irradiance; these confirm the predictions made on the basis of the older data.

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2. It is well established now that UV-B irradiation causes immunological changes in a mouse, resulting in an impaired ability to reject a transplanted tumour induced by UV-B in a syngenetic mouse. This suggests that UV-B irradiation will also impair the animal's ability to reject a tumour induced by UV-B in its own skin.

This was confirmed in direct experiments. These demonstrated that preirradiation of a part of a mouse's skin with UV-B reduced the resistance against the induction of tumours by UV-B in other parts of its skin. Pre-irradiations in doses insufficient for the induction of tumours are sufficient to cause the systemic effect described.

In spite of epidemiological and clinical impressions, there is still no direct evidence that UV-B plays a role in causing malignant melanomas. An experimental project was started to investigate this possibility.

B. A report was completed on non-aerosol applications of fluorocarbons in the Netherlands. 3/ The report deals with present use and trends in the use of chlorofluorocarbons for refrigeration and air conditioning, foam plastics, solvents and others. For the next five years no major changes are expected for CFC use in these applications.

The report further deals with possible abatement measures and alternatives for CFCs.

NORWAY

Ozone monitoring and observations

Observations of total ozone are continued at the Physics Department, University of Oslo, with the Dobson spectrometer. This is part of the observation series aimed at calibrating satellite observations. Calibrations of another ozone instrument are now completed. This instrument will be put into operation in the near future in Tromso (70° latitude).

Previous studies of upper stratospheric ozone continued at the Institute. Observations of scattered sunlight above 40 km during sunset (depression angle 5°) combined with model studies make it possible to detect ozone variations in this height region. Such studies are under way. Since ozone perturbations by man's activity are believed to be rather sensitive at these heights, the present study is aimed at detecting possible trends in future upper stratospheric ozone.

Modelling

Model studies of ozone chemistry in the stratosphere and troposphere have been done at the Institute of Geophysics, University of Oslo for several years. The study on possible man-made effects on ozone continues. A 2-D model of the

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3/ C.F.P. Bevington, T.F.N. Johnson and R.J. Phillips, Non-aerosol Applications of Fluorocarbons in the Netherlands; 's-Gravenhage, 1982: ISBN 90346 0085.

troposhere and stratosphere, where transport is based on diabatic heating rates, has been developed. The model makes use of residual mean transport with strongly reduced eddy diffusion in the stratosphere, compared with most other 2-D models. A chemical scheme which considers the diurnal variations in solar radiation and the concentrations of chemical species is included in the model.

The model reproduces total ozone variations rather well, with marked hemispheric differences. Large column densities of ozone are obtained at high latitudes during late winter in the northern Hemisphere. Similar marked increases are not obtained in the southern Hemisphere. The distribution of long-lived species (H_2O, N_2O, F-11, F-12) are well represented in the stratosphere.

Ozone perturbation estimates are in agreement with previous studies. Average global steady-state reduction due to F-11 and F-12 alone are estimated to be 4.5 per cent. However, changes in total ozone are found to be highly seasonal and latitude-dependent. Ozone reductions are found to be most pronounced at high latitudes during winter and spring seasons, where they are in the range of 6-10 per cent. Reduction due to methyl chloroform is estimated to be approximately 25 per cent of the reduction due to F-11 and F-12, with present release rates. The model studies show a marked discrepancy with observations in tropospheric inventory of F-11 and F-12 over the last few years. The models show a slower increase in concentrations with time than the observations. This may indicate that the published release rates are underestimated. Future studies will emphasis on possible tropospheric changes in ozone. Tropospheric processes are more complex and less well understood, and the uncertainties are still very large.

Regulatory questions

In January 1982 the Ministry of Environment refused to approve the establishment of a factory for production of extruded polystyrene. The reason for this was partly the amounts of CFC which would be used and released each year compared with the former use of CFC as propellants in aerosol cans; partly it was deemed that there were alternative products on the market which do not use CFC in production.

Norway has, as a result of the incident mentioned above, introduced a permit system for all new industries which will have CFC emissions from productions or/and products. Also, already established industries which wish to expand their production capacity must apply for a permit.

SWEDEN

Research

1. The Swedish Meteorological and Hydrological Institute in Norrköping has recently bought a Brewer spectrophotometer for measuring UV-B. The purpose is to start a long-run programme for measuring the variations of the intensity of UV radiation.

2. <u>At the Institute of physiological Bothanics at the University of Lund</u>, studies of the effects of UV on photosynthesis have just started. The work is mainly focused on laboratory studies of the influences of UV on biological and chemical processes in plants, and will investigate what effects a probable future increase of UV radiation would have on different plants, including agricultural plants.

Co-operation with Indian agricultural scientists has just started.

<u>Regulatory actions</u>

<u>Environmental Protection Board</u>

1. There has been ban on the use of CFCs in aerosols from 1 July 1979.

2. With respect to CFC use in foam plastic industries, no ban exists, however, the industries have to have special permits when starting such industries. At present, special conditions are included in the permit requiring industry to search for alternatives to CFCs and also investigate the possibilities for recycling.

SWITZERLAND

A 1-D mesospheric model of ozone and all the relevant trace substances calculating and explaining the day-night variation of all these substances has been constructed and run at the Laboratory for Atmospheric Physics at ETH-Zurich.

Sponsored by CMA, a four month intercomparison between microwave technique (Institut of Applied Physics, University of Berne) and the Umkehr method used at Aire-sur-l'Adour has been carried out in the winter 1981/82 for measuring ozone between 30 and 50 km.

Regular Umkehr measurements with two Dobson instruments in parallel are carried out at the climatic observatory at Arosa run by the Laboratory for Atmospheric Physics at ETH; about 15 vertical distributions per month are obtained with each instrument. In addition to the manual total ozone observation carried out at Aire it is planned to make continuous total ozone observations (every few minutes) with an automatic Dobson instrument beginning in the summer 1983 for investigating short-time variability and the influence of sky conditions on the measurements.

Regular ozone soundings (three times per week) are made at Payune, using the Brewer-Mast electrochemical sonde, in collaboration between the Swiss Meteorological Institute and the Laboratory of Atmospheric Physics at ETH-Zurich.

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

Since the fifth meeting of CCOL the UK has continued its long-standing commitment to research on the ozone layer. The work can be conveniently reported under three headings - atmospheric measurements, laboratory kinetic studies, and stratospheric modelling.

1. Atmospheric measurement

(i) Ground-based measurements

The Meteorological Office has continued measurement of columnar ozone abundance by Dobson instruments at Lerwick, Bracknell and St. Helena, and carried out calibration of those at Mahé (Seychelles) and Singapore.

The British Antarctic Survey maintains Dobson spectrophotometer stations at Argentine Islands and Halley Bay. During 1982-3 a programme of ozone sonde flights was carried out at Argentine Islands in collaboration with NASA. The vertical distribution of ozone was measured by electrochemical concentration cell. Balloons were launched to coincide with overpasses of NIMBUS 7 and Solar Mesosphere Explorer satellites. Fifty five ascents were successfully completed.

(ii) Aircraft measurements

The Meteorological Office is undertaking the analysis and interpretation of all past stratospheric data from Canberra flights up to 1980, particularly those from a campaign during 1977-80 to examine the meridional gradient of water vapour around the longitude of the Greenwich meridian.

A campaign is planned for April 1983 to examine stratospheric-tropospheric exchange, with the C130 Hercules aircraft of the Meteorological Research Flight based in Scotland. Tracers to be measured by on-board instruments include O_3, H_2O, CF_2Cl_3, CCl_4 and CH_3CCl_3 in addition to high frequency (20Hz) measurements of meteorological variables.

(iii) Balloon-borne measurements

The Upper Atmosphere Group of the National Physical Laboratory (NPL) has been one of the key participants in the international Balloon Intercomparison Campaign (BIC); the first phase of this experiment took place in autumn 1982 at the National Scientific Balloon Facility, Palestine, Texas; the second phase is scheduled for spring 1983. Experimental groups from the Belgium, Canada France, Italy, Japan, United Kingdom, the United States, and are taking part in this campaign funded by NASA, CMA, the Commission of the European Communities and the groups' own funding agencies. Measurements are being made on atmospheric species which are the key to understanding the chemistry of the stratosphere including the NO_x family, HCl, chlorine monoxide and ozone itself. The intercomparison is intended to assess the accuracy and precision of measurements by different methods and to provide near simultaneous measurements in the same air mass.

Four separate balloon-borne payloads were launched simultaneously. The NPL grating spectrometer (described in the progress report to the fifth session of CCOL) was flown with five other instruments on a gondola managed by NPL. Unfortunately, the balloon carrying the gondola was defective so the flight had to be terminated and the experiment was reflown two weeks later. All the instruments on the NPL gondola used the limb sounding remote sensing technique to derive concentration profiles as a function of altitude. Each was able to monitor one or more species belonging to the NO_x family plus other stratospheric constituents. The gondola was fully steerable in azimuth

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so that the instruments could be made to look at the same air mass. Half the instruments used emission spectroscopy and looked west in the period just before and immediately after the sunset transition. The remaining instruments used absorption spectroscopy with the sun as source and collected data during the transition. Intercomparison of the data, which are still being analysed, should yield important information on the usefulness of the two techniques at sunset (or sunrise), when the rate of change of several species is greatest.

Two sets of stratospheric air samples obtained in collaboration with the Max-Planck Institute, Lindau were analysed at Harwell during 1982. The first balloon launched from Gap in the French Alps reached 17 km altitude and the second from Aire sur l'Adour in Landes provided a full set of 24 samples over the altitude range of 11 to 33 km. The samples were analysed for some 20 stable trace gas species including a comprehensive group of chlorofluorocarbons and chlorocarbons. Vertical profiles for carbon tetrachloride and methyl chloroform were successfully obtained for the first time, loss of the species on storage in the sample bottles having been successfuly overcome following laboratory simulations. The results are still being assessed, but it is already clear that the vertical profiles of several chlorine species photolysed in the stratosphere support the recent downward revision of the molecular oxygen absorption coefficient in the ultra-violet region of the spectrum. Profiles for some hydrocarbons were also obtained, and the data for ethane support current model predictions for chlorine atom concentrations in the lower stratosphere.

The Rutherford Appleton Laboratory is developing a rapid-response microwave heterodyne spectrometer operating at 183-184 GHZ, to be flown on a balloon-borne platform for measurement of H_2O and O_3 in the stratosphere and mesosphere. The instrument will provide a vertical resolution of $\sim$100 m by measuring during ascent and/or descent, up to an altitude of $\sim$40 km, and a vertical resolution of $\sim$6-7 km from float altitude to about 80 km altitude by determining the pressure-broadened line shapes of the molecular transitions. The experiment will initially be flown during the MAP-GLOBUS campaign at Aire sur l'Adour, in September 1983, and annually thereafter as opportunities arise.

There have been no recent flights of the National Physical Laboratory's light-weight filter radiometer for the measurement of water vapour. However, the data collected during the Water Vapour Intercomparison Campaign (1981) have been analysed and compared with the other measurements which were made simultaneously: the data have been published in the Upper Atmospheric Programs Bulletin (issue 81-4). It is planned to carry out certain improvements to this instrument to extend the altitude range over which measurements can be made.

The Meteorological Office hope, subject to NASA approval, to fly a spectrophone instrument on a balloon in April 1983 from Palestine, Texas, to measure directly the heating of the stratosphere caused by the absorption of solar radiation by volcanic aerosol from the El Chichon eruption.

(iv) <u>Measurements on current satellites</u>

Daily analyses of meteorological variables are being produced by the Meteorological Office for levels up to 1 mb using data from the Stratospheric Sounding Unit on TIROS N. These analyses are being used for dynamical studies

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in conjuction with a numerical stratosphere-mesophere model. The Stratospheric Sounding Unit, provided by the Meteorological Office and flown on NOAA's TIROS-N series satellites, has proved capable of making very consistent temperature measurements. Stratospheric warming associated with the eruption of El Chichón has been observed. (Nature 301, 406-407 (1983)).

(v) Measurements on future satellites

Upper Atmosphere Research Satellite (UARS)

The Improved Stratospheric and Mesospheric Sounder (ISAMS) is multi-channel infra-red limb-sounding radiometer, planned jointly by Oxford University and Rutherford Appleton Laboratory, which will fly on the Upper Atmosphere Research Satellite scheduled for launch in 1989. ISAMS will measure, with near-global coverage and with a resolution at the tangent point of 5 km, the vertical concentration profiles of the minor constituents NO, N_2O, NO_2, H_2O, HNO_3, CH_4 and possibly CO, as well as temperature and zonal wind speed.

The primary scientific objectives of ISAMS are:

(a) The study of minor constituents which take part in ozone chemistry, to assess the effect of artificial production of such constituents;

(b) To study the interplay between dynamic, photochemical and radiative processes, to obtain some understanding of stratospheric climate;

(c) To measure the distribution of important constituents through the altitude region where they are dissociated in order to estimate production and loss rates.

Rutherford Appleton Laboratory and the Meteorological Office are participating through the NASA science teams in the Halogen Occultation Experiment (HALOE) to be flown on UARS. HALOE is a multichannel infra-red solar occultation experiment designed to measure the stratospheric concentrations of HCl, HF, CH_4, NO, COS, H_2O, CF_2Cl_2, O_3, HNO_3 and CO_2, with a vertical resolution of 2 km to produce horizontal and vertical maps of conentrations, and to determine annual variations in the measured species.

Space Shuttle

Rutherford Appleton Laboratory is also taking part in the Atmospheric Trace Molecules by Spectroscopy (ATMOS) experiment scheduled for 1984. ATMOS is a Fourier spectrometer solar occultation experiment which will measure the vertical distributions of a number of minor stratospheric constituents with 2 km resolution to include:

Source molecules	: CFMs, H_2O, CH_4, N_2O
Reservoir molecules	: O_3, HNO_3, HCl, HF, NO, H_2O_2, $ClONO_2$
Radical molecules	: ClO, H_2O, NO_2

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Rutherford Appleton Laboratory has been invited to participate with the Federal Republic of Germany and Switzerland in the Microwave Atmospheric Sounder (MAS), a limb-sounding microwave heterodyne spectrometer to be flown on the Shuttle from 1986 onwards. The main objective of the MAS experiment is to study the composition and dynamic structure of the stratosphere and mesosphere (altitude range 20 - 100 km), with particular reference to the study of anthropogenic influences on the ozone layer. MAS operates at frequencies of 60, 183-184 and 204 GHz, and will measure, for the first time on a global basis, the distributions of temperature, pressure, O_3, H_2O and ClO in the stratosphere and mesosphere. The 1m antenna will provide a vertical resolution at the tangent height of 2 km for the constituents and 10 km for temperature and pressure.

2. Laboratory measurements

(i) Spectroscopy

(i) Rutherford Appleton Laboratory is building a facility to provide basic spectral absorption cross-section data, so that the chemical composition of the middle atmosphere may be inferred from remote sensing instruments. The measurement programme will include studies of spectroscopic line data in support of HALOE and ATMOS.

The spectroscopy facility comprises several absorption cells, in which gases may be held for long periods at temperatures and pressures which closely simulate those found in the middle atmosphere, and a versatile interferometric spectrophotometer capable of achieving very high spectral resolution. The absorption cells provide path lengths from 5 cm to 1 km, and allow molecular transition line strengths to be measured over four orders of magnitude. The high spectral resolution will allow line shapes and widths to be measured over a wide temperature range, enabling many outstanding problems in stratospheric remote sensing to be addressed.

(ii) Chemical kinetics

O_x cycle

The primary step in the ultraviolet photolysis:

$$O_3 \; + \; h\nu \qquad O(^1D) \qquad + \qquad O_2(^1\Delta g) \qquad\qquad (1)$$

is of major importance as a source of excited atoms and molecules. Oxford University has confirmed its early work on the wave length dependence of quantum yield for (O^1D) formation by more detailed recent studies. However, none of these later investigations has addressed the question of $O_2(^1\Delta g)$ production at wave lengths longer than the spin-allowed limit ($\sim$310 nm). Evidence has now been obtained that the quantum yield remains unity (measured) for at least as long as 334 nm. Thus O_2 ($^1\Delta g$) production rates at low altitudes/high zenith angles are much higher than ordinarily calculated. While O_2 ($^1\Delta g$) probably plays little part in the direct oxygen-only ozone cycle, its long atmospheric lifetime could cause it to modify the chemistry of trace constituents, especially unsaturated ones.

At Edinburgh University work of relevance to atmospheric chemistry is being undertaken on chemiluminescent reactions in the oxygen afterglow. Current interest is centred on the mechanism of the production of highly excited molecular oxygen in the $(A^3\Sigma_u^+)$, $C(^3\Delta_u)$, and $C(^1\Sigma_u)$ states. The rates of quenching of these states by atmospheric gases are being measured in order to elucidate the mechanism of the formation of atmospheric O^1S, which is thought to be formed by collisions between excited molecular oxygen and ground-state oxygen atoms, i.e.

$$O(^3P) + O_2 = O(^1S) + O_2 \qquad (2)$$

A thorough understanding of such processes will be important in the calculation of mesospheric odd-oxygen concentrations from measured emission rates for the process:

$$O(^1S) \longrightarrow O(^1D) + h\nu \quad (557\ nm) \qquad (3)$$

HO_x cycle

Experiments have been carried out at Cambridge University to develop new methods for detecting HO_2 by mid-infra-red spectroscopy. A tunable diode laser is being used to scan a narrow region of the v_3 band of HO_2 near 1100 cm^{-1} with Doppler limited resolution and at high repetition rates (10^4Hz). The reaction

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (4)$$

has been studied using HO_2 radicals generated by flash photolysis and a rate coefficient of $2.4 \times 10^{-13} \exp(560/T)\ cm^3\ s^{-1}$ obtained for the pressures which exist in the stratosphere. Much higher sensitivities can be achieved by laser magnetic resonance spectroscopy using a $^{12}C^{18}O_2$ laser to observe the v_3 band of HO_2. This method will be used to measure coefficients of reactions of HO_2 at total pressures up to 50 Mb, giving data which can be applied directly to stratospheric problems.

Preliminary work has begun at Edinburgh University to examine the rates of gas-phase reactions of both hydroxyl and hydroperoxyl radicals using resonance fluorescence detection for OH and chemical titration followed by resonance fluorescence for HO_2.

At Oxford University the radical-radical process:

$$OH + ClO \longrightarrow \text{products} \qquad (5)$$

is being studied by conventional discharge-flow methods in an attempt to resolve conflicting views about the over-all kinetics, as well as the nature and efficiencies of the product channels. The approach used is to measure concentrations of as many species as possible. Resonance fluorescence allows the concentrations of OH, Cl, etc. to be determined directly, and ClO and HO_2 via titration.

The reactions of HO_2 play a central role in the chemistry of the stratosphere (and the troposphere), since HO_2 is chemically coupled to OH, the major oxidizing species for atmospheric trace gases. As part of a continuing kinetics programme on HO_2 at Harwell, the reaction of Cl with HO has been studied using an improved molecular modulation technique. Two channels have now been identified for this reaction:

$$HO_2 + Cl \longrightarrow HCL + O_2 \qquad (6a)$$
$$HO_2 + Cl \longrightarrow OH + ClO \qquad (6b)$$

Channel (6b) was previously thought to be unimportant, but has now been positively identified from direct observation of ClO product. The data are currently being evaluated to determine both k_{6a} and k_{6b} at pressures near 1 atmosphere.

NO_x chemistry

The reaction between $O(^1D)$ atoms and N_2O in the stratosphere affects the ozone layer due to the formation of NO. Gas phase measurements have been carried out at the University of East Anglia on the $O(^1D)/N_2O$ system using FTIR, and the spectra indicate formation of both NO and NO_2. The detection of this latter compound introduces a quantifiable correction to the value of ϕ NO 184.9 as previously measured by various researchers.

One radical of considerable importance in atmospheric ozone chemistry is NO_3, the kinetics and reactivity of which have been relatively neglected. Many investigations have used the thermal decomposition of N_2O_5 as a source of NO_3.

$$N_2O_5 + M \rightleftharpoons NO_3 + NO_2 + M \qquad (7)$$

Subsequent analysis of kinetics (and spectroscopic) data then generally requires modelling of a complex scheme, and the results are ambiguous. However the major atmospheric source of NO_3

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (8)$$

has also been used in the laboratory at Oxford University. Sufficiently high concentrations of O_3, and low concentrations of NO_2, were used to convert NO_2 to NO_3 virtually stoichiometrically. Ozone was circulated in a totally enclosed flow system by a reciprocating pump and estimated by optical absorption. Measurements were made of the absolute absorption cross-section of NO_3, a parameter relevant to the photolysis of the radical. Both photolytic

$$NO_3 + hv \longrightarrow NO_2 + O \qquad (9a)$$
$$\longrightarrow NO + O_2 \qquad (9b)$$

steps are possible, and the consequences of reaction (8) in the atmosphere depend on the absolute and relative quantum efficiencies of reactions (9a) and (9b). The reverse of reaction (7) - association of NO_3 with NO_2 - has also been investigated. Future work planned on the NO_3 system includes measurement of the association kinetics as a function of third body (nature and concentration) and of temperature. Radical-radical processes will be studied involving NO_x, HO_x, and possibly ClO_x species (eg. $NO_3 + NO_3$, $NO_3 + O$, $NO_3 + OH$ etc.).

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ClO_x chemistry

The production process of a chlorine (or bromine) atom and a halogenocarbon radical from halofluorocarbon photolysis in the stratosphere has been well studied in recent years. However, while the reactions involving the halogen atom have been much investigated there is little known about the processes in which the halogenocarbon radical participates. Research at the University of East Anglia has been centred on quantifying the photo-oxidation reactions of CF_2Cl and CF_3 radicals using Fourier Transform Infra-red (FTIR) spectroscopy as a means of monitoring end-products such as carbonyl difluoride (COF_2). Thus ϕ COF_2 189.9 has been measured for the photolysis of CF_2Cl_2 and CF_3Br in oxygen. The values are 1.0 ± 0.1 for both compounds, and represent measurements not performed directly on COF_2 in previous work. Future studies are directed towards the identification of expected intermediates, e.g. CF_2ClOO formed in the photo-oxidation by means of the matrix isolation technique at 4^oK using FTIR for analysis.

Oxford University uses reaction (1) as a source of $O(^1D)$ for the production of CF_3Cl radicals by the reaction:

$$O(^1D) + CF_2Cl_2 \longrightarrow ClO + CF_2Cl \qquad (10)$$

The technique employs a photolytic flow system with mass spectrometric detection of reactants and products. The initial interest centred on the branching ratio for reaction (10) compared with over-all quantity of $O(^1D)$. More recently, the emphasis has been on the subsequent fate of the CF_2Cl radicals. In a system containing excess ozone up to 3 further O_3 molecules can be removed by each CF_2Cl radical. The initial attack of CF_2Cl on O_3 is rapid, but subsquent processes (probably involving peroxy-species) are slower. From the atmospheric point of view, the important conclusion is that both Cl atoms in CF_2Cl_2 are now explicitly shown to be available for the catalytic ozone destruction cycle. Results are now being obtained and analysed for the CFCs, CF_3Cl and $CFCl_3$. Future studies using this technique will concentrate on the kinetics of the initial attack of CF_2Cl (or CF_3, $CFCl_2$ etc.) radicals on O_3 and on O_2.

Chlorine nitrate is a significant temporary reservoir species for active ClO_x and NO_x species in the mid-stratosphere, and consequently its chemistry has a substantial effect on calculated ozone depletion due to stratospheric pollutants. The formation of chlorine nitrate, $ClONO_2$, in the association reaction of ClO with NO_2

$$ClO + NO_2 + M \xrightarrow{k_1} ClONO_2 + M \qquad (11)$$

has been studied at Harwell using long-path absorption of coherent infra-red radiation from a diode laser. Chlorine nitrate is the only stable end-product of this reaction at room temperature. Time-resolved measurements of $ClONO_2$ formation showed no evidence for any involvement of unstable isomers of $ClNO_3$ in the reaction. These measurements gave a value of $k_{11} = (1.8 \pm 0.4) \times 10^{-31}$ cm^6 $molecule^{-2}s^{-1}$ at 295^oK and an upper limit of 5 ms for the lifetime of any isomeric products at this temperature. This implies that isomer formation is not significant for the

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chemistry of the stratosphere, and that consensus value of k_{11} as measured from decay of ClO reactant can be used to calculate the formation rate of chlorine nitrate in the stratosphere. The experiments also showed that the reaction of Cl atoms with $ClONO_2$ is a factor of 50 higher than the literature value, and this has important consequences for interpretation of other laboratory experiments.

3. Stratospheric modelling

The Harwell 1-D model is being updated to include revised photolysis rate coefficients for a number of species following the recent increase in calculated solar irradiance in the range 195 nm to 220 nm. This results from the recent revision in preferred values for molecular oxygen absorption cross-sections in the Herzberg continuum. Calculated profiles for halocarbon species, including minor CFCs and chlorocarbons such as methyl chloroform and carbon tetrachloride, will be compared with experimental data obtained in the 1982 balloon launches referred to earlier. This should provide an independent check on the revised oxygen cross-sections and the extent to which inappropriate eddy diffusion coefficients contribute to the well-documented discrepancy between observed and calculated profiles of $CFCl_3$ in the stratosphere.

Cambridge University has carried out modelling studies of the decay of ozone near the South Pole during the Antarctic summer. This work, done in collaboration with the British Antarctic Survey, is being prepared for publication.

Theoretical modelling of the composition of the stratosphere at the Meteorological Office has focused on the covariance of ozone and water vapour in a general circulation model, (J. Geophys. Res 86, 5303-5320 (1981)) and upon the possible utility of the diurnal variation of ozone in the upper stratosphere as an experimental test calling for high relative rather than absolute accuracy in the measurements (Q.J. Roy. Met. Soc. 109, 281 (1983)). Calculation of photochemical evolution in parcels moving on isentropic surfaces is also under-way.

A programme of two-dimensional stratospheric modelling has begun at Rutherford Appleton Laboratory with the primary aim of investigating the coupling between dynamical, radiative and photochemical processes. Three main areas will be (i) the study of long-time-scale (of the order of a few years) integrations to investigate the budgets of stratospheric trace gases and the sensitivity of the model to the representation of physical processes; (ii) comparison of model fields with satellite and balloon data, and the use of such data to constrain the model; (iii) detailed investigation of diurnal variations, with particular emphasis on comparison with co-ordinated balloon campaigns. A detailed comparison of the model fields with CH_4 and N_2O data from the University of Oxford SAMS instrument on Nimbus 7 has been carried out. The agreement is very good in the case of CH_4. For N_2O there are differences in the upper stratosphere which could have photochemical or dynamical origins. This work is to be submitted for publication soon.

Two-dimensional modelling using the residual diabatic or residual circulation was formerly carried out at the University of Oxford. The same researchers, now at Rutherford Appleton Laboratory, have submitted a paper on this work for publication. Further extensions of the work, but relying more on satellite-derived wave climatologies, are planned.

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UNION OF SOVIET SOCIALIST REPUBLICS

Total ozone content measured in the USSR during the solar eclipse on 31 July 1981

During the solar eclipse on 31 July 1981, in accordance with the measurement programme, the USSR State Committee for Hydrometeorology and Control of Natural Environment performed increased meteorological observations from the Soviet stations located along the eclipse trajectory. At the same time, measurements of the total ozone content (TOC) were made from some stations.

The researchers of the Central Aerological Observatory measured TOC using a Dobson spectrophotometer at the meteorological station of Bratsk. The researchers of the Main Geophysical Observatory made these measurements using network ozonemeter M-83. Tables 3, 4 and 5 show the data from the stations where conditions were favourable for observations. The researchers of the Institute of Atmospheric Physics made measurements of TOC from aircraft Jak-40 at an altitude of 8 km using device DMK-4; table 5 demonstrates the total ozone content in the atmosphere over 8 km. Table 1 shows the situation of the solar eclipse at the stations on 31 July 1981.

Data on TOC were obtained by researchers of the Central Aerological Observatory (table 2), the Main Geophysical Observatory of the USSR State Committee for Hydrometeorology and Control of Natural Environment (tables 3, 4 and 5) and the Institute of Atmospheric Physics of the Academy of Sciences of the USSR (table 6). Moscow time is used for all the tables.

Analysis of the data shows that the influence of the total solar eclipse on the total ozone content seems to be negligible.

Table 1

Solar eclipse situation,

Moscow time, 31 July 1981

(T_1- beginning of the eclipse, T_2 - beginning of the total eclipse, - duration of the total eclipse, T_4 - termination of the eclipse, - maximal phase of the eclipse)

	Station name	T_1	T_2	$\sim$	T_4	ϕ_m
		hm	hms	s	hm	
	a/ within total eclipse band					
1	Bratsk	4 48	5 59 46	106	7 17	1.008
2	Vitim	5 02	6 17 35	90	7 37	1.004
3	Tinda	5.12	6 30 01	117	7 50	1.008
	b/ out of total phase band					
4	Nikolayevsk-on-Amur	5.35	6 55	-	8 12	0.98
5	Semipalatinsk	4.28	5 34	-	6.45	0.93

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Table 2

Data on TOC obtained in Bratsk, 31 July 1981

Time	TOC	Time	TOC
4.52	0.317	5.50	0.295
5.00	0.301	5.55	0.299
5.08	0.301	6.00	0.303
5.20	0.301	6.09	0.304
5.25	0.301	6.15	0.298
5.30	0.302	7.00	0.299
5.35	0.298	7.10	0.302
5.40	0.300	7.15	0.304
5.45	0.300		

Table 3

Data on TOC obtained in Vitim, 31 July 1981

Time	TOC	Time	TOC
3.00	0.323	8.00	0.325
3.30	0.330	8.30	0.330
4.00	0.343	9.00	0.330
6.50	0.350	9.30	0.325
7.00	0.355	10.00	0.325
7.10	0.350	10.30	0.335
7.20	0.343	11.00	0.335
7.30	0.330		

Table 4

Data on TOC obtained in Nikolayevsk-on-Amur, 31 July 1981

Time	TOC	Time	TOC
5.30	0.295	7.12	0.320
6.22	0.325	7.15	0.320
6.30	0.310	7.18	0.330
6.39	0.325	7.21	0.325
6.46	0.305	7.24	0.340
6.48	0.310	7.27	0.320
6.51	0.335	7.30	0.330
6.54	0.318	7.40	0.320
6.56	0.325	7.50	0.330
7.00	0.348	8.00	0.320
7.03	0.345	8.10	0.325
7.03	0.323	8.30	0.315
7.06	0.325	9.00	0.320
7.09	0.330	9.30	0.350

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Table 5

Data on TOC obtained in Semipalatinsk, 31 July 1981

Time	TOC	Time	TOC
4.00	0.334	5.52	0.382
4.01	0.340	5.56	0.364
4.10	0.368	6.00	0.362
4.20	0.342	6.01	0.364
4.21	0.348	6.10	0.352
4.30	0.361	6.20	0.356
4.40	0.388	6.30	0.341
4.41	0.391	6.32	0.323
4.50	0.359	6 40	0.353
5.00	0.355	6.50	0.374
5.04	0.362	7.00	0.346
5.08	0.380	7.03	0.335
5.12	0.361	7.05	0.345
5.20	0.365	7.30	0.346
5.24	0.360	8.00	0.334
5.28	0.375	8.30	0.355
5.31	0.360	9.00	0.360
5.32	0.362	9.30	0.344
5.34	0.378	10.00	0.338
5.35	0.380	10.30	0.345
5.37	0.365	11.00	0.347
5.40	0.367	11.30	0.345
5.41	0.370	12.00	0.350
5.44	0.370	12.30	0.354
5.48	0.380	13.00	0.345

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Table 6

Data on TOC obtained in Tinda region at an altitude of of 8 km, 31 July 1981

Time	TOC	Time	TOC
5.18	0.280	6.36	0.285
5.22	0.283	6.38	0.283
5.25	0.285	6.40	0.280
5.33	0.285	6.44	0.280
5.35	0.283	6.52	0.280
5.38	0.283	6.53	0.285
5.46	0.283	6.56	0.283
5.48	0.283	6.58	0.281
5.49	0.282	6.59	0.285
5.51	0.283	7.02	0.283
5.54	0.283	7.03	0.284
5.55	0.284	7.06	0.281
5.56	0.282	7.11	0.281
5.58	0.283	7.13	0.283
5.59	0.285	7.15	0.285
6.00	0.280	7.17	0.282
6.08	0.281	7.20	0.283
6.10	0.280	7.22	0.281
6.12	0.285	7.26	0.283
6.17	0.287	7.30	0.281
6.20	0.290	7.35	0.282
6.24	0.287	7.37	0.280
6.25	0.289	7.39	0.281
6.34	0.290	7.41	0.283

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EUROPEAN ECONOMIC COMMUNITY

During the last four or five years the Commission of the European Communities supported ozone research by co-ordinating modelling and measurement activities in member States. Study groups were formed in order to perform joint simulation studies and to gather data for testing the CFC depletion hypothesis. At workshop organized in January 1981 in Brussels about 30 experts from nine countries (including USA and Canada) produced a report entitled "Evaluation of the effects of chlorofluorocarbons on atmospheric ozone: Present status of research", which was published by the Commission in November 1981 (Doc. XII/CLi/9/81). This report represented an update of the results of the reports issued in 1979 by the United States National Academy of Sciences, NASA and the British Department of Environment.

At present, ozone research is funded under the R & D Programmes "Environment protection" and "Climatology", which started in 1981 and will end in December 1985. There exist several cost-sharing research contracts in this area with different groups in several member States. Some of the highlights of the research being promoted are briefly summarized below.

Six European research groups are being supported for participation in an international Stratospheric Balloon Intercomparison Campaign. The first phase of this campaign (supported also by NASA and CMA) took part in fall 1982, and the second phase is scheduled for April 1983.

A group from the Federal Republic of Germany is receiving fund for balloon-borne measurements of stratospheric trace gases in the southern hemisphere during this year. Another group from the Federal Republic of Germany is undertaking monitoring of stratospheric temperatures under the climatology programme.

An interesting result is an observed increase in the stratospheric temperature of about 5°K in the tropics following the El-Chichón eruption. These temperature measurements show a high positive correlation with LIDAR measurements of volcanic stratospheric aerosols made by a group in the United States.

Two-dimensional modelling of the stratospheric dynamics, radiation and chemistry is being funded. The results produced by one of these models are being compared with results derived from analysis of satellite observations of temperature, CH_4 and N_2O and H_2O performed by the same group.

Under the Climatology programme modelling studies of the radiative impact of ozone and other trace gases and aerosols on climate are receiving considerable support.

Apart from providing funds for research, the Commission is also undertaking supporting activities. For instance, at the request of the IAMAP - International Ozone Commission (IOC), it will be co-sponsoring the Quadrennial International Ozone Symposium to be held in Greece in 1984.

On the side of action for the protection of the ozone layer the EEC Council of Ministers took a decision in 1980 which has resulted in a 34 per cent reduction of in the use of CFCs 11 and 12 in aerosols by by the end of

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1981 in comparison with the levels of use in 1976, rising to 37 per cent by the end of 1982, for the EEC as a whole. As a result of a 1982 decision the Commission undertook an action programme aimed at reducing emissions of CFCs in the non-aerosol sectors of their use. Under this programme codes of practice on the use of CFCs in refrigeration, solvents and rigid polyurethane foam were prepared for application by the relevant industries. In the field of flexible foam production a pilot project has been undertaken in Denmark to examine the feasibility of recycling the CFC used.

WORLD METEOROLOGICAL ORGANIZATION

A. Introduction

1. WMO has continued to carry out activities in keeping with its responsibility as lead agency in several fields of the World Plan of Action on the Ozone Layer. These activities are carried out within the WMO Global Ozone Research and Monitoring Project established in 1976.

B. Purpose of document

2. This document informs the UNEP Co-ordinating Committee on the Ozone Layer of progress made by WMO of direct concern to the implementation of the World Plan on the Ozone Layer, since the fifth session of the Committee (Copenhagen, October 1981), and makes some proposals for future activities and support.

C. Discussion

3. During the 17 months since the Copenhagen CCOL meeting, WMO Ozone Project activities have continued to concentrate primarily on:

- Improving the Global Ozone Observing System (GOOS), including proliferation of Umkehr measurements;
- Clarifying physical processes and phenomena which possibly affect ozone photochemistry and ozone trends;
- Studies of potential climatic effect of ozone and other radiatively active minor trace gases; and
- Studies of the effect of aerosol contamination of the stratosphere on Umkehr evaluation.

Total ozone

4. The Dobson spectrophotometer is the mainstay instrument in the global total ozone observing network, upon which many other activities in the World Plan on the Ozone Layer depend to some degree. However, the instrument is delicate to operate and is subject to changes in its characteristics with time. It is therefore a necessary and continuing exercise to expand efforts to maintain the global network in a satisfactory condition. Starting in 1976, up to the end of 1982, WMO, with support from UNEP, has arranged for about

half of the active Dobson instruments to be upgraded, relocated and/or calibrated. In 1982 alone, Dobson spectrophotometers Nos. 6, 7, 12, 17, 52, 69, 78, 81 and 105 have been put into perfect working order with the assistance of experts volunteered by Canada, the United Kingdom and the United States.

5. WMO is supporting the use of a travelling Brewer spectrophotometer to check on the calibration of network Dobson instruments. There are plans for this instrument to be taken to the South-West Pacific region (i.e. Australia, New Zealand, the Philippines and Singapore). The other method of quickly spotting malfuctioning Dobsons, by the use of travelling standard lamps, which was initiated in late 1981, is continuing. It has been revealed, for example, that Dobsons Nos. 6, 12, 81 and 111 are badly in need of recalibration.

Vertical ozone distribution

6. Although the importance of continuous and reliable measurements of the vertical ozone distribution is well recognized, progress in this field is slow and requires increased emphasis on the subject by member countries, in accordance with the call made by the WMO Executive Committee. In this regard, a letter was addressed directly to Dobson operators by the IAMAP Ozone Commission, urging them to make Umkehr measurements as frequently as possible. Weekly balloon-borne ozone sonde measurement programmes have been initiated in Prague and Sofia, and WMO has supported the training of one observer as requested.

7. It is expected that an important improvement in the frequency of Umkehr measurements will be achieved through the joint initiative with the United States Environmental Protection Agency, the United States National Atmospheric and Oceanic Administration and the Chemical Manufacturers Association to automate seven Dobsons in the global network to take frequent Umkehr measurements. Collaboration of nearby LIDAR-operating institutions is now being sought by WMO to allow for aerosol correction of the Umkehr evaluation, data permitting.

8. Work is also continuing to revise all historical rocket ozone data using information provided by the WMO/FAA/NOAA/NASA rocket ozone sonde performance study, which will allow the establishment of firm reference profiles.

9. WMO has co-sponsored field measurements of vertical ozone distribution by various techniques (e.g. Umkehr, ECC, Brewer-Mast, LIDAR, DASIBI) held in Gap France in 1981, and further support has been pledged for a second ozone data gathering campaign, planned for September 1983, as a European contribution to the Middle Atmosphere Programme. The data from these two campaigns, and in particular the more elaborate true comparisons planned by NASA (also co-sponsored by WMO) for June 1983, will be very useful in firmly establishing performance characteristics of some uncommon methods and instruments. It is expected that the data will indicate which methods are worth giving special emphasis, especially in looking into ozone concentrations in the 30 - 45 km layer.

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10. During recent years the need for knowledge on the behaviour of ozone concentrations near the ground has greatly increased as a result of the dangerous concentrations which can arise from anthropogenic sources. Within the WMO Ozone Project continuous comparisons of three different physical methods of making ozone measurements (using wet and dry chemical or optical sensors) were carried out by the Hohenpeissenberg Observatory in the Federal Republic of Germany. The results were published by (W. Attmannspacher and R. Hartmannsgruber) in Berichte des Deutschen Wetterdienstes, No. 161 in 1982. The conclusion is that the tested instruments are useful for continuous measurements of ozone near the ground, but only if careful maintenance and control by a good ozone generator is made. Interference by water vapour and by NO_2 was observed in several sensors; however, such interference is usually negligible away from industrial plants and very foggy areas.

Other items

Trend detection

11. The WMO Executive Committee at its thirty-second session (May 1980) allocated high priority to studies aimed at clarifying physical processes which influence ozone trends and the assessment of such trends, if any. In this regard it was felt necessary to arrange for the detection of ozone trends to be discussed extensively in conjuction with known instrumental errors and the combined effect of various natural processes and possible anthropogenic influences. It was against this background, therefore, that WMO, in collaboration with the International Ozone Commission of IAMAP, organized a Meeting of Experts on Sources of Errors in Detection of Ozone Trends at the headquarters of the Canadian Atmospheric Environment Service in Toronto from 26 to 30 April 1982. The meeting focused discussion on the following main points: sources of errors and Dobson and vertical ozone distribution data quality, impact of errors in trend detection, possible retrospective improvement of data records and detection of ozone trends in the future.

12. The report stated that due to high natural variability and to many complicating factors such as instrument calibration errors, improper observational procedures, discontinuities in data records, influence of volcanic aerosols, instrumental drift, SO_2, etc., analyses of the available data and subsequent interpretations of the results require great care and understanding. The over-all 2 uncertainty of the total ozone trend estimate is estimated currently to be between 1.9 and 3.8 per cent per decade. It was noted, however, that combined scenario models indicate that some anthropogenic effects on the ozone layer may be partially compensated by others, raising the possibility of a non-detectable trend in total ozone during the past and current decades. Several important recommendations were formulated to improve past, current and future data from all ozone-measuring systems, which, if successfully applied, would put the ultimate trend detection limit of the combined total ozone observing system (ground-based, in situ, Umkehr and satellites) at better than 3 per cent per decade. The report of the meeting was published as WMO Ozone Project Report No. 12, and was given wide distribution.

13. In the meantime, not yet published statistical analyses of monthly averages of Umkehr data from 13 stations, in which the effect of aerosols induced in the evaluation of the ozone concentration at the top layers is taken into consideration (see also paragraphs 15-17 below), indicate with 95 per cent confidence that during the period 1970-1980, detectable depletion of partial ozone concentration of about 0.3 per cent per year in the 34-43 km range (layers 7 and 8) has occurred. These preliminary results need to be treated with caution because the aerosol adjustment is made using the only available atmospheric transmission data from one station.

New ozone absorption coefficients

14. In recent years, a number of studies have demonstrated ozone measurement inconsistencies which have been attributed to errors in laboratory measurements of ozone absorption coefficients. In addition, a number of results suggest that the present WMO scale (as adopted in 1968 on the recommendation of the Ozone Commission) may give results which are a few per cent too high. Re-determination of ozone absorption coefficients was initiated in the appropriate laboratory in the United States National Bureau of Standards, and WMO has supported evaluation of the preliminary results.

15. First assessments suggest that the present WMO scale for total ozone measurement with the Dobson spectrophotometer yields data which are approximately three per cent too high. For indirect ozone profile measurements using solar ultra-violet wavelengths, viz., the ground-based Dobson Umkehr method and the satellite BUV method, the new coefficients will produce both a change in scale and a change in the shape of the derived ozone profile. For direct balloon-borne soundings there would be only a uniform change in scale with no change in shape.

16. There is a consensus that efforts to obtain final re-determination of the absorption coefficients should be accelerated, and that the IAMAP Ozone Commission should make firm recommendations to WMO not later than mid-1984. Following this information, the rather demanding work on re-evaluation of all ozone data could be initiated. Of course the change in scale mentioned in the previous paragraph will be small, but it will be necessary to ensure precision in the results of ozone data analyses.

St atospheric aerosol effect

17. It is well known from theoretical studies that stratospheric aerosols, introduced usually by major volcanic eruptions, produce serious errors (about 10 to 20 per cent and more in the uppermost layers), in the evaluation of vertical ozone profiles from Umkehr measurements. The unpredictability of volcanic eruptions makes it impossible to plan experiments in advance. Therefore, when the Mexican volcano El Chichón erupted in April 1982, introducing an estimated 30 to 50 Mt of dust and gases into the stratosphere, WMO immediately encouraged the initiation of special measurements, and provided partial support to scientists from the Canadian AES and NOAA to participate in NASA-initiated dedicated studies.

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18. However, it is not only the scattering effect of volcanic aerosols which affects ozone data. The impact of volcanic SO_2 on total ozone measurements leads to spurious effects in ozone data which may mask a possible downward trend. Enormous effects have shown up in TOMS data taken over the initial plume of El Chichón. Once the volcanic cloud spreads out, the effect will be small (about 2-5 per cent) and not easily recognizable, and so very likely to affect future statistical studies of ozone trends.

19. In view of the above considerations, stratospheric aerosol LIDAR measurements should be strongly supported, and a system for correction of the ozone data needs to be established and implemented internationally.

Climate impact of future ozone and trace gas changes

20. Another major task of the WMO Ozone Project is to encourage and assist studies which will clarify the possible climatic impact of future changes in the concentrations of ozone and other minor constituents of the atmosphere. WMO therefore, in consultation with the International Ozone and Radiation Commission of IAMAP, organized a meeting on this subject which took place at NCAR (Boulder, Colorado) from 13 to 17 September 1982. The objectives of the meeting were to review and assess the current understanding of the various aspects of the trace gas-climate problem, to identify areas where there is considerable uncertainty and to formulate appropriate recommendations for future work.

21. The trace gases principally responsible for the long-wave radiative opacity of the present-day atmosphere are H_2O, CO_2 and O_3. On an annual and global basis, ozone alone contributed about 20 per cent of the total thermal downward flux from the stratosphere to the troposphere. The experts pointed out that several other radiatively active gases in the atmosphere, including N_2O, CH_4, NO_x, CCl_4 and chlorofluoromethanes (CFMs), contribute roughly 2^oK to present-day surface temperatures. Considering that these latter gases are undergoing augmentation of their concentration, the discussion concentrated on how they might interact photochemically amongst themselves and with ozone, and potential that might result in the vertical distribution of temperature and ozone. Several of these minor trace gases have strong absorption bands in the 7-13 um spectral region where the background atmosphere is relatively transparent. For example, the five CFM absorption bands in this region are roughly one order of magnitude stronger than the CO_2 14 μm band. Hence, projected increases in the amounts of these gases in the atmosphere could enhance the "greenhouse" effect, which might result in global mean surface warming. In this regard, climate model calculations published by several different groups indicate that the enhancement of the atmospheric long-wave opacity due to increases in the quantities of trace gases could produce global mean surface warming comparable to that projected as a result of increasing CO_2 over the next 60-80 years.

22. Another significant effect on the climate sensitivity could occur as a result of changes in and/or redistribution of the trace gas concentration with altitude, as might happen with ozone. For example, if the tropospheric concentration of ozone were to increase during the next century (a tendency indicated by reliable ozone soundings during the last decade), absorption in

the 9.6 μm ozone band could have an appreciable heating effect on surface temperatures of about 0.9°K. It is interesting to note that on a "per molecule" basis, O_3 changes in the lower stratosphere and upper troposphere are a few times more effective than changes in other regions of the atmosphere in causing surface temperature changes. At the same time, a decrease of ozone concentration at levels above 35 km could lead to cooling in that part of the stratosphere of about 10°K.

23. The meeting also discussed radiative-chemical and dynamical interactions between the different trace gases which, in certain cases, could result in additive and in other compensating radiative effects. Results of calculations using the 1981 WMO/NASA photochemical reaction rates indicate that increases of CO_2 alone could increase the surface temperature by about 0.25 and 0.4°K, for the periods 1952-1982 and 1982-2012 respectively. However, the same calculations suggest that the surface warming caused by increases of other gases is the same as CO_2 in the 1952-1982 period, and becomes slightly larger in the 1982-2012 period; for example, for the latter period, anthropogenic emissions other than CO_2 could warm the surface by 0.4°K. It is important to note that the other-than-CO_2 warming effect can be attributed equally to the direct radiative effects of NO_x, CFCs, CH_4 and N_2O, and to the indirect radiative effect associated with these O_3 perturbations induced by anthropogenic emissions. The combined effect on the stratospheric temperature for the period 1952-2012 indicates a small warming between tropopause (12 km) and 18 km, while the middle and upper stratosphere is cooled with a maximum cooling of about 5.5°K occurring around 48 km, which is a few kilometres higher than a possible maximum O_3 depletion. As in the case of the O_3 perturbation, the distribution of the temperature change for the period 1982-2012 is very similar to that for the total period. The magnitude of stratospheric temperature change is, however, smaller, with a maximum temperature decrease of about 3.5°K around 48 km.

24. It was concluded that the role of trace gases in the climate system is very complex, and that there are several unique issues. These require further studies of tropospheric chemistry, chemistry/climate interactions, stratospheric transport and stratosphere/troposphere radiative-dynamical interactions, including latitudinal effects. In view of these facts, there exists an urgent need for consolidating results, and international co-ordination of efforts aimed at clarifying the problem is very desirable. WMO, jointly with the IAMAP Radiation Commission, is initiating planning for comparisons of radiative codes used in climate models as one early and absolutely necessary step.

25. The WMO Executive Committee, at its session in June 1981, was informed of progress in measurements of minor constituents and of new values of photochemical rate constants which confirmed the potentially serious impact of human activities on the ozone layer. The Committee therefore requested the CAS Working Group on Atmospheric Ozone to assess new developments in this field and to prepare a third WMO statement on the matter if necessary. The third WMO statement was prepared on the basis of the detailed review on the State of the Statosphere 1981, prepared with the participation of more than 100 scientists, which was reported to the fourth session of CCOL. The WMO statement was released on 14 January 1982 and was widely distributed.

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26. Section E below contains a listing of reports published (or in preparation) in the WMO Ozone Project Report Series, which are of direct relevance to the World Plan of Action on the Ozone Layer.

D. Action proposed

27. The Committee is invited to note the information contained in this document. More specifically, it may wish to urge countries and interested institutions to intensify their efforts, and to collaborate in:

- Continuous regular recalibration of ozone-observing instruments;
- Detecting irregularities by means of the travelling Brewer and standard lamps;
- Encouraging reliable ozone soundings and frequent Umkehr measurements (automated when possible) and analysis of the data;
- Correcting data from long-term ozone observing stations, following the procedures outlined in WMO Ozone Report No. 12;
- Continuing studies of physical processes and phenomena which possibly affect ozone photochemistry and ozone trends, in particular solar and volcanic effects;
- Detection of changes in the tropospheric ozone concentrations and improvement of the upper tropospheric chemistry;
- Completing determination of new ozone absorption coefficients and arranging recalculations of all previous vertical ozone distributions taken by Umkehr and satellites;
- Exploring and developing methods for correction of Umkehr calculations for aerosol effect using LIDAR information;
- Clarifying the radiative effects of ozone and other minor constituents and incorporating them into climate models, e.g. by accelerating studies on tropospheric/stratospheric chemistry and chemical/dynamic interactions;
- Giving particular attention to simultaneous measurements of minor constituents of importance to the ozone budget.

E. previous reports published in connexion with the WMO Oxone Project

1. WMO Report on Atmospheric Ozone submitted to the UNEP Meeting of Experts designated by governments, intergovernmental and non-governmental organizations on the Ozone Layer, Washington, D.C., 1-9 March 1977

2. Report of the WMO Meeting of Experts on Ozone Modelling and Stratospheric/Tropospheric Exchange Processes, Geneva, 25-29 April 1977

3. Report of the WMO Meeting of Experts on UV-B Monitoring and Research, Geneva, 16-20 May 1977

4. Report of the WMO Meeting of Experts on Measurements of Rare Species Relevant to the Ozone Budget, Seattle, 18-21 August 1977

5. Report of the WMO Meeting of Experts on Stratospheric Circulation Analysis and Ozone, Washington, D.C., 9-13 July 1979

6. Operations Handbook. Ozone Observations with a Dobson Spectrophotometer, June 1980

7. Report of the WMO Meeting of Experts on 2-D Ozone Models, Toronto, January 1980

8. Report of the WMO Meeting of Experts on Rare Atmospheric Constituents of Importance to the Ozone Layer, Washington, D.C., March 1980

9. Report of the WMO Meeting of Experts on Assessment of Performance Characteristics of Various Ozone Observing Systems, Boulder, July 1980

10. Review of the Contribution of Ozone and Other Minor Gases to Atmospheric Radiation Régime and Their Possible Effect on Global Climate Change, December 1981

11. Report of WMO/NASA/FAA/NOAA Meeting of Experts on the Stratosphere 1981 - Theory and Measurement, Hampton, Virginia, May 1981

12. Report of the WMO Meeting of Experts on Sources of Errors in Detection of Ozone Trends, Toronto, 26-30 April 1982

13. Review of Dobson Spectrophotometer Total Ozone Measurement Accuracy (in press)

14. Report of the WMO Meeting of Experts on Potential Climatic Effects of Ozone and Other Minor Trace Gases, Boulder, Colorado, 13-17 September 1982.

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

OECD has recently issued two reports on the chlorofluorocarbons/ozone depletion issue. The Report on Chlorofluorocarbons (1982) contains a summary of the state of scientific knowledge as of 1981 in the areas of stratospheric chemistry and modelling, and health and environmental effects. It also contains a lengthy discussion of the uses of CFCs and of substitutes, alternative technologies and methods for reducing emissions of CFCs. The second report, Emissions Scenarios for CFCs (1982), discusses the results of modelling work done in several OECD member countries on a set of mutually agreed-upon scenarios. Several scenarios were postulated for CFC emissions, and they were run against a background scenario for emissions of other substances capable of perturbing the ozone. These substances included NO_2,

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NO_x, CO, CO_2 and CH_4. In addition, the report discusses work done in the United States and Canada on UV-B mapping. Much of the work generated for the preparation of this report has been reported independently and is reflected in the previous and current reports of the CCOL.

Currently, OECD is attempting to examine the socio-economic impacts of reducing the use of CFCs. The report will contain a summary and synthesis of existing work on costs of reducing the use of CFCs. Unfortunately, the data needed to significantly extend the analysis of impacts on industry and employment is generally not available in member countries, and even where governments have the data, they are often unable to release it for reasons of confidentiality. In the area of analysis of benefits to human health and the environment due to lowered emissions of CFCs, the lack of dose response relationships for most effects limits the work. This report will be completed during the summer of 1983 and submitted to the autumn 1983 meeting of the Environment Committee.

INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS

During the last years, ICSU has continued to carry out activities related to the ozone problem within its special committees such as SCOPE (Scientific Committee on Problems of the Environment) and SCOSTEP (Scientific Committee on Solar-Terrestrial Physics), unions such as IUGG (International Union of Geodesy and Geophysics) and its associations IAGA (International Association of Geomagnetism and Aeronomy) and IAMAP (International Association of Meteorology and Atmospheric Physics). A Middle Atmospheric Program (MAP) has been initiated for a duration of at least five years. SCOPE deals "with scientific problems that have major influence on the world environmental scene", and always bears in mind the desirability of maintaining and strengthening its relationship with UNEP and other parts of the United Nations system concerned with environmental matters.

In August 1983, at the XVIII General Assembly of the International Union of Geodesy and Geophysics, to be held in Hamburg, there will be a Middle Atmosphere Science Symposium under the sponsorship of IAMAP and IAGA. This symposium will include papers on the photochemical trace species, chemistry of ions and aerosols, etc.

From 3 to 7 September 1984, an Ozone Symposium organized by the IAMAP International Ozone Commission will be held in Halkidiki, Greece. This symposium will include papers on ozone-climate interactions, laboratory measurements of chemical rate constants and absorption cross-sections observations of trace constituents and their budgets, analysis of surface-based and satellite ozone observations, etc.

CHEMICAL MANUFACTURERS ASSOCIATION

Modelling

In 1980-1981 a full chemical scheme was successfully incorporated into the 2-D model funded by the CMA Fluorocarbon Program Panel (FPP). During 1981-82, considerable effort was spent on the further refinement and optimization of several key components of the 2-D code.

Incorporating detailed simulation of diurnal behaviour of radical species permits comprehensive comparisons of model calculations with the concentrations of those observed species known to vary significantly during a diurnal cycle. This unique capability is useful and perhaps essential in the interpretation of certain phenomena. For example, some improvement between the calculated and observed column NO_2 can be achieved by use of a fully diurnal, instead of a diurnally averaged, 2-D model. This model, however, still cannot fully account for the observed NO_2 minimum occurring at high latitudes during winter months, leading to the belief that certain conversion processes for NO_2 are not included in the air accepted chemical scheme.

Much of the major overestimation by models of the HNO_3 concentrations at around 35 km has been removed by incorporating the diurnal variations of OH and NO_2 into the model. Analysis of difficulties in reconciling the NO_2 observations at high latitudes during winter-time suggests that current theory may be missing a stratospheric sink for N_2O_5. N_2O_5 is, according to current models, the major form of NO_x under winter conditions. Several reactions that may be responsible for transforming winter-time NO_2 into HNO have been identified. Future work will assess the impact of these added reactions on stratospheric chemistry.

A comprehensive comparison between 2-D theory (which includes the effects of latitudinal, seasonal and diurnal insolation and a complete set of photochemical reactions with NASA 1982 recommended rates) and a wide range of atmospheric measurements at different latitudes, altitudes and seasons shows agreement within a factor of 2, generally, but there are several notable discrepancies. For instance, current models tend to predict too much CFC-11 and CFC-12 (particularly CFC-11) around 30 km at mid-latitudes. This discrepancy may result from an underestimation of solar flux at 200-220 nm by current models. There is recent evidence that the O_2 cross-sections in this spectral region (the Herzberg continuum) are lower than previously estimated. When these smaller cross sections are incorporated in the model, the principal results are: (1) improved agreement between measured and calculated CFC-11 and 12 profiles, (2) shorter lifetimes for CFC-11 and 12 and (3) smaller calculated steady-state ozone depletion from the effect of CFCs alone (3.2 per cent vs. the 4.5 per cent calculated using 1982 chemistry and the old O_2 cross sections).

The aforesaid 2-D model has been used to identify certain shortcomings of the current 1-D models. For example, one error arises due to the inability of 1-D models to account for the latitudinal gradient of species concentration and photolysis rates in the lifetime calculation. Preliminary results indicate that transport in two dimensions leads to a shorter calculated residence time as compared with 1-D model calculations. This finding clearly illustrates that the calculated photolysis lifetime depends on the latitudinal variations of both gas concentrations and photolysis rates, as well as their correlations.

Incorporating the revised rate constants (NASA Panel, 1982) into the 1-D model leads to the principal findings that the calculated ClO at around 40 km is in improved agreement with observations, and that the steady-state ozone depletion due to CFCs alone is revised downward to 4.5 per cent from the

6.1 per cent calculated using 1981 rates. These ozone depletion numbers are based on releases of CFCs alone, and do not reflect the effect of coupled perturbations due to anticipated increased emissions of CH_4, CO_2, N_2O and NO_x.

The calculated extent of change in total column ozone by the year 2010 for selected scenarios is listed in the following table.

Scenario	Percentage change in total column ozone by the year 2010
CFC constant[a]	-1.5
CFC growth[b]	-1.8
CFC constant[a] + NO_x^c + 0.2%-yr^{-1} N_2O + 0.55%-yr^{-1} CO_2 + 1.2%yr^{-1} CH_4	+1.2
CFC growth[b] + NO_x^c + 0.2%-yr^{-1} N_2O + 0.55% yr^{-1} CO_2 + 1.2%-yr^{-1} CH_4	+0.9

a Constant emission at 1980 levels.

b 3 per cent yr^{-1} growth from 1980 to 2000, followed by constant emissions at the 2000 level.

c Increases based on United States Department of Transportation estimates.

From these calculations it is apparent that even by the year 2010, there is little difference in the extent of ozone change between calculations for constant and for growth scenarios for CFCs. Use of a scenario that couples increasing CH_4, NO_x, N_2O, and CO_2 emissions with CFC emissions leads to a slight increase in the calculated amount of ozone, in contrast to the small decrease calculated when only CFC emissions are included in the model. Time-dependent calculations of stratospheric ozone profiles have also been made with the model incorporating coupled perturbations.

After it was suggested that the reaction of NaOH with HCl could be an important sink for stratospheric chlorine, the role of sodium in stratospheric chemistry was examined. The impact of sodium species on the stratospheric chlorine budget was found to be limited by the availability of sodium in the stratosphere, where the mixing ratio of total sodium is not expected to be larger than 0.1 ppbv. Recent revisions in the rates for the photolysis of NaCl and NaOH have led to renewed assessment of the importance of sodium and related chemistry. It has been found that the reactions $O(^3P)$ + NaO_2 and NaO + H_2O must be fast in order to explain the observed profiles for some sodium species. Modelling results suggest that sodium could have some importance to HO_x chemistry.

Atmospheric chemistry

The FPP programme to elucidate stratospheric chemistry centres on species and reactions likely to affect the interactions between chlorine-containing species and ozone.

Complementing the balloon observations were ground based measurements at the Kitt Peak National Observatory and at the Holloman Air Force Base, and observations from an aircraft flown by the National Center for Atmospheric Research.

A second series of measurements, scheduled to take place in May 1983, in conjunction with observations in support of the NASA Climate Program, will complete one of the most extensive and well-characterized field measurement campaigns ever undertaken.

A continuation of the data reduction from the SIBEX balloon campaign was funded in 1982 to permit a more complete assignment of spectral lines. The conclusions are due for publication shortly.

Funding of field measurements by FPP in 1983 includes a flight using the newly developed reel-up/reel-down technique and incorporating a new generation of instrumentation for in situ detection of ClO and related species.

Microwave measurements from Mauna Kea have been successfully used for determination of the ClO vertical profile and the diurnal variation of ClO, and for the detection of HO_2. FPP continues to fund IR spectroscopy from mountain sites in the United States and Europe. Significant developments are expected from the continuing analysis of the historical solar spectral record at Kitt Peak Observatory. Some evidence for the presence of temporary reservoirs, so far undetected in the stratosphere, has been provided by balloon-borne IR spectrometers. In 1983, FPP is funding latitudinal surveys of trace species using ground-based IR spectroscopy.

Work continues on the intercomparison of conventional Umkehr measurements with IR and microwave techniques for the determination of ozone profiles. This research has assumed special importance in view of the problem of correcting Umkehr measurements for the effects of stratospheric aerosols.

FPP has funded some measurements in the troposphere, including the Atmospheric Lifetime Experiment (ALE) and investigations of possible sinks for CFCs (e.g., in heterogeneously assisted processes) (see separate section on ALE).

Laboratory studies are essential for quantitative understanding of field measurements, and FPP has funded both the development of techniques and the accurate measurement of the temperature and pressure dependences of spectral features, e.g. tunable diode laser spectroscopy of the vibrational-rotational bands of HO_2. Of particular interest in 1983 will be a balloon flight of a copper vapour laser spectrometer for simultaneous measurement of a series of radical species in the HO_x cycle.

Ozone trend analysis and ozone data

The FPP-funded groups at the University of Wisconsin and Princeton University have continued their studies on the analysis of stratospheric ozone data for evidence of ozone changes. Nimbus 4 satellite and Dobson

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ground-based ozone data have been extensively analysed in terms of changes in total ozone (the amount in a column of air) and in ozone at different altitude levels (i.e., profile zone).

No evidence of an ozone depletion has been detected in total ozone from 36 ground stations over the period 1970-1980. The trend has been slightly positive (viz., less than 0.5 per cent per decade), with trend detection thresholds in the range from ± 1.0 per cent to ± 1.3 per cent. (The detection threshold is that level above which a change both would be judged statistically significant at the 95 per cent confidence level and could not be reasonably explained by natural variation alone.)

The present-day ozone change estimate based on model calculations that incorporate effects due to CFCs, CO_2, CH_4, N_2O and NO_x is +0.3 per cent. When the uncertainties in the theoretical model predictions and ozone trend calculations are taken into consideration, there is no inconsistency between calculations and observations.

Analyses of Nimbus 4 satellite ozone data for the period 1970-1977 suggest an instrument drift of -0.5 per cent/year in total ozone and an apparent larger instrument drift in profile ozone in the region 38-48 km. A comparison of satellite and ground-based measurements supports the conclusion that the ground-based Dobson network provides globally representative trend estimates in the period of the 1970s for both total ozone and ozone vertical profiles. Satellite data analyses will continue when Nimbus 7 data tapes are available in a form suitable for trend analysis.

Both previously mentioned research groups found an effect in the early 1960s that correlated with the Soviet nuclear tests in 1961 and 1962. A volcanic eruption (Agung) occurred at about the same time, making it difficult to interpret the cause of the 1962-1963 perturbation in ozone. The inclusion of a calculated nuclear test effect and a solar cycle variation did not alter the conclusion that there was no change in total ozone during the 1970s.

Including meteorological data (e.g., temperature, pressure and vorticity) in the ozone trend models leads to some reduction in the trend standard errors, but to little change in the actual trend values.

Both groups also detected no significant change in ozone in the period 1970-1980 at the 40 km altitude level, based on analyses of Umkehr ozone data from 13 ground-based stations. However, preliminary analysis of data on atmospheric transmission of solar radiation measured at Mauna Loa, Hawaii, indicates that trend analysis of ozone concentrations in the region of 34-48 km may be affected by aerosol dust. A procedure that adequately accounts for these interfering effects of stratospheric aerosols is being sought.

A task group of NASA, NOAA, Atmospheric Environment Service (AES) and University of Wisconsin researchers has been set up by NASA to study the profile data from satellites Nimbus 4 and 7.

A joint project by EPA, NOAA and FPP is under way at NOAA in Boulder to automate Umkehr ozone monitoring stations. The purpose is to have at least six strategically located Dobson stations automatically taking ozone profile measurements of very high quality on a regular basis (i.e., every day, weather permitting).

FPP has recently committed partial funding for a project to gather improved atmospheric transmission data to study aerosol effects on stratospheric ozone measurements. If NOAA can obtain the balance of the necessary funding, this project will enhance the quality of upper stratospheric ozone data as measured by ground-based stations.

Atmospheric Lifetime Experiment (ALE)

The four original ALE monitoring stations have been in operation since 1978, and a fifth station located on the Oregon coast was added to the network in 1980. The ALE programme monitors concentrations of CFCs 11 and 12, CCl_4, N_2O and CH_3CCl_3. Preliminary results from three and a half years of data indicate that any tropospheric sinks for CFC 11 or 12 must be very small in comparison to the photolytic processes in the stratosphere. Publication of results from the first three and a half years of this programme is in progress, and the full data base will be made available from the NASA library toward the end of 1983. FPP funding of the stations' operations will cease in November 1983, when sufficient data will have been collected for an accurate lifetime determination. The investigators are actively seeking supplementary funds to continue the global monitoring role of these stations.

Production and release of CFC-11 and CFC-12

Production and sales data for CFC-11 and CFC-12 have been collected from CFC manufacturers on a world-wide basis and have been provided to CCOL. These figures show that estimated world production of CFCs 11 and 12 peaked in 1974, and that the 1981 production was 11 per cent below the 1974 level. The world estimates include assumptions of continued increase in countries not directly reporting to the independent accountants used by FPP. Releases of CFCs are calculated from the production and sales figures, and have also been revised during the past year to reflect ongoing studies by FPP. A description of the revisions has also been included with the most recent calculations.

ANNEX IV

EXECUTIVE SUMMARY OF THE ASSESSMENT OF OZONE LAYER DEPLETION AND ITS IMPACTs - APRIL 1983

1. The UNEP Co-ordinating Committee on the Ozone Layer held its sixth session in Geneva from 5 to 8 April 1983. The Committee examined contributions presented to it by various countries and organizations, and reviewed research conducted as regards the observations, evaluations and modelling necessary for the study of the stratosphere. On the basis of existing and new information the Committee reached the following conclusions.

2. The ozone layer may be affected by several trace substances a number of which are produced by man's activities. None of them acts independently; they are strongly coupled in a complex manner.

3. If one considers only CFC 11 and CFC 12 releases at their present rates, current calculations estimate an eventual reduction in the total ozone column of somewhere between 3 and 5 per cent depending on the model chosen, compared to about 5 - 10 per cent estimated in the previous CCOL report. The change from the 1981 figure is due to new data on certain chemical reaction rates. If present releases of other chlorocarbons continue at present rates, then they could increase the eventual ozone depletion due to CFC 11 and 12 alone by about a third.

4. The predicted depletion of the ozone layer in the upper stratosphere due to chlorofluorocarbon releases is still about the same as earlier estimated.

5. Calculations for several other individual perturbations have been performed. For example, a doubling of CO_2 shows an increase in total ozone similar in magnitude to the decrease calculated for CFCs.

6. However, it should be recognized that the range of predicted ozone reductions does not adequately represent the true uncertainty in our knowledge, which is substatially greater.

7. In recognition of the simultaneous and complex impacts of human activities on atmospheric ozone, more realistic scenarios have been developed to study the coupled nature of potential ozone changes. The changes in the concentrations of CO_2, N_2O, NO_x, CH_4 and halocarbons may all have affected past ozone amounts. The estimate of total column ozone changes in recent times is below the present detection limit.

8. Recent multiple perturbation calculations estimate little change in the total ozone column over the coming decades, but do predict substantial redistribution in the vertical profile of ozone.

9. Continued improvement of the data base on atmospheric trace species has contributed to the resolution of some past problems in interpretation and pointed out new areas of possible concern.

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10. The generally recognized concern about the quality of stratospheric measurement data has led to vigorous efforts in a series of international intercomparison campaigns.

11. No evidence of changes in total ozone has been observed, notwithstanding the significant continuing progress made in statistical analysis of the ozone record. The relatively large natural variability of atmospheric ozone, and the possibility from model calculations of a cancellation of effects at different altitudes, creates difficulties when trying to detect changes in the total column ozone by observation. However, it should be possible to detect distortions of the vertical ozone profile.

12. Observational data indicate an ozone increase in the northern hemisphere troposphere over the last 15 years which is qualitatively consistent with the model-predicted impact from past subsonic aircraft operations and other NO_x emissions. Observations in the upper stratosphere are not yet fully adequate for deriving statistically significant trends. Further combined ground-based and satellite data analyses are expected to produce statistically significant results within the coming few years.

13. As far as possible climatic consequences, are concerned, multiple-scenario models suggest that the distortion of the vertical ozone profile might become more important than changes in the total amount. Calculations indicate that early next century the combined radiative effects of ozone and other trace gases on the surface temperature would be of the same order as that calculated for CO_2 at that time.

14. Estimated world production of CFCs 11 and 12 (including an upward revision of the assumed growth rate for producers not reporting to the Chemical Manufacturers Association) fell by 18 per cent between 1976 and 1980. Most of the decrease occurred in 1974 and 1977; since then the decrease has levelled off and the revised estimates show an increase of 2 per cent between 1980 and 1981. The validity of this increase, and its implication for estimates of future production levels, depends on the validity of the assumption made about the growth rates of non-CMA producers.

15. The Committee emphasized that it was important for member countries and international organizations such as WMO, with the support of UNEP, to continue to collaborate in studies on the ozone layer, and to provide data on production, use, and release of chemicals which have a potential impact on the ozone layer.

16. If atmospheric ozone decreases, more solar ultra-violet radiation, in the UV-B range, will penetrate to the earth's surface and into surface waters. Computer calculations of solar UV-B radiation reaching the earth's surface have been made for a variety of combinations of UV-B radiation wavelengths, latitude, season and time of the day for normal and depleted total ozone amounts. Health and biological effects can be expected to result from such an increase of ultra-violet radiation. Most of the known effects of UV-B are damaging effects, so that there is concern for the consequences, especially with regard to agricultural production, fisheries and human health.

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17. Recent research results indicate that many terrestrial plants and aquatic organisms may undergo damage by increased UV-B; this applies to important crops such as wheat and rice, and to aquatic organisms such as plankton, fish eggs and larvae. The damaging effects on UV-sensitive terrestrial plants of enhanced UV-B radiation in combination with other stresses, such as water or mineral deficiency, are greater than the sum of the effects produced by the stresses independently.

18. With regard to human health, it is well established that an increase in solar UV-B would lead to an increased incidence of non-melanoma skin cancer, especially in light-skinned people. There are several indications that sunlight may be one of the causative factors of malignant melanoma, which affects people of all skin types. It has not been proved whether UV-B is involved.

19. Recent research indicates that UV radiation alters several responses of the immunological system.

20. The Committee emphasized that it was important for member nations and organizations to study the biological effects of increasing levels of UV-B and to make quantitative assessments of these effects, especially with regard to the productivity of agriculture and fisheries, and to human health.

ANNEX V

Advice on scientific and technical matters provided by the Committee to the Ad Hoc Working Group of Legal and Technical Experts for the Elaboration of a Global Framework Convention for the Protection of the Ozone Layer

1. During the first part of its second session, the *Ad hoc* Group of Legal and Technical Experts requested the Co-ordinating Committee to forward to it advice on technical and scientific matters. The Committee decided that the following views transmitted to the Working Group.

2. The Committee considered that the best scientific definition of the ozone layer would be one that included both stratospheric ozone and tropospheric ozone, excluding pollution in the boundary layer. The ozone layer should therefore be considered as atmospheric ozone contained in the planetary boundary layer, excluding local and regional pollution in the lower levels.

3. However, while suggesting the above scientific definition, the Committee appreciated that from a legal viewpoint it might be considered expedient to adopt some other definition.

4. The Committee discussed two papers placed before it which had been prepared for the second part of the second session of the *Ad Hoc* Working Group, dealing with the possible contents of annexes and/or protocols to a global framework convention for the protection of the ozone layer concerning:

(*a*) Research and monitoring;

(*b*) Information exchange;

(*c*) A list of substances capable of modifying stratospheric ozone.

5. With respect to annex 1 to the convention, on research and monitoring, it was felt that emphasis must be placed on flexibility, as it might well be necessary for annexes and/or protocols to be changed or adapted after adoption as research issues changed. The annex should therefore include a mechanism for updating which would draw on the work of the Co-ordinating Committee, particularly with respect to the World Plan of Action on the Ozone Layer, and also on the Committee's updated research recommendations.

6. The Committee declined to take a position in favour of either of the two versions of annex 1, but instead suggested that the Working Group should study both versions and select their requirements from either paper as appropriate.

7. In considering the list of chemical substances capable of modifying stratospheric ozone, several delegations thought that a categorization of the chemical substances was necessary. Two approaches were possible:

(*a*) A list determined within a scientific framework, considering only how they impact on the ozone layer; or

(b) A list determined within a regulatory framework, considering those substances which were capable of being subject to regulatory action.

8. The Committee considered that the choice between the two approaches involved a fundamental decision to be made by the Working Group.

9. The Committee felt that a list of substances arranged in order of their degree of impact on the ozone layer would be most useful. However, it was pointed out that such a list would be most difficult to compile in view of the many coupled perturbations which would have to be taken into account in determining an individual substance's impact.

10. Another type of categorization suggested involved grouping the substances as follows:

(a) Those that could be regulated;

(b) Those that would pose problems in regulatory action;

(c) Those that could not be regulated.

11. This approach was supported by several delegations. However, the members were unanimous that the prime criterion in compiling any list must be potential impact of the substance on the ozone layer rather than the ease of controllability of any such substance. Therefore, it was necessary first to categorise substances by effects and, as necessary, amplify the requirements from the point of view of regulatory action.

12. The Committee considered that increases in CO_2, N_2O and CFCs 11 and 12 posed the greatest potential threat of ozone layer depletion, but cautioned that there were other substances whose effects on atmospheric ozone were unknown. It was further noted that different countries had different needs in determining a list of chemicals to be regulated.

13. One delegation noted that while the list of chemicals capable of modifying ozone contained a reference to annex I, no reference was made to annex II. It suggested the addition of the following phrase in the preamble to the list:

"These substances should also be considered in the application of annex II".

14. The Committee concluded its discussion by noting that many of the participants at the Committee's sixth session would also attend the second part of the second session of the Working Group, and would be prepared to expand further on the advice contained in the present paper if the Working Group so wished.
