Environmental Assessment of

OZONE LAYER

Depletion and Its Impact

as of April 1984

Bulletin No.9 — January 1985

A yearly bulletin on ongoing and planned research activities

UNEP
United Nations Environment Programme

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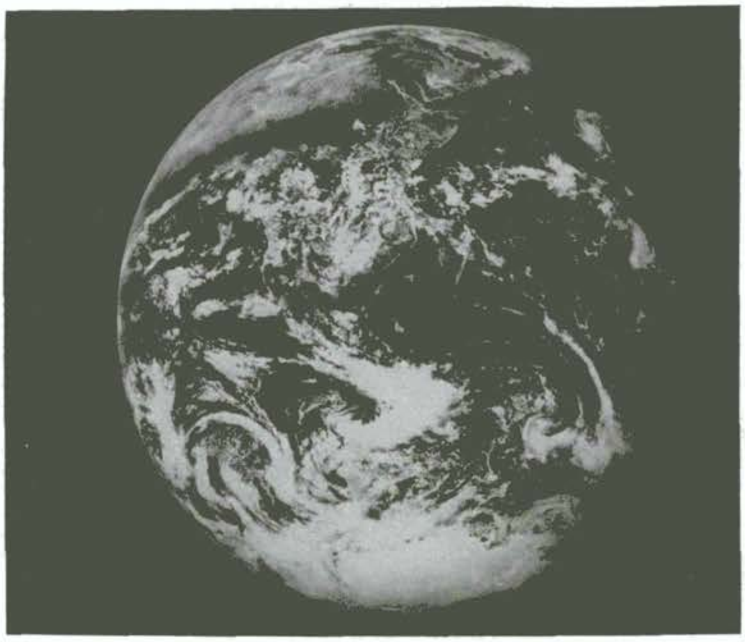

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INTRODUCTION

The Co-ordinating Committee on the Ozone Layer (CCOL) is composed of representatives of agencies and non-governmental organisations participating in the implementation of the World Plan of Action on the Ozone Layer, and of representatives of countries which have major scientific programmes contributing to the Plan. The Committee makes recommendations relevant to the continuing development and co-ordination of the Plan of Action. The recommendations are made to the UNEP Executive Director who reports to the Governing Council.

CCOL held its seventh session from 15 to 19 October 1984. The timing of this session accorded CCOL opportunity to provide specific information and advice to the ad hoc Working Group for the Elaboration of a Global Framework Convention for the Protection of the Ozone Layer. The Ad hoc Working Group, it will be noted, held its fourth session from 22 to 26 October at the Palais de Nations, Geneva.

CCOL examined research results relevant to the World Plan of Action on the Ozone Layer and, on the basis thereof, made a new assessment of ozone layer modification and its impact. An executive summary of the assessment, specifically prepared to meet the needs of the Working Group in its elaboration of the draft framework convention, draft technical annexes and a draft protocol for the control of chlorofluorocarbons, was made available to the Working Group at the opening of its fourth session (UNEP/WG.110/3). The executive summary is reproduced in section I of this Bulletin.

Bulletin No. 9 shows an important change from previous issues. Its new title, "Environmental Assessment of ozone layer modification and its impact", reflects the uncertainty that exists with respect to future budgets of trace gases with the potential to modify the ozone layer. Although the chemistry and physics of the atmospheric processes which control ozone are now better understood than ever before, the ability to predict accurately future atmospheric concentrations of chlorine species, carbon dioxide, methane, nitrous oxide and other oxides of nitrogen has not yet been achieved. Moreover, since the ways in which these chemicals interactively affect ozone depend, to a large extent, upon their concentrations relative to one another, with some substances such as methane and carbon dioxide being producers rather than depleters of ozone, it has become increasingly difficult to offer a single realistic scenario for future steady-state ozone, including the prediction whether or not ozone is destined to increase or decrease. It does not follow, however, that CCOL took the view that the risk associated with ozone changes had diminished - on the contrary, there was general agreement that, a potential danger to human health and to other biological processes and systems, together with serious implications for climate, still existed as a consequence of ozone layer modification. To that extent, the legislative process being developed for the protection of the ozone layer is a timely exercise that should be supported by all nations.

The full assessment of ozone modification and its impacts can be found in section II of the Bulletin, together with 44 recommendations for future research and activities in support of the World Plan of Action on the Ozone Layer.

Section III contains recent research results and information on ongoing and planned research programmes undertaken by CCOL members and which are relevant to the Plan of Action. Once again, this section is incomplete, and members are reminded of their responsibility to supply such information.

Production and sales data for chlorofluorocarbons 11 and 12, up to and including 1983 provided by the Chemical Manufacturers Association (CMA), are contained in section IV. As it is impossible to accurately estimate production and emissions, other than those from manufacturers reporting to the CMA Fluorocarbon Programme Panel, assessments of production by countries other than those listed in schedule I have been discontinued. UNEP has been asked by both CCOL and the Working Group to continue its efforts to obtain technical data on the production capacity, release and production of chlorofluorocarbons 11 and 12 and other substances with the potential to modify the ozone layer (see Bulletins 7 and 8). Countries which manufacture and use such substances are asked to co-operate with UNEP in the collection of the necessary data.

The Governing Council of UNEP, at its twelfth session requested, that CCOL examine, if possible within two years, the likely effects on the ozone layer of the substances considered as having the potential to modify it. It also listed in Annex I to the draft convention, such substances which should be evaluated singly, interactively and under appropriate emission scenarios. In response to the request, the Committee endorsed a UNEP proposal to join with WMO, NASA and other organizations in a programme to assess the current understanding of the physical and chemical processes which control atmospheric ozone and assess its susceptibility to change due to natural and anthropogenic perturbations. This will be achieved by the convening, in 1985, of a number of working groups to determine the impact on the ozone layer of specific substances or processes. At its next meeting in February 1986, CCOL will consider the report of the overall assessment, to which each working group will have contributed an individual chapter.

SECTION I

EXECUTIVE SUMMARY OF THE ASSESSMENT OF OZONE LAYER MODIFICATION AND ITS IMPACT - OCTOBER 1984

1. The UNEP Co-ordinating Committee on the Ozone Layer held its seventh session at Geneva from 15 to 19 October 1984. The Committee examined contributions presented by various countries and organizations, and reviewed research conducted into atmospheric observations, mechanisms, modelling and effects relating to changes in atmospheric ozone. As a result of its review of new and existing information, the Committee reached the following conclusions:

2. There are a number of trace gas species whose changing in atmospheric concentrations are expected to affect the amount and distribution of ozone. Moreover, there is strong coupling between the effects of the different species, so that it is not realistic to consider the consequences of changes in a single species in isolation. Species for which there is evidence of change include organochlorine compounds (notably CFCs 11 and 12), carbon dioxide, methane, nitrous oxide and other oxides of nitrogen.

3. The production of CFCs 11 and 12 by the companies participating in the CMA data collection programme fell to 599 kilotons in 1982 and rose to 644 kilotons in 1983. These figures are considered to represent about 90 per cent of total world production, but it is no longer possible to make reliable estimates of the world total. The 1983 value represents a 21 per cent reduction from the peak level in 1974, with the bulk of the reduction occurring between 1974 and 1977. The decrease since 1976 is composed of two parts; a 51 per cent decrease in aerosols use (432 to 211 kilotons) and a 36 per cent increase in non-aerosol uses (318 to 433 kilotons).

4. Atmospheric concentrations of CFCs 11 and 12, carbon dioxide, methane and nitrous oxide are currently rising at 5-7 per cent, 0.5 per

cent, 1-2 per cent, and 0.2 per cent per year respectively. Several other halocarbons besides CFCs 11 and 12 also have increasing concentrations; for example, CFC 113 and methyl chloroform are currently rising at about 15 per cent and 6 per cent per year respectively. One should recognize that the current large growths in halocarbons are due to the fact that they are far from equilibrium.

5. Knowledge of the chemistry of atmospheric trace gases has continued to advance both by a reduction of the uncertainty in the established data base and by a recognition of new aspects which would affect predicted ozone concentrations. The new aspects merit further consideration in the near future.

6. Model calculations which take into account the changing concentrations of all the source gases have been performed to describe ozone from 1970 to 1980. These models calculate a 0.4 per cent increase in total column ozone in the atmosphere which is made up of a decrease in the ozone from 32-40 km ranging from 2 to 4 per cent and an increase in the ozone in the lower stratosphere and the troposphere.

7. Analysis of total column ozone recorded at 36 Dobson stations gives no evidence of statistically significant trends during the 1970s. The results for the period since 1970, with the 95 per cent confidence limits from two research groups are +0.02 ± 0.94 per cent and -0.59 ± 1.16 per cent per decade respectively. This is consistent with model calculations taking into account changes of trace gases i.e. CFCs, carbon dioxide, methane, nitrous oxide and other oxides of nitrogen.

8. A statistically significant ozone depletion of 2-3 per cent per decade has been observed over the period 1970 to 1980 in the upper stratosphere (32 to 42 km). This result is consistent with recent one-dimensional model calculations encompassing the same period. However, problems concerning the spatial distribution of the 13 Umkehr observing stations and the single-station aerosol adjustment method should be further examined.

9. An ozone increase in the Northern Hemisphere troposphere over the past 15 years has been found in studies of ozone sonde observations. This result needs careful reassessment, to account for both instrumental changes at certain stations and boundary layer pollution effects where urban or regional pollution may be significant.

10. Evidence of the large natural variability of ozone was observed with a major decrease in total column ozone in 1983, which is so far unexplained. For example, at Arosa, Switzerland, the lowest annual mean of total ozone in nearly 60 years of record was observed. The decrease followed soon after the eruption of El Chichón, and achieved its maximum amplitude with the El Nino climatic anomaly during the winter of 1982-1983. Such natural variations will complicate the estimation of ozone trends.

11. The magnitude and sign of the predicted change in total ozone for multiple trace gas scenarios over the next century depends critically on the scenarios assumed. Reasonable projections (see paragraph 4) suggest little change in total ozone (less than 1 per cent) over the next few decades, unless there is sustained growth in CFC use leading to a several-fold increase in production.

12. Even though little change in total ozone during coming decades calculations show, a substantial redistribution in the vertical profile of ozone is predicted. For example a large percentage decrease of about 14 per cent at 40 km over the next two decades is calculated, using the following scenario: constant CFC emissions at 1977 rates, increasing carbon dioxide, methane and nitrous oxide, at rates of 0.5 per cent, 1.0 per cent, and 0.2 per cent per year respectively. This decrease is accompanied by a corresponding increase at lower altitudes.

13. The calculated effects over long periods are sensitive to assumed source gas scenarios. For example, a typical model, assuming the same scenario as discussed in paragraph 12, gives an increase in total ozone of 1.8 per cent in year 2050 (relative to the present). If instead a sustained 3 per cent per year growth in CFC emissions is assumed

(corresponding to a factor of 6.8 growth in emissions by the year 2050), with the same scenario otherwise, a decrease in total ozone of 3.5 per cent is obtained.

14. In the hypothetical situation where releases of CFCs 11 and 12 alone remain at their 1977 rates, (which would contribute a concentration of approximately 8 ppb odd chlorine by the year 2100), current calculations estimate an eventual steady-state reduction in the total ozone column of about 3-5 per cent, and as much as a 40 per cent reduction near 40 km. If releases of other chlorocarbons continue at present rates, they would increase the eventual ozone depletion due to CFCs 11 and 12 alone by about a third. This is similar to the estimates in the report of the sixth session of the Committee.

15. In the hypothetical situation where atmospheric chlorine alone increases (with carbon dioxide, methane and nitrous oxide constant), current calculations show a non-linear relationship with greater than 10 per cent total ozone reductions occurring when the odd-chlorine levels would exceed those of odd nitrogen in the stratosphere. (This would require odd chlorine mixing ratios of 15-20 ppb) Alternatively, if growth in carbon dioxide, methane and nitrous oxide similar to that described earlier is included, time-dependent calculations suggest that this non-linear relationship will also eventually be reached if sustained growth in CFC emissions is greater than 3 per cent per year.

16. In general, globally averaged 2-D model calculations of changes in ozone tend to agree with the 1-D model calculations. However, the 2-D results indicate substantial variation with latitude and season. Larger ozone decreases are calculated at high latitudes relative to those at the tropics, and for late winter and early spring. For the hypothetical individual CFC and nitrous oxide perturbations the latitudinal gradient of ozone depletion is calculated to be a factor of about three. To date no fully realistic multiple-scenario calculations have been performed with 2-D models.

17. The generally recognized concern about the quality of stratospheric measurement data has led to vigorous efforts in a series of international intercomparison campaigns. The results will be available in early 1985.

18. In general, the model calculated distributions of stratospheric trace species are consistent with measured distributions. Very few of the currently available data sets critically constrain model calculations.

19. A major deficiency of current model calculations is the inability to reproduce the measured value of ozone in the upper stratosphere, where the chemistry is believed to be the simplest and best understood.

20. It should be recognized that all models have known deficiences, and may also be deficient in other (as yet unknown) aspects. Model predictions of ozone change still remain substantially unvalidated; the range of predicted ozone depletions does not adequately represent the true uncertainty.

21. Recent developments in our ability to measure atmospheric species should enable us to improve our understanding of atmospheric composition in order to test the validity of theory and to observe trends in the concentration of key consituents. This latter capability should provide evidence of significant changes in atmospheric chemical composition.

22. With respect to the impact on climate, multiple-scenario models suggest that the distortion of the vertical ozone profile might become more important than changes in total column ozone. Calculations indicate that, early next century, the combined radiative effects of ozone and other trace gases on surface temperature would be of the same order as those calculated for carbon dioxide for that time.

23. Although current atmospheric scenarios predict a range of both positive and negative ozone changes, biological studies have focused on the effects of an ozone decrease. If atmospheric ozone decreases, more solar ultraviolet radiation in the UV-B range will penetrate to the

Earth's surface and into surface waters. Health and biological effects can be expected to result from such an increase of ultraviolet radiation. Most of the known effects of UV-B radiation are damaging effects, so that there is concern for the consequences, especially with regard to human health, agricultural production and fisheries.

24. Although there are many uncertainties involved in the simulation of enhanced levels of solar UV-B radiation, research results indicate that many terrestrial plants are affected by exposure to levels of UV-B radiation obtained from simulating ozone decreases as small as 5 per cent. There is evidence in higher plants, including such important crop plants as soya beans and wheat, for physiological effects and for differential effects among species of cultivars resulting from UV-B exposure. Although there is no clear evidence from field studies of a relationship between direct effects of UV-B radiation at relevant levels and a decrease in the quantity of yield, the nutritional value of soya beans is affected by exposure conditions obtained from simulating a 16 per cent ozone decrease. The damaging effects to 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.

25. There are large uncertainties regarding the natural mortality of aquatic organisms and the role of current levels of UV-B exposure in the mortality rate. However, various experiments using exposure levels of UV-B radiation simulating ozone decreases ranging from 5 to 25 per cent have demonstrated damaging effects on fish larvae, shrimp larvae, crab larvae and the zooplankton and phytoplankton essential to the aquatic food web. These damaging effects range from mild to severe, and include decreases in growth, productivity, survival, mortality and community diversity.

26. With regard to human health, it is well established that there is a direct relationship between exposure to UV-B radiation and the incidence of non-melanoma skin cancer. A 1 per cent decrease in ozone

concentration with unchanged exposure habits would result in about a 4 per cent increase in the incidence of non-melanoma skin cancers. Non-melanoma skin cancers occur in people of all skin types; the incidence is highest in light-skinned people. There are several indications that sunlight may be one of the causative factors of malignant melanoma. For at least one type of melanoma, there are indications that UV-B radiation is involved.

27. Recent research indicates that UV radiation alters several responses of the immunological system. The doses of UV-B radiation causing these immunological changes are much smaller than the doses which induce tumours.

28. The Committee emphasized that it was important for member nations and organizations to study with increased intensity the biological effects of exposure to UV-B radiation simulating both decreased and increased ozone concentrations, and to make quantitative assessments of those effects, especially with regard to human health and to the productivity of agriculture and fisheries.

29. The Committee also emphasized that it was important for member countries and international organizations, such as the World Health Organization and the World Meteorological Organization, with the support of the United Nations Environment Programme, to continue to collaborate in studies on the ozone layer, especially evaluations of the state of the ozone layer and the nature and scale of any likely modification thereof; and to examine the sources and possible effects of the substances listed in annex 1 of the Draft Convention for the Protection of the Ozone Layer. Furthermore, the Committee stressed the need to provide data on production capacity, production, use and release of chemicals which have the potential to modify the ozone layer.

SECTION II

AN ASSESSMENT OF OZONE MODIFICATION AND ITS IMPACT - OCTOBER 1984

A. Ozone observations

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 an 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 and abrupt changes following the realignment and recalibration of instruments) and high natural variability (synoptic, seasonal, solar, etc.).

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, Boulder, Colorado, United States, or a regional (secondary) standard instrument. Most of the Dobson ozone data reported to the World Ozone Data Centre (WODC) at 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 calculations of trends. Drifting of instrument readings has been demonstrated, and frequent intercomparisons (once every three to four years) are therefore considered essential.

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 equable 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.

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 do report regularly, a significant fraction (approximately 20 per cent) provide data derived from lower quality filter instruments. It is noted, however, that the lower quality filter instruments are in the process of being upgraded and the data will be so delineated for publication. 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.

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 ultraviolet radiation back-scattered by the earth and the atmosphere (BUV, SBUV, TOMS) and nadir-emitted infra-red radiance in the 9.6 μm 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 ultraviolet instruments and the surface-based Dobson network, there is 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.

The Ozone Commission has recommended the use of new ozone absorption coefficients for evaluation of back-scattereed ultraviolet (BUV) type satellite ozone measurements. It is likely that the new coefficients will also be recommended for use with the Dobson instrument, after slit functions and wavelengths settings have been re-evaluated. Preliminary studies indicate that the use of the new absorption coefficients will substantially reduce the systematic biases between Dobson, BUV, SBUV and TOMS total-ozone measurements to less than 3 percent.

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. It is noted that the United States NOAA operational satellite series is to include an improved SBUV type instrument. This is, currently, scheduled to be launched on a biennial basis with the first launch in November 1984. The data from these instruments, with those available from the SBUV instrument on board the Nimbus 7 spacecraft, (1978-present), form the initial part of the long-term satellite ozone monitoring programme.

Because of absorption of solar ultraviolet 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. It is noted that the Brewer ozone spectrophotometer is designed to measure ozone and sulphur dioxide separately. While it is thought that the effect on total ozone trend determination of troposphere pollution is relatively minor, this should be the subject of further examination.

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 call for more confirmative observations. These factors strongly support the argument for obtaining vertical ozone distribution data.

So far, ground-based Umkehr measurements constitute the largest time series 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. Implementation of an automated Dobson observing system has begun with five stations completed in 1984 and two more scheduled for 1985. Further programmes of this type are to be encouraged. LIDAR measurements of aerosols in proximity to Umkehr stations are necessary for correcting for the optical effects of stratospheric aerosols from volcanic and other sources.

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 fewer than a dozen stations make weekly ozone sounding by balloon and only a few have continuous records for periods greater than 10 years. International intercomparisons of various types of operational ozone sondes have twice been conducted at Hohenpeissenberg and in Haute Provence and, more recently, at Palestine, Texas. The comparisons at

Palestine were more complete in that several research sondes of potentially greater accuracy were involved. The Palestine results indicate considerable variability among the systems, the general range being ± 20 per cent. However, special sensitivity is noted above 25-30 kms, where the operational sondes appear to give results that are too low. Efforts should be directed towards the continuation and improvement of balloon-borne ozone sondes in parallel with the increase in remote measurements of vertical-ozone distribution by, for example, the Umkehr method which are, however, inadequate below about 15 km.

Three solar ultraviolet 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 μm ozone band for profile measurements, while another (SAGE) uses solar occultation in the visible regions. The data from these satellite instruments are available from the United States National Space Science Data Center. It is noted, however, that current plans are to reprocess the BUV and SBUV data bases with a uniform algorithm and by utilizing the ozone absorption coefficients recently recommended by the International Ozone Commission. The SAGE data are also to be reprocessed to allow for temperature adjustments not previously considered in the routine analysis. However, until such time as these reprocessed data are available, due caution must be exercised in the data interpretation. 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-based measurements, they provide the best means for the early detection of perturbations of the vertical-ozone profile. As stated above, the United States NOAA operational satellite series beginning in November 1984, is scheduled to include an improved SBUV-type instrument with biennial launch thereafter. These data, with those available from the SBUV instrument on board Nimbus 7 (1978-present) form the initial part of the long-term satellite ozone profile monitoring programme.

At present, rocket-borne measurements provide the only in situ data available in the region above about 40km. Unfortunately, the data prior to 1984 have been questioned, and, beginning with the 1984 data, major improvements have been made in the instrument and data algorithm. Again, due caution must be exercised in the interpretation of the earlier data.

For the region below about 40km, several balloon-borne systems are being examined through the intercomparison held at Palestine, Texas. Of note is the development of an improved, operational electrochemical sonde, suitable for flight up to about 40km, which is to be deployed in early 1985. System launching at three sites (Hilo, Hawaii; Boulder, Colorado; and either Poker Flat, Alaska or Edmonton, Canada) is planned on a once-per-week basis in support of the SBUV instrument on the NOAA operational spacecraft.

New observational sensors: In order to assess the value of new sensors, it might be appropriate to list briefly the requirements for such sensors:

Total ozone and profile information up to approximately 60 kms of altitude;
Day and night observing capability;
Observations independent of aerosols;
Observations independent of meteorological conditions such as Cloud cover and precipitation;
Capability of continuous operation; and
Global coverage.

In recent years, two new observing techniques have been developed, both of which have the potential to meet at least some of the above-mentioned criteria, namely the superheterodyne or microwave technique, and LIDAR.

The relevance of microwave sensors to ozone research was reviewed by a working group of the International Ozone Commission in 1984. The conclusion reached was that microwave sensors have demonstrated their capability of measuring ozone profiles in the altitude range from 25 kms to approximately 80kms. These measurements are unaffected by aerosols and only slightly disturbed by meteorological conditions. An intercomparison of a microwave sensor with a nearby Umkehr station has shown good agreement, but a longer period (greater than one year) is required to make a more definite statement about the accuracy. At present, microwave sensors are limited to wavelengths larger than 1 mm. However, rapid progress is being made in sensor technology in the sub-mm range. These sensors will allow the extension of the number of minor constituents which can be investigated to such important molecules as OH, NO and NO_2.

LIDAR systems can provide profiles with excellent altitude resolution from less than 100 m up to about 50kms. In addition, LIDAR provides information on aerosol content which can be used to correct the results from "Umkehr" observations. However, LIDAR is limited to clear-sky conditions. Ground-based LIDARS have been successfully used to measure ozone and NO_2. Intercomparisons of the LIDAR-derived ozone profile with ozone sonde data show excellent agreement.

Global Ozone Observing System (GOOS). 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 continual intercomparisons of routinely used ozone sondes with special high-accuracy instruments, in both the laboratory and the field.

B. Ozone data analysis

The relatively large natural variability of atmospheric ozone complicates the detection of trends. The ground-based Dobson network indicates that between 1958 and 1982, several periods of increases and decreases in ozone concentrations have occurred involving changes of one to several per cent, each lasting several years. There are some indications of a possible solar-cycle variation which are as yet difficult to confirm with any statistical certainty.

Analysis of total column ozone recorded at 36 Dobson stations gives no evidence of statistically significant trends during the 1970s. The most recent analyses have been designed to remove the effects of nuclear testing, solar variability, and instrument recalibrations. The results for the period since 1970, with the 95 per cent confidence limits from the two research groups doing this work are + 0.02 ± 0.94 percent per decade (Wisconsin/Chicago group) and -0.59 ± 1.16 percent per decade (Princeton group). This is consistent with model calculations taking into account changes of trace gases i.e. CFC's, carbon dioxide, methane, nitrous oxide and other oxides of nitrogen.

A major negative perturbation in total column ozone was observed in 1983. Although global in extent, the effect was most pronounced in the Northern Hemisphere. At Arosa, Switzerland, for example, the lowest annual measure of total-ozone in nearly 60 years of record was observed. It followed soon after the eruption of El Chichón (May 1982) and was concurrent with the El Niño (January 1983) climatic anomaly. Considerable work will have to be done to determine the cause of the ozone changes and their association, if any, with the above-noted natural events. This is important, from the viewpoint not only of testing theoretical prediction models but also of extending our knowledge of natural total-ozone variations and their impact on trend direction.

Total-ozone measurements from the Nimbus-4 satellite using the back-scattered ultraviolet (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 render possible 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 from the combined systems should be no worse than 1 per cent.

Furthermore, with respect to the instrumental drift in the Nimbus-4 BUV, it is reasonably certain that a similar uncorrected drift exists in the vertical profile retrievals. However, there are insufficient ground-based comparisons to provide a meaningful estimate of this drift. Consequently, and because the spatial coverage of this particular instrument was incomplete and degraded with time, the Nimbus-4 BUV ozone profile data should not be used for the estimation of trends. It is noted, however, that improvements incorporated into the follow-on SBUV instrument on Nimbus-7 resulted in virtually complete spatial coverage and that the causes of instrument degradation were monitored. Moreover, the SBUV-2 to be flown on the NOAA operational spacecraft has, in addition, an on-board Mercury lamp which will serve as a calibration source and will be backed up by an SBUV instrument flown on 10-day shuttle missions (SSBUV) at about six month intervals. The SSBUV instrument will be recalibrated both before and after flight, thus providing basic calibrations comparison of the operational spacecraft.

A statistical analysis of stratospheric ozone profile data from the Umkehr method has been considered for the detection of trends. In the statistical trend analysis, time series models have been estimated using monthly averages of Umkehr data for the whole of 1980 at each of 13 Umkehr stations and at each of the five highest Umkehr layers. The time series regression models incorporate seasonal, trend (zero trend up to 1970, linear 1970-1980) and noise factors plus an additional factor to account explicitly for the effects of stratospheric aerosols. The analysis also accounts for step functions in the record of certain stations, where changes of instrument, recalibration or instrument damage are known to have occurred. A random effects model is used to combine the 13 individual station trend estimates to form an overall trend estimate. The analysis indicates statistically significant trends in Umkehr layers 7 and 8 of the order of -0.2 to -0.3 per cent per year over the period 1970-1980, with little trend in the lower layers, nos. 5 and 6. These results are consistent with recent one-dimensional model calculations encompassing the same period (see figure 1).

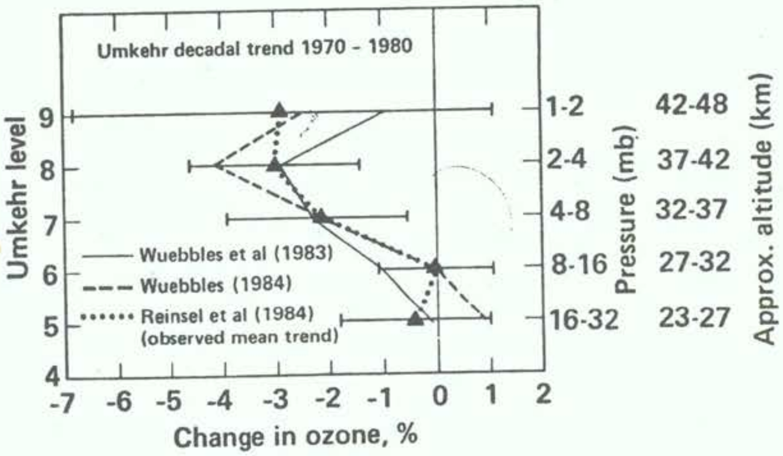


Figure 1

Trend analysis of stratospheric ozone profile data obtained by the Umkehr method

There are three elements of uncertainty in the trend results described in the previous paragraph. First, there is the effect of the 11-year solar cycle both on statistical interpretation of observed data and in the model calculations. Secondly, there is the representativeness of the 13 station Umkehr network in terms of global trends. Thirdly, there is the use of turbidity data from the background air pollution monitoring station at Mauna Loa as a measure of stratospheric aerosols at all stations. With respect to the solar-cycle variation, current model calculations suggest that there could be an eleven year variation in ozone at Umkehr layers 7, 8 and 9. That such a variation is not readily discerned represents a possible substantial problem that must be resolved. The impact on the current trend estimates for the period 1970-1980, however, is such that the results should not be invalidated. With respect to the question of representativeness, this is a major uncertainty which can be resolved only when a greater length of satellite-derived record becomes available. For the stratospheric aerosol corrections, the major feature was the long-term signature of the Mt. Agung eruption which was explicitly treated in the statistics. It is important, however, to have an independent check on the aerosol impact of the 1982 El Chichón volcanic eruption.

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. However, it is noted that the ozone sonde data are currently being re-evaluated to include the effect of changes in instrumentation and the effect of the adjustment of the profile to conform to a Dobson total-ozone value. Results should be available in the near future.

Tropospheric ozone. The vertical distribution of ozone within the troposphere has been measured on a regular basis at some 20 stations in the Northern Hemisphere and at about 4 stations in the Southern

Hemisphere using electrochemical ozone sondes. Recent evidence has suggested an increase in the tropospheric ozone content. In view of current efforts to examine the quality of the observations and the spatial distribution of the variations, great care must be exercised at this stage in interpreting the current trend values.

Trends in stratospheric temperature. As the current multi-species models predict the major impact on temperature to be in the mid-to upper stratosphere, it is imperative that this parameter be examined for corroborative evidence. While long-term measurements have been made from meteorological rocket sondes since about 1965, a major change in instrumentation was incorporated into the United States network in the early 1970s. This has complicated the trend analysis of these data and a considerable effort is being made to resolve this problem.

With respect to the availability of satellite data, it is noted that global, daily stratospheric analyses have been available from the United States NOAA operational spacecraft since November 1978 and that this is a continuing programme. These data, however, depend on information derived from ground-based instruments (i.e. the rocket sondes) for continued calibration. The fact that the number of rocket sonde stations has, over the last few years, been reduced, especially at high latitudes of the Northern Hemisphere, presents a potentially serious problem for the calibration programme which is currently under study. It is emphasized, however, that the previous remarks are pertinent to the region above about 30mb ($>$25km). As regards the lower stratosphere of the Northern Hemisphere, a more numerous body of rawinsonde observations exist such that meaningful trends can be determined.

C. Detection of ozone trends due to human activity

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 trends result from a summation of 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 when using sophisticated statistical techniques. Nevertheless, the statistical estimation of trends in individual layers offers the possibility of a better diagnostic capability.

D. Sources of sinks of trace gases

Over the past few years, we have become aware of a growing number of atmospheric trace-gas species whose concentrations have 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 trophospheric and stratospheric chemistry. The list of such species includes CFCs, other halocarbons, carbon dioxide, methane, nitrous oxide, other nitrogen oxides, carbon monoxide and water vapour. All of these gases are infra-red active and may contribute to an increase in the temperature of the troposphere. In contrast to these other radiatively active trace species, only CO_2 would directly change (decrease) the temperature of the stratosphere to a significant extent. Of these trace gases, most information is available concerning CFC 11, CFC 12 and CO_2. The key issues to be addressed are the tropospheric concentrations of the source gases, the rates of change of the source-gas concentrations in the troposphere, identification of the key sources and sinks for these source gases, and how the source gases are transformed into active species in the stratosphere.

1. CFC 11 and CFC 12

The production of CFCs 11 and 12 by the companies participating in the CMA data collection programme fell by 7 per cent relative to the 1981 figure to 599 kilotons in 1982 and rose by a similar amount to 644 kilotons in 1983. The 1983 value represents a 21 per cent reduction from the peak level of 1974, with the bulk of the reduction occurring between 1974 and 1977. The 1983 production rate was very close to the 1981 value (See figure 2).

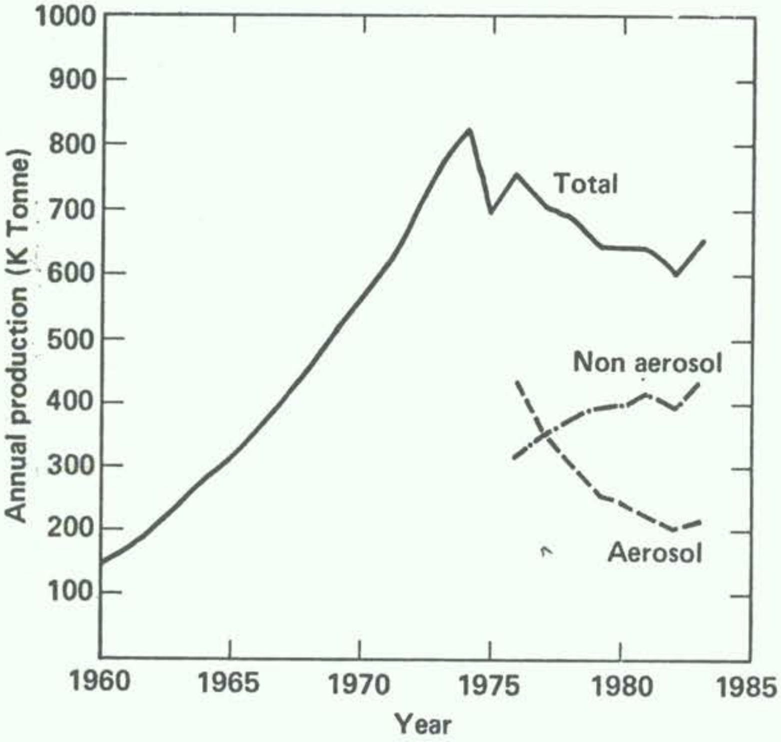


Figure 2
The production of CFC 11 and 12, by companies participating in CMA 1960 to 1983

In previous years, CMA had assessed world production by estimating production in countries and companies which do not participate in the CMA data collection programme. However, CMA has now decided to discontinue this exercise because the estimation of non-CMA production relied heavily on published data for 1968-1975 for one non-CMA producer only, which indicated a growth of 18 per cent per annum. The continued extrapolation of such a high rate for a number of years without any verification cannot be justified, and may be introducing serious errors. Indeed, there is evidence from the measurement of global abundances, that production of

CFC 12 was being over-estimated. However, it is still considered that production by companies reporting to CMA represents about 90 per cent of world production.

Additional data from CMA show that the pattern of CFC 11 and CFC 12 usage has changed substantially since 1976, the first year for which such data are available. Aerosol usage has declined from 432 kilotons in 1976 to 211 kilotons in 1983, a fall of 51 per cent, while non-aerosol usage has increased from 318 kilotons to 433 kilotons over the same period, a rise of 36 per cent (See figure 2).

Observations show that the concentrations of CFC 11 and CFC 12 in the atmosphere have been rising at a rate of 5-7 per cent per year. This large rate of increase reflects the fact that these gases are, at present, far from being at equilibrium in the atmosphere. The rate of increase would level off, eventually falling almost to zero, as steady state is approached, if release rates were to remain constant.

Further measurements from the five-station observing network of the Atmospheric Lifetime Experiment (ALE) have confirmed the absence of any significant tropospheric sinks for CFC 11 and CFC 12. The lifetime observed for CFC 11 was about 70 years, in good agreement with model calculations made assuming a stratospheric sink only. There is greater uncertainty in the lifetime calculated for CFC 12 (about 100 years), arising partly from the difficulty referred to above of determining global production and release.

Although the ALE network has achieved the principal purpose for which it was set up, four of the five stations are being incorporated into the Global Atmospheric Gases Experiment (GAGE) to provide continuing data on CFCs 11 and 12 and other natural and man-made gases of atmospheric signifieance, particularly methyl chloroform, carbon tetrachloride and methane.

2. Other halocarbons

No organization currently collects global production data for halocarbons, other than CFCs 11 and 12, that may affect the ozone layer and there are only some rather uncertain estimates that can be used in model calculations. These indicate that other chlorocarbons contribute about one-third as much chlorine to the stratosphere as CFCs 11 and 12 combined. Currently, the main contributions come from methylchloroform and carbon tetrachloride, but there are a number of other chlorocarbons which make small contributions. Estimates by industry sources suggest that the production of methyl chloroform was essentially constant for the years 1979 to 1981 inclusive, and that the high growth in production observed in the 1970s has now ceased.

Extensive atmospheric measurement data are now available for methyl chloroform (CH_3CCl_3) and carbon tetrachloride and more fragmentary data for chlorofluorocarbons other than CFC 11 and 12. These show that atmospheric concentrations of methyl chloroflorm, carbon tetrachloride and CFC 113 have been rising at 5-8 per cent, 1-3 per cent and 15-20 per cent per year respectively. As in the case of CFC 11 and CFC 12, these rates would decline in future as the concentrations approach equilibrium, if production were to remain constant.

On a molecule to molecule basis, bromine is a more effective catalyst than chlorine for the destruction of stratospheric ozone. If organo-bromine compounds in the atmosphere were to increase from their present value of 25-30 ppt to 100 ppt, then ozone reductions of several per cent are predicted with current models. The principal contributor to organo-bromine atmospheric concentrations at present is methyl bromide, which is of both natural and anthropogenic origin. Other man-made compounds could become more important in future. There continues to be a clear need to acquire relevant global release data and to extend the corresponding atmospheric measurements.

3. Carbon Dioxide

Carbon dioxide is important in the radiative cooling of the stratosphere; its concentration, together with that of ozone, largely determines stratospheric temperatures which in turn affect the rate coefficients of the chemical reactions that control stratospheric ozone.

Tropospheric CO_2 concentrations have increased steadily over the last hundred years or more and are now over 340 ppm and rising at about 1.5 ppm per year; this increase is attributed to the burning of fossil fuels and the effects of deforestation. However, the rate of increase of CO_2 concentration (approximately 0.5 per cent per year) is considerably less than estimates of source increases even for fossil-fuel burning alone (approximately 2 per cent per year) owing in part to the reservoir effects of oceanic sinks. Our current understanding of the global carbon cycle is inadequate to explain CO_2 trends quantitatively, especially the role of the oceanic and terrestrial biosphere.

Increasing CO_2 leads to increases in total ozone through stratospheric temperature changes. Current estimates are that a doubling of CO_2 from the pre-industrial level to 600 ppm will occur about the year 2060.

4. Methane

Methane plays a major role in controlling stratospheric ozone concentration by limiting the effectiveness of the chlorine cycle in catalysing ozone destruction, by contributing to the water vapour budget and by influencing the concentration of HO_x. There is good evidence that the tropospheric methane concentration has been rising since 1978 at a rate of 1 to 2 per cent per year to its present value of 1.65 ppm. More tentative evidence indicates increases of about 0.5 per cent per year during the period 1965 to 1975. Ice core data suggests that, in the sixteenth to seventeenth centuries, the concentration was only 0.7 ppm. If the rate of increase over the past five years were to continue well into the next century, then methane would play an increasingly important role in determining the future concentration of ozone. Consequently, it is of prime importance to discover the reasons for the increase in atmospheric methane and the likelihood of its continuation over the next few decades. At present, it is not clear whether the increase is due to increases in the magnitude of methane sources or to a decreased rate of tropospheric removal by OH radicals; the lifetime of methane in the atmosphere is uncertain by up to a factor of two. Increased production of methane could be due to an increase in world cattle population, increased rice production in wet soils or some other more speculative cause.

5. Nitrous oxide

Several sets of data indicate that nitrous oxide concentration has been increasing at a rate of about 0.2 per cent per year since 1960 at least, reaching a value of 300 ppb in 1980. It is uncertain whether the increase is due to an increased rate of combustion of fossil fuels or to denitrification of an increasing fertilizer consumption. Understanding the life history of N_2O is important since it controls the concentration of nitrogen species in the stratosphere and this, in turn, plays a crucial role in controlling the effects of the chlorine cycle in the catalytic destruction of ozone, with particular reference to the chlorine concentration at which non-linearity in ozone depletion occurs.

6. Other nitrogen oxides

Anthropogenic production of NO and NO_2 at the earth's surface as a result of fossil fuel combustion and biomass burning, has undoubtedly increased during the past century. The competing consequences of still further increases in fossil-fuel combustion and potential regulatory action make future emissions difficult to predict. However, the lifetime of odd nitrogen in the lower troposphere is very short (a few days) so that it is generally assumed that little of the NO_x produced at the surface reaches the upper troposphere or lower stratosphere. However, surface emissions of NO_x may be affecting the lowest few kilometres of the troposphere. Current model calculations suggest that emissions of NO_x by subsonic aircraft make a significant contribution to the nitrogen budget in the upper troposphere. It is estimated that emissions of NO_x by aircraft increased by a factor of six between 1955 and 1975 corresponding to an annual increase of some 9 per cent per year. One source has suggested that an annual increase of 7.4 per cent per year should be adopted for the years 1975 to 1990. An increase in ozone in the mid-troposphere over the last 15 years may possibly be attributed to aircraft emissions of nitrogen oxides and accompanying hydrocarbons. A re-evaluation of historical and future aircraft emissions is required.

7. Carbon monoxide

The tropospheric concentration of OH radicals is largely determined by the atmospheric concentration of carbon monoxide and, to a lesser extent, by methane itself. Increases in carbon monoxide would lead to a reduction in tropospheric OH and a consequential increase in methane. Some sets of data indicate that tropospheric carbon monoxide concentrations have been increasing by about 1 per cent per year in the recent past; other data suggest a larger increase. Since carbon monoxide is also a product of methane oxidation, there is the possibility of a positive feedback mechanism in which increasing methane retards the rate of its own removal resulting in still further increases. More needs to be known about the sources and sinks of both methane and carbon monoxide. Extended sets of observational data are required to define the growth rate and lifetimes with better precision.

8. Water vapour

Water vapour in the stratosphere is important because it is the source of the hydroxyl radical. It enters the stratosphere mainly through the tropical tropopause (with the Indonesian and Indian monsoon regions being particularly important) where "cold trap" action results in very low concentrations in the lower stratosphere (about 2 - 3ppm near the tropopause). The temperature of the tropical tropopause is the main influence on the flow of water vapour, and hence any change in this temperature could have profound effects.

Above the tropopause, concentrations increase with height from 2-3 ppm to 5-6 ppm, consistent with a stratospheric source from oxidization of methane. Co-located satellite measurements of methane and water vapour are consistent with there being no other major sources or sinks. Thus increased methane concentrations would also lead to increased water vapour in the upper stratosphere. Likewise, increased tropospheric temperatures resulting from a CO_2 increase could lead both to increased tropospheric water concentrations and by altering the exchange rate between the troposphere and stratosphere, to changes in water vapour in the lower stratosphere.

E. Atmospheric chemistry

Our understanding of the chemistry of atmospheric trace species has continued to improve as a result of laboratory measurements of rate coefficients, cross sections, primary photo-dissociation quantum yields and products of elementary reactions. Since the last CCOL session, new data have been reported for a number of key reactions previously identified as important for the ozone budget. This has led to small refinements and reduced uncertainty in the recommended parameters for the basic odd-oxygen removal chemistry involving HO_x, NO_x and Clx species. In addition, rate coefficients have been measured for a number of reactions for which data were not previously available, in particular, reactions involving the NO_2 radical. These studies have not provided any major novel or unexpected results.

Although there are still some problems in relating the data base to chemical kinetics theory, the consistency in the experimental results of the important reactions gives reason for considerable confidence in the reliability of their rate coefficients. This rather satisfactory situation can be largely attributed to the great improvement in the experimental techniques for study of gas phase kinetics and photochemistry.

No major new processes have been incorporated into photo-chemical models since the last CCOL session, but several novel chemical aspects of a more speculative nature have been addressed. These include the slow chemical reactions of non-radical reaction partners (e.g. $ClONO_2$, HCl, H_2O, N_2O_5 and HO_2NO_2 etc.), which may occur either homogeneously, or heterogeneously on aerosol particles; reactions involving sodium of mesospheric origin; and excited-state chemistry. Data relating to the mechanisms of the oxidization of hydrocarbons and halocarbons has also been reported.

The following discussion will emphasize the impact of new results on established chemistry and also on some of the more speculative aspects, with particular reference to ozone perturbation calculations. The large majority of the processes for which the data base is thought to be well established have been fully dealt with in previous CCOL reports and will not be covered again here. In experimental work, emphasis has continued to be placed on:

(a) The analysis of reaction products with the object of better definition of the products of multiple reaction pathways; (b) Investigation of rate parameters and mechanisms over the full range of atmospheric temperature and pressure since extrapolation of results from outside this range is sometimes unreliable; (c) Studies of the influence of the partial pressures of other gases such as water vapour or oxygen on reaction rates; (d) Laboratory investigations of simple chemical systems involving ozone reactions with HO_x, ClO_x or NO_x species, as it has been recognized that this approach may lead to the possible identification of relevant novel chemical processes.

The report of the CCOL at its sixth session drew attention to the importance of tropospheric chemistry, both in controlling the input of surface-derived source gases to the stratosphere and with respect to the contribution of tropospheric ozone to the total ozone column. Efforts to improve our understanding of tropospheric chemistry, particularly that relating to the budgets and life cycles of sulphur, nitrogen and carbon-containing species have expanded greatly in the last two years. These studies have revealed a complex picture of tropospheric trace gas behaviour which is not so readily amenable to study using the approach adopted successfully for stratospheric chemistry. This arises from the variation in space and time of the sources of photo-chemical activity, and of the dynamical behaviour of the lower atmosphere. However, real progress towards understanding the chemistry of the troposphere is expected as a result of the ongoing programmes.

Extensive chemical kinetics research has continued to emphasize the importance of temporary reservoir species such as HOCl, HO_2NO_2, N_2O_5 and $ClONO_2$. The improved measurements of key kinetic and photochemical parameters involving these species, reported in the period since the last CCOL session, has not led to any significant change in the calculated ozone depletion due to ClX perturbations. The possible importance of additional chemical pathways for ClX species in the highly perturbed stratosphere will need to be considered.

<u>Reactions involving</u> O_x, HO_x, NO_x <u>and ClX coupling</u>. No significant new experimental data relating to the kinetics of reactions of the oxygen species $O(^3p)$, $O(^1D)$, O_3 or O_2* have been reported and the data base is considered to be well established. The branching ratio for NO formation in the reaction, of $O(^1D)$ with N_2O, which is the major source of stratospheric NO_x, is a critical parameter in model calculations. There are differences in the laboratory studies of this reaction which have been attributed by some, to kinetic energy effects from photochemically generated $O(^1D)$. This needs clarification. There remains some concern about the possible roles of excited states of O_2 ($O_2$1D and $O_2$1) and work is in progress to identify the sources of these excited molecules, especially from radical + radical reactions. At present, there is no evidence that these states have any important effects on the overall chemistry of the stratosphere.

The penetration of solar ultraviolet radiation into the atmosphere is controlled by absorption by molecular oxygen between 100 and 240 nm and by ozone between 200 and 320 nm. In the past, there have been inconsistencies between measured solar ultraviolet fluxes and those calculated from laboratory measurements of the relevant absorption cross section of O_2 and O_3. It was inferred that the laboratory measurements of the O_2 absorption cross-sections in the Herzberg Continuum, 180-220 nm, may have been too high, by a factor of two, and recent laboratory experiments designed to overcome problems associated with extrapolation to stratospheric pressure and temperature have confirmed this. Incorporation of these lower values into models results in enhanced calculated penetration of solar-radiation flux into the atmosphere. The resulting increased photolysis rates lead to an improvement in the agreement between measured and calculated profiles for CFC 11, CFC 12, N_2O and HNO_3 but reduces the level of agreement for profiles of ozone. Accurate values for ozone cross-sections for 200 $\pm$ 20 nm are still required to refine the solar-flux calculations.

Recent laboratory measurements of the ozone absorption cross-section from 230 to 340 nm show no significant difference below 280 nm compared with the previous measurements used in the stratospheric models. But, at longer wavelengths, the temperature effect leads to increasing differences reaching 10 per cent at 300 nm. The temperature dependence should be considered carefully for modelling applications with the simultaneous variation of the quantum yield of the $O(^1D)$ production, particularly in the lower stratosphere.

HO_x species play a key role in the upper stratosphere, where the following reactions:

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$O + HO_2 \rightarrow OH + O_2$$

provide the major O_3 loss process in the unperturbed atmosphere. In the lower stratosphere, OH is the key radical controlling formation and removal of active ClX and NO_x species through the reactions:

$$OH + HCl \rightarrow H_2O + Cl$$
$$OH + NO_2 + M \rightarrow HONO_2 + M.$$

The data base has improved greatly so that today there is a reliable consensus based on measurements for the rate parameters for all the key HO_2 reactions with H, O, OH, NO, HO_2 and O_3 which control the abundance and partitioning of OH and HO_2 radicals. Earlier work indicating unexpected kinetic effects has been confirmed in experiments which now provide better characterization of the reactive channels and the presure, temperature and water vapour dependence of the rate coefficients. Additional studies of $HO_2 + O_3$ are still required.

Removal of odd hydrogen in the lower stratosphere occurs mainly by the reactions of OH with nitric and peroxynitric acid:

$$OH + HNO_3 \rightarrow H_2O + NO_3$$
$$OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$$

Changes in the recommended rate coefficients for the reactions have previously resulted in significant revisions of calculated ozone changes. The negative temperature dependence and small pressure dependence of the reaction of OH with HNO_3 is now well established, and new data have been reported for the temperature and pressure dependence of the reaction:

$$HO_2 + NO_2 + M = HO_2NO_2 + M.$$

The problem of conflicting results for the temperature dependence of OH + HO_2NO_2 is still not resolved and the products of this reaction have not been verified. Moreover, the temperature dependence and products of the photo-dissociation of HO_2NO_2 are still not established. These gaps in the data base still lead to some uncertainty in the description of the behaviour of HO_2NO_2 in the lower stratosphere.

The most significant new developments in NO_x chemistry relate to the kinetic data reported for NO_3 reactions. There have been several direct measurements of the rate coefficients for the reaction $NO_3 + NO_2 + M = N_2O_5 + M$, and the equilibrium constant for this important temporary reservoir species (N_2O_5) is now established. Data for reactions of NO_3 with NO, Cl, ClO and numerous hydrocarbon species have been reported. The new information on NO_3 reactions has not modified the previously held view of the major features of NO_3 chemistry.

No major changes in the data base for the major odd-chlorine reactions have emerged. Minor revision of the rate coefficients for the reactions O + ClO and OH + HCl has resulted from several new studies of each reaction. The new values are approximately 10-20 per cent lower and higher respectively and, since they have opposite effects on the ozone destruction cycles, the overall effect of these revisions on calculated ozone depletion is minimal. Recent kinetics studies of the HO + ClO reaction have revealed some inconsistencies, in both the kinetics and products channels. Earlier conclusions that the HCl forming channel is negligible may need modification in the light of consistent observations of only 85 per cent yield of the HO_2 and Cl products. Direct observations of HCl as a product is urgently required, since this reaction channel could provide an important loss mechanism for odd chlorine in the upper stratosphere, where large O_3 reductions due to ClX are predicted.

New data on the temporary reservoir species HOCl and $ClONO_2$ have confirmed previous conclusions that HOCl plays a minor role and only one significant chlorine nitrate isomer is formed in the ClO + NO_2 + M reaction. Photo-dissociation is the major sink for these temporary reservoirs. Minor changes in the product channels for $ClONO_2$ photo-dissociation are indicated by recent results, which suggest that $O(^3p)$ formation occurs approximately 10 per cent of the time.

1. Bromine chemistry

Ozone destruction by active bromine species, Br and BrO, may occur by means of a catalytic cycle analogous to that of ClO_x and also by coupling with ClO_x cycles through the fast reaction of BrO with ClO. Although photochemical kinetic data have been reported for most of the relevant reactions, the uncertainty in the data base is larger than that for ClO_x reactions. Nevertheless, it is clear that ozone destruction by BrX is more efficient than that by ClX on a molecule basis, because of the rapid conversion of the reservoir species, HBr, to active BrO_x species by the reaction:

$$OH + HBr \longrightarrow Br + H_2O.$$

This leads to a large proportion of the total stratospheric bromine being present in the active form.

2. Oxidization of hydrocarbons and halocarbons

The observed increase in atmospheric methane concentrations underlines the need to understand its oxidization mechanisms. In the stratosphere, the reaction $Cl + CH_4 \rightarrow HCl + CH_3$ 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 products are CH_3O, CH_3O_2 and formaldehyde. New data confirm that reaction with O_2 is the only important route for CH_3O in the atmosphere. Particular areas of uncertainty, are the rates of the reactions: $CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$, $CH_3O_2 + O_3 \rightarrow$ products and $HO_2 + HCHO \rightarrow$ products, and the temperature dependence of the OH + CO reaction. The effects of these uncertainties on stratospheric ozone perturbation calculations are negligible but they are important for the tropospheric ozone and OH budget. There is also improved knowledge of the kinetics and mechanisms for oxidization of 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. Many gaps remain, however particularly in the photochemistry of intermediate species such as carbonyl compounds, which are potential HO_x sources through photolysis, and the organic peroxynitrates (e.g. peroxyacetylnitrate) which can act as sinks for odd nitrogen in the troposphere and lower stratosphere.

A considerable amount of attention has been directed over the past few years, to the photo-oxidization mechanisms of the chlorofluoromethyl radicals derived from the initial breakdown of the CFCs by photolysis or by reaction with $O(^1D)$. Model calculations have generally assumed that the release of Cl from the CF_xCl_y radicals is rapid compared to the overall CFC lifetime and detailed chemical steps for this process are normally ignored. However, calculations in which the intermediate species Cl_2O and CFClO are included give stratospheric ClX concentrations a few per cent lower than the simplified treatment. Furthermore chlorofluoromethyl peroxynitrates formed by the reaction of $CF_xCl_yO_2$ with NO_2 may act as a minor temporary reservoir for NO_x and ClX in the lower stratosphere. These effects need to be explored further in model calculations.

3. New chemical considerations

The stabilization of the data base for established reactions has rendered feasible investigation using modelling techniques and laboratory experiments of the possible role of less well quantified processes in stratospheric chemistry. The potentially most important effects result from reactions involving the temporary reservoir species. The homogeneous reaction of N_2O_5 with water vapour is known to be very slow, but a rapid surface reaction can take place. If this reaction were to occur on the surface of stratospheric aerosol, the reaction sequence: $H_2O + N_2O_5 \rightarrow 2HNO_3 \rightarrow 2OH + 2NO_2$ could provide a significant source of HO_x in the lower stratosphere. A similar effect could result from $ClONO_2$ and HO_2NO_2 reactions with water. The reaction $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ has also been observed in the laboratory, but the rate and nature of the reaction has not been established with certainty. Such chlorine reactions could be important for stratospheric chemistry, since they could release active chlorine from these reservoir species thus increasing the predicted magnitude of ozone depletion. In addition the $ClONO_2 + H_2O$ reaction would increase calculated ozone depletion due to ClO_x. The occurrence of these reactions on the surface of stratospheric aerosol could also be important. Studies of the reactivity of these species in both the gas phase and on aerosol surfaces are clearly needed.

The possibility of additional chemical pathways for ClO in a highly ClX perturbed stratosphere has also been addressed. The formation of assymetrical ClO_3 in the reaction of ClO with O_2 has been investigated experimentally, with a view to assessing a possible odd-oxygen source through photolysis of ClO_3, i.e.:

$$ClO_3 + h\nu \rightarrow OClO + O$$

$$OClO + h\nu \rightarrow ClO + O$$

Recent results suggest that ClO_3 formation is too slow to be significant. Other possible pathways to Clx species, such as the ClO + ClO reaction, are also being investigated.

Since the sixth session of the CCOL, a certain amount of progress has been made in quantifying some of the more speculative aspects of stratospheric chemistry raised previously. These include reactions of excited-state species, e.g. N_2 (A), which could provide a source of N_2O via reaction with O_2. Reactions of HO_2(A) and OH* could modify HO_x chemistry. While numerous excitation mechanisms for these species have been shown to be important in the stratosphere, non-reactive quenching processes appear to dominate the loss mechanism of the excited states for HO_2(A) and OH*, but the picture is still less clear for N_2(A).

Considerable improvements have been made in the kinetic data base for reactions involving sodium. It has been suggested that sodium could influence upper stratospheric ozone through catalytic release of Cl from HCl, through the formation and photolysis of NaCl. The gas phase reactions of NaO and NaOH with HCl to form NaCl are thought to be extremely rapid. There is still considerable uncertainty regarding the photolysis rate of NaCl, which is essential for the release of chlorine and the regeneration of sodium. However, the major uncertainty relating to the importance of sodium chemistry is our lack of knowledge of the abundance of gaseous sodium and its oxides in the stratosphere.

4. Solar-flux variability

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 ± 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 ultraviolet regime above 100 nm. While the best calibrations give a precision of better than ± 10 per cent, examination of different sets of observations that are often regarded individually as satisfactory, reveals consistent differences of ± 20 per cent and in certain cases as much as a factor of two. The most recent values obtained using rockets have mean values for 1 nm intervals which generally differ by about 10 per cent.

The degree of penetration of solar UV radiation in the stratosphere is determined by the absorption of molecular oxygen (O_2) leading to production of O_3 through photodissociation to oxygen atoms (O) and to its final product ozone (O_3). Recent satellite and rocket observations have shown that the solar spectral irradiances of the various spectral regions (Chappuis bands in the visible, Huggins bands in the UV-B and even the Hartley band at wavelengths less than 310 nm) corresponding to the photo-dissociation of O_3 do not vary with solar activity (± 1 per cent). Twenty-seven day cyclic changes in the solar irradiance have been detected in the region of the Herzberg Continuum, leading to the photodissociation of O_2 at wavelengths less than 240 nm. Between 240 and 210 nm, the variation is about 1 per cent increasing to approximately 5 per cent near 200 nm.

An extrapolation of these data to a solar 11-year cycle requires the adoption of a solar index. Since there is no general agreement to date regarding the adoption of an indicator of solar activity, the question as to the magnitude of the solar-cycle variation in the photo-dissociation region of the spectrum of O_2 still remains.

F. Atmospheric observations

Atmospheric observations are required to check the validity of models at all accessible points. The comparison of theory and observation is essential if we are to test our ability to describe the present atmosphere. Various in situ and remote-sensing techniques are now being used to determine the atmospheric concentrations of a large number of chemical species from the ground and from aircraft, balloon and rocket platforms. This type of data is required to test the radiative-chemical aspects of the models. To date, there have been some measurements of most of the key atmospheric constituents, with the exception of the temporary reservoirs, e.g., $ClONO_2$, HO_2NO_2, etc., which have, at best, been only tentatively identified.

While many of these observations have been isolated measurements of single species, they have not only demonstrated the presence of these species in the atmosphere, but also provided a vital, though limited, test of our knowledge of atmospheric photochemistry. Obtaining measurements of these key species with the accuracy, precision, and temporal and spatial resolution required to test critically the validity of the photochemical models, is a difficult task due to the low atmospheric concentrations of these species i.e., parts per million to sub-parts per trillion. It is now well recognized that the simultaneous measurement of several photochemically coupled species in the same air mass is necessary for the required critical test of photochemical theory; such tests are not possible from isolated measurements of single species. To date, however, there have been only a limited number of such simultaneous measurements with which to test the theory.

There has also been substantial progress during the last two years on formulating strategies that will test most effectively the validity of the photochemical models, including studies of the diurnal behavior of gases, studies of the changing chemical composition of an air parcel with time, ratio measurements of species, correlation studies of O_3 with temperatures and correlation studies of O_3 with HO_x, ClO_x and NO_x species. Before comparing theoretical descriptions of the present atmosphere with observations, it is vital to have an understanding of the accuracy and precision of the 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. Once the quality of the data has been determined from the various intercomparison campaigns that have recently been conducted, and the newly developed instrumentation discussed below is demonstrated, it should be possible to make the type of measurements required to test critically the photochemical models. The data collected from the recent remote-sensor campaign, described below, will provide the most comprehensive set of data of known quality with which to test photochemical models. It should also be noted that a capability to measure several species globally from satellites has been demonstrated, and that a data base is now available to test certain features of the chemical, radiative and dynamical aspects of multidimensional models. In the longer term, these field and satellite programmes will overcome the greatest problem, i.e., the shortage of data.

As indicated earlier, one of the major shortcomings to validating theory is a lack of understanding of the accuracy and precision of atmospheric measurements. Consequently, there has been a major effort to conduct a series of international intercomparison balloon measurement campaigns aimed at determining the accuracy with which the vertical distributions of key atmospheric constituents can be obtained. In two of these campaigns, numerous different instruments using similar and dissimilar experimental techniques were employed to measure simultaneously a wide range of key atmospheric constituents in the same air mass. Provisional data from these campaigns have been presented at several recent international symposia, and in most cases, the accuracy appears to be in the range of 10-20 per cent after certain problems in the analysis of some of the data sets were solved. This data is currently being finalized and should be available within the next few months. They include:

(a) Several campaigns employing both in situ and remote-sensing balloon-borne and rocket-borne ozone instruments;

(b) Two campaigns utilizing remote sensing balloon-borne instruments (13 on the first, and 18 on the second) using eight different techniques including grating spectrometers, radiometers and Fourier transform interferometers, to measure several key atmospheric constituents including HNO_3, NO_2, NO, HCl, HF, O_3, N_2O, CH_4, H_2O, HD, 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. These balloon measurements were supported by ground-based and aircraft-borne instruments which measured the total column content for a number of chemical species, and also, by meteorological and atmospheric aerosol data;

(c) Three campaigns employing in situ and remote sensing balloon-borne water vapor instruments;

(d) In one campaign, two in situ grab sampling techniques for source gases, including N_2O, $CFCl_3$ and CF_2Cl_2 were utilized.

Several additional intercomparison campaigns of balloon-borne instruments are clearly needed including:

(a) In situ and remote sensing techniques for ClO;

(b) In situ and remote sensing techniques for NO and NO_2.

Over the last two years, several newly developed in situ and remote sensing techniques have been demonstrated, though the data has not yet been published, for species for which there had been inadequate measurements, e.g. OH. In addition, some existing techniques have been - or are being, improved and this will result in greater sensitivity for a number of species, e.g., ClO and O_3 by balloon-borne microwave emission and HO_2 by matrix isolation EPR detection. This newly developed and improved instrumentation will augment existing instrumentation so as to measure nearly all key atmospheric species over a significant altitude range with the accuracy and precision required to test critically our description of atmospheric photochemistry. An exception to this may be in the important area of the temporary reservoirs, where there are no reliable measurements to date, and where the prospects for future measurements are difficult to assess. In principle, there may be hope of utilizing a high resolution infra-red interferometer or another possible approach may be the infra-red detection of these species trapped at 77K on an inert gas matrix.

Techniques that have been demonstrated over the last two years include:

(a) Two balloon-borne far-infra-red emission interferometers for remote sensing detection of OH;

(b) Balloon-borne laser induced fluorescence systems for in situ and ranging detection of OH;

(c) A ground-based microwave emission system for remote detection of HO_2;

(d) A balloon-borne laser diode absorption system for in situ detection of NO and NO_2.

A platform, called reel-up/reel-down, has also been demonstrated whereby an instrumented package can be lowered and subsequently raised approximately 10 km on a cable relative to a balloon-borne platform floating in the mid-upper stratosphere. This allows the atmosphere to be probed with highly sensitive in situ fluorescence instruments having a high vertical resolution (approximately 30 m) many times per balloon flight. This results in a substantial enhancement of the scientific information return; e.g. on the diurnal variability of chemically coupled species and fine structure in the vertical distribution of the chemical composition, both of which critically test chemical models of the atmosphere.

The only two parameters for which there are long-term extensive satellite and ground-based global data sets are ozone and temperature. However, a significant step forward occurred with the validation and release of data obtained by instruments flown on the Nimbus 7, Atmospheric Explorer II, and Solar Mesospheric Explorer Satellites. This includes seven months of Limb Infrared Monitor of the Stratosphere (LIMS) data (HNO_3, NO_2, O_3, H_2O, temperature), the first year of Stratospheric and Mesospheric Sounder (SAMS) data (N_2O, CH_4, temperature), the first two years of Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS) data [O_3 (column and vertical distribution) and solar flux] and the first two years of Stratospheric Aerosol and Gas Experiment (SAGE) data (O_3, NO_2, aerosols). In addition, five years of polar stratospheric aerosol data are available from the SAMS II experiment. These data have been processed and archived in the National Space Science Data Center at Washington, D.C. Moreover, the data from the SME satellite (O_3, NO_2, aerosols and solar flux) are now becoming available.

Our current knowledge of the vertical distribution of source gases and reactive trace species will now be briefly reviewed, with emphasis on those species which can directly influence the concentration of ozone in the stratosphere. However, it should first be reiterated that recent developments in our ability to measure atmospheric species should enable us to improve our understanding of atmospheric composition in order to test the validity of theory and to observe trends in the concentrations of key constituents. This latter capability should provide evidence of significant changes in atmospheric chemical composition.

1. Source gases

Individual vertical profiles at several latitudes have been obtained for H_2, CH_4, N_2O, CF_2Cl_2 and $CFCl_3$, while, in addition, zonally averaged vertical profiles have also been obtained for N_2O and CH_4 from satellites. 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 all aspects of the available quantitative details. The most notable discrepancy is the underestimation of vertical fall-off. The new lower O_2 cross sections reduce the magnitude of this discrepancy but do not eliminate the problem. It should be noted that transport parameterization can also affect the theoretical calculated vertical profiles. These differences have little impact on the overall 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 present lack of an extensive data base for these species prevents more refined analysis.

2. Odd-oxygen family

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. $O(^1D)$ has not been measured in the stratosphere because of its low concentrations. 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; however, the data base is limited and, therefore, not adequate to test critically these models. Atmospheric O_3 is discussed in another section of this report.

3. Odd-hydrogen family

Although the odd-hydrogen species (HO_x) play a central role in stratospheric photochemistry, knowledge of atmospheric concentrations of HO_x species (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 published data at present, and this constitutes a serious gap in our knowledge. This limited data base is understandable considering the difficulty of the measurements. However, several new techniques have recently been developed to measure the vertical distributions of OH and HO_2 radicals. These techniques have already been deployed and the data obtained are currently being evaluated. This type of data will render possible a critical testing of the understanding of HO_x photochemistry, when obtained in conjunction with other relevant data, e.g. H_2O and O_3 concentrations. Published ground-based measurements of the total column of OH, and of the distribution of HO_2 above approximately 25 km, do reflect some constraint on these key species, and are indeed consistent with model predictions. The OH distribution with altitude and latitude have been calculated using LIMS NO_2 and HNO_3 data by assuming photochemical equilibrium. The derived OH concentrations appear to compare well with theory between 30 and 35 km. The situation for hydrogen peroxide is less satisfactory, since there are no positive observations of this species in the stratosphere, but, prospects for its detection in the near future are good. 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, and this is urgently needed due to its control of NO_x and ClO_x photochemistry. The partitioning of NO_x and ClO_x species between active radicals and inactive reservoir species is believed to be controlled by the atmospheric concentration of OH, i.e., the ratios ClO:HCl and NO_2:HNO_3 are both controlled by OH in model calculation.

4. Odd nitrogen family

The odd-nitrogen species considered important in the chemistry of the stratosphere are NO, NO_2, NO_3, N_2O_5, HNO_3, HO_2NO_2 and $ClONO_2$. The results of measurements of NO, NO_2, NO_3 and HNO_3 have been reported in the literature, but the lack of reliable measurements of the temporary reservoir species (N_2O_5, HO_2NO_2 and $ClONO_2$) constitutes a major gap in the understanding of nitrogen chemistry. Odd-nitrogen chemistry is important in that it is believed to play a dominant role in limiting O_3 concentrations in the stratosphere and it interacts strongly with odd-chlorine and odd-hydrogen chemistry.

Atmospheric-concentration profiles of the dominant odd-nitrogen species (NO, NO_2 and HNO_3) have been measured by a variety of techniques. In general, the agreement between measurements by the different techniques lies well within the slight day-to-day variability observed by a single technique. However, until recently, there have been very few simultaneous measurements by different techniques to test instrument accuracies. The recent BIC campaign addressed this problem and the results, which will be available in the near future, will be used to evaluate the relative accuracies of many of the long-path instruments that have been used to measure NO, NO_2 and HNO_3.

There have been no measurements of total odd-nitrogen concentrations (NO_y) in the stratosphere. However, NO_y profiles in the 30 to 40 km region can be inferred from NO_2 and NO profiles measured by satellite and balloon-borne instruments (HNO_3, HO_2NO_2, NO_3 and $ClONO_2$ contribute only very minor amounts to the total; and N_2O_5 contributes a somewhat larger and diurnally variable amount to the total in this region; NO is only present during daylight hours when the bulk of NO_y is in the form of NO and NO_2). Of these measurements, the best available indicator of stratospheric concentrations of NO_y to compare with one-dimensional models are the early evening measurements of the mid-latitude NO_2 concentration profiles. In this region and at this time, NO_2 is calculated to comprise 50 per cent (at 30 km) to 90 per cent (at 40 km) of NO_y. In the 30 to 40 km altitude region, chemical processes predominate over transport processes, and the chemistry that controls the partitioning among NO_y species is believed to be reasonably well understood.

For global budgets of NO_y, satellite data provide the most comprehensive data sets for comparison with models. Three satellite data sets of stratospheric NO_2 concentrations exist (LIMS, SAGE and SME), but only one (LIMS) includes night-time measurements of NO_2 concentrations. Averaged NO_2 concentration profiles for March, April and May, 1979 from the LIMS early night data (four to five hours after sunset) for the middle latitudes (Northern and Southern Hemispheres) show an increase with altitude from about 9ppbv at 30 km to a broad concentration maximum of about 16.5ppbv extending from 36 km to 40 km with a one sigma error of about 25 per cent. This average NO_2 profile can be converted to an NO_y profile using calculated NO_2 to NO_y ratios which are primarily determined by ozone concentration and temperature. The data are consistent with a uniform NO_y mixing ratio in the range 18 to 21 ppbv between 30 and 40 km. Specifically, the NO_y profile is calculated to be 18ppbv at 30 km, 21ppbv at 36 km and 18ppbv at 40 km.

Due to large diurnal variations in NO and NO_2 concentrations (under daytime conditions NO_2 comprises only 15 to 35 per cent and NO only 14 to 80 per cent of NO_y at 30 to 40 km), other measurements are not directly comparable with the NO_y data derived from the night-time NO_2 data. However, the satellite (SAGE) sunrise and sunset NO_2 data measured during March, April and May, 1979, are consistent with the NO_y profile deduced from the LIMS data and the calculated NO_2 to NO_y ratio. Also, most NO and NO_2 measurements from balloon-borne instruments (as summarized in The Stratosphere 1981 - Theory and Measurement, published by WMO in co-operation with NASA) are consistent with the NO_y values given above when the calculated ratios for NO to NO_y and NO_2 to NO_y are used to convert to NO_y profiles. However, there are several NO concentration profiles measured using a rocket-deployed in situ technique that implies NO_y values about one half as large as those given above.

The general consistency between data sets measured with a variety of different instruments, both in situ and remote, and specifically the consistency between balloon-generated data and satellite data, tends to verify NO_y concentrations derived from the LIMS data. However, a much more comprehensive study to compare NO_y budgets derived from the large volumes of satellite NO_2 data as well as the more limited balloon NO and NO_2 data sets should be conducted. Even though one or two models calculate NO_y values below 15ppbv, many of the current one-dimensional models calculate NO_y values at 30 to 40 km in the 18 to 22ppbv range, a range consistent with the values derived above.

In general, the shape of model calculated profiles of NO and NO_2 in the middle latitudes agree with the shapes of measured profiles throughout the stratosphere. The only discrepancy between measured and calculated profiles of the dominant odd-nitrogen species is the slight over-estimation of HNO_3 by models above 30 km. However, it appears that the available measurements of NO_x by species do not provide a critical test of model performance.

The main deficiency in odd-nitrogen measurements is the lack of reliable data for the temporary reservoir species N_2O_5 and HO_2NO_2. Only a tentative identification of N_2O_5 and an upper limit for HO_2NO_2 have been reported.

5. Odd-chlorine family

The stratospheric odd-chlorine species (ClO_x) are Cl, ClO, HOCl, $ClONO_2$ and HCl. Measurements of ClO and HCl have been reported, but reliable measurements of HOCl and $ClONO_2$, which are needed to assess their importance to stratospheric chemistry, are not available. The interaction of the odd-chlorine species with species of the odd-nitrogen, odd-hydrogen and odd-oxygen families may be important in determining the future concentrations of atmospheric ozone.

Knowledge of atmospheric ClO has been improved recently by ground based microwave measurements. These measurements largely confirm previous balloon-based vertical profile measurements. This technique has also been used to measure the diurnal charge in the column amount of atmospheric ClO. The results of model calculations agree rather well with these movements. The large calculated diurnal variation of ClO is primarily due to the rapid exchange between Cl/ClO and $ClONO_2$/HOCl. However, published results of ground-based infra-red measurements of ClO indicate an upper limit for the column ClO density that is a factor of three to five below both the microwave and the balloon-based measurements. This upper limit was derived on the basis of the observed signal-to-noise ratio and the lack of any spectral feature that could be attributed to ClO. Preliminary analysis of new spectra shows a line that can be attributed to ClO, but the interpretation of these data is complicated by interferences due to adjacent HNO_3 lines. A complete analysis of these data and a re-evaluation of the relevant line strengths should be available in the near future.

The agreement between balloon-based ClO profile measurements and the model-calculated profiles is reasonably good, with the calculated profiles being at the upper edge of the measured profiles throughout most of the stratosphere (ignoring the two unexplained balloon-based profiles that fall well outside the other eight profiles measured by the same technique). The earlier discrepancy at 40 km, where models underestimated ClO, has apparently been resolved. This is due to larger calculated ClO concentrations at this altitude, as a result of changes of the rate coefficients of $O+HO_2$, O+ClO and OH+HCl. The column density of ClO measured by the ground-based microwave instrument is approximately 30 per cent lower than the column density calculated using the mean values of the ballon-based profiles. It should be noted, however, that the balloon-based ClO data exhibit rather large flight-to-flight variability (a factor of three to four) which is neither easily explained nor seen in the ground-based microwave data.

Measurements of HCl consist of vertical profiles from 14-40 km and ground and airborne total column measurements. Profile 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 35-40 km possibly indicate an HCl mixing ratio (approximately 2 ppbv) somewhat higher than calculated values. Recently observed latitudinal variations in the HCl column are modelled fairly successfully.

Temporal trends in HCl and HF atmospheric concentrations have been determined from the airborne total column measurements, which have wide latitudinal coverage but are made only sporadically. Calculated trends for these species are in reasonable agreement with the measured trends. However, preliminary analysis of ground-based infra-red data indicate a trend in HF that agrees with the airborne measurements and calculations, but a trend in HCl that is considerably below the airborne measurements and calculations. These data are from only one location but are continuous in time. As the trend in HCl concentrations is critical to the understanding of stratospheric ClO_x, these results must be cross-checked by other data sets.

The important temporary reservoir species $ClONO_2$ and HOCl have not been reliably detected in the atmosphere. However, two techniques may produce measurements of $ClONO_2$ in the near future. Improvements in the spectral resolution and in the signal-to-noise ratio in addition to the ability to remove interfering lines mathematically , should lower the detection limit for the FTIR technique to a value below the calculated $ClONO_2$ concentrations. A technique in which the $ClONO_2$ is trapped in a solid CO_2 matrix and is then analysed by FTIR will, in principle, have a detection limit well below the model calculated $ClONO_2$ concentrations.

G. Current status of model predictions

It is now well recognized that the changing concentrations of a number of anthropogenically influenced source gases may be altering the global atmospheric ozone distribution and temperature structure. Many previous evaluations of possible changes in ozone have considered only the effects of individual species. However, because of the non-linear interactions between the various chemical cycles, the most realistic model analyses of possible future changes in ozone must consider the simultaneous effects of the time-dependent scenarios for variations in concentrations of all chemically and radiatively important gases. These gases include CFC-11 , CFC-12, other chlorocarbons (CFC-113, CFC-114, CFC-115, CFC-22, CH_3CCl_3, CCl_4) CO_2, CH_4, CO, N_2O and NO_x, the last from both surface and aircraft emissions.

Nevertheless, for historical purposes and for interpreting the role of a given type of perturbation, there is still value in considering the effects of each individual species alone, as discussed below. Such single-source calculations also render possible simple evaluations of the effects resulting from revised rate coefficients or changes in other models inputs. Therefore, single-species perturbations will be discussed, following discussion of the more realistic combined scenario studies, in order to describe the individual source-gas influences on chemical cycles in the atmosphere.

As in the past, most of the model studies of potential perturbations to ozone and temperature have been made using one-dimensional (1-D) models. However, assessments with 2-D models are also now becoming available from a number of groups in North America and Europe; these 2-D results, where available, are discussed throughout the remainder of this section.

1. Individual perturbations

Most one-dimensional models used to study the effects of single perturbations also include the coupling of chemistry and temperature, while the 2-D results available for chlorofluorocarbons, methane and nitrous oxide perturbations do not include temperature feedback. Most of these calculations have been carried out with steady-state models assuming 1977 rates for ground release of chlorofluorocabons CFC-11 and CFC-12, and prescribed factors for the increase in the ground concentrations of nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2) and for the tropospheric injection of odd nitrogen (NO_x) by subsonic aircraft or surface sources. The table below gives a summary of representative model results for changes in total ozone and surface temperature. All temperature changes were normalized to a value of 2K for a doubling of CO_2. This is a typical value for radiative-corrective models, whereas most general circulation models give 2.5-4.5K. In comparison with last year's results, small differences are mostly due to alterations in the O_2 and O_3 absorption cross-sections.

Table 1. Changes in total ozone and surface temperature at steady state for individual species perturbations

Scenario	Change in Total Ozone (percentage)	Change in Surface Temperature (^oK)
CFCs (1977 rate)	-5	+0.5
CH_4 x 2	+3	+0.4
N_2O x 2	-10	+0.3
CO_2 x 2	+3	+2

Steady-state odd-chlorine concentrations calculated with 1977 CFC emission rates result in a change of total ozone of about -5 per cent in fully coupled radiative-convective models and -3 to -4 per cent in models without temperature feedback. The maximum changes in ozone of 40 per cent occur near 40 km in the steady-state CFC perturbations. The corresponding surface temperature change is about +0.5K due primarily to the CFC greenhouse effect with some influence also from the change in ozone. Two 2-D models, which do not include the temperature feedback, give a global average ozone change of -3.0 and -3.4 per cent in good agreement with the typical value of -3.5 per cent from 1D models without temperature feedback. The largest ozone depletion in the 2D models is calculated to take place at high latitudes in the late winter and early spring, the minimum effect on ozone (-2 to -3 per cent) would be in the tropics in late summer. If the releases of other chlorocarbons were to continue at present rates, they would increase the eventual calculated ozone depletion due to CFCs 11 and 12 by about one third.

Doubling of methane results in a calculated increase of total ozone by about 3 per cent, with about one-third of the increase occurring in the troposphere and two-thirds in the lower stratosphere. With increased methane, calculated stratospheric ozone reduction by odd chlorine is decreased or even reversed through the reaction of Cl with methane. Increased CH_4 also produces more stratospheric water vapour and therefore more odd hydrogen, which adds to calculated upper stratospheric ozone reduction. The surface temperature change results from the combined effects of CH_4 increase (about two-thirds of the effect), increase in stratospheric water vapour (about one third), and increase in ozone (about one sixth). A 2-D study gave approximately a 2.5 per cent global average increase in total ozone with a maximum increase (3 per cent) in the tropics and small decrease (1 per cent) in the high-latitude summer hemisphere.

Odd nitrogen produced from the reaction $N_2O + O(^1D) \rightarrow NO + NO$ provides the primary loss mechanism for ozone in the stratosphere. Coupling of odd-nitrogen species with the odd-chlorine and odd-hydrogen families converts the ozone-destroying catalysts (NO_2, ClO, OH, HO_2) to inactive reservoir species ($ClONO_2$, HNO_3, HNO_4) and can therefore reduce calculated ozone destruction. Doubling of N_2O causes appreciable reduction in stratospheric ozone below 40km. At current rates of N_2O concentration increase, the N_2O perturbations on ozone over the next century are likely to be smaller than those projected for constant CFC emissions.

Increase of tropospheric odd nitrogen by subsonic aircraft or surface emissions enhances calculated ozone production. In terms of the estimated aircraft fleet for 1990, a global increase of 0.3 per cent in total ozone, with most of the effect in the troposphere, has been calculated using 1-D models. Since most of the effects from aircraft emissions would be expected to occur over a limited latitude range, further analysis with 2-D and 3-D models is required.

Increasing CO_2 decreases calculated stratospheric temperatures by its infra-red cooling effect, slowing down temperature-dependent ozone destruction reactions. With doubled CO_2, stratospheric ozone is calculated to increase by about 3 per cent. The CO_2 greenhouse effect results in a surface temperature increase of about 2K.

Should there be an increase in tropospheric carbon monoxide (CO), calculations show a decreased OH concentration and an increase in tropospheric ozone. Tropospheric OH limits the amount of hydrogen-containing species (e.g. CH_4, CH3Cl, CH_3CCl_3) which rise into the stratosphere.

Although not examined in detail here, emissions of bromine-containing gases could also lead to a significant reduction in stratospheric ozone, if anthropogenically related emissions of such gases as methyl bromide, ethylene dibromide, FC-13B and FC-12B1 were to increase substantially.

Several recent modelling results have shown a non-linear dependence of the total ozone column as a function of the upper atmospheric odd-chlorine level ($ClX = Cl + ClO + HCl + ClONO_2 + HOCl$). Two distinct types of non-linearity have been discussed: for small changes in chlorine ($\Delta ClX < 5$ ppb) above the natural chlorine level of about 1 ppb, and for large chlorine perturbations ($\Delta ClX > 15$ ppb).

At small levels of chlorine loading, some models show a linear decrease in ozone with added ClX, while others give non-linear results, including cases for which the calculated ozone change is positive. The newly reported non-linearity for small ClX perturbations is different from earlier results and has implications for calculated short-term ozone trends. Several details of the models, including the method of diurnal averaging and the eddy diffusions coefficient used, appear to cause these model differences. In general, models with a more detailed treatment of diurnal concentration changes give more linear results.

Over the last year, model sensitivity studies have been made showing a rapid decrease in the total ozone column when the ClX level approximately exceeds that of stratospheric odd nitrogen ($NO_y = NO + NO_2 + NO_3 + 2 \times N_2O_5 + HNO_3 + HO_2NO_2 + ClONO_2$). The non-linearity for large ClX perturbations may have significant implications for the interpretation of effects if CFC emissions increase substantially. These results suggest that as ClX increases, the calculated total ozone decreases non-linearly with each additional increment in ClX. Some typical results are given in figure 3.1. For purposes of comparison, models calculate a change in ClX level relative to background of 8-9 ppb in the eventual steady state (about the year 2100) with nominal 1977 release rates for CFC 11 and 12. Atmospheric measurements suggest that present total odd-nitrogen level (NO_y) is about 18-21 ppb, with an uncertainty of ± 25 per cent.

The shape of the calculated curve of O_3 versus ClX depends sensitively on the levels of both NO_y and CH_4. This is illustrated in figure 3.1 and summarized in table 2. The level of ClX giving a calculated steady state ozone reduction of 10 per cent, for several

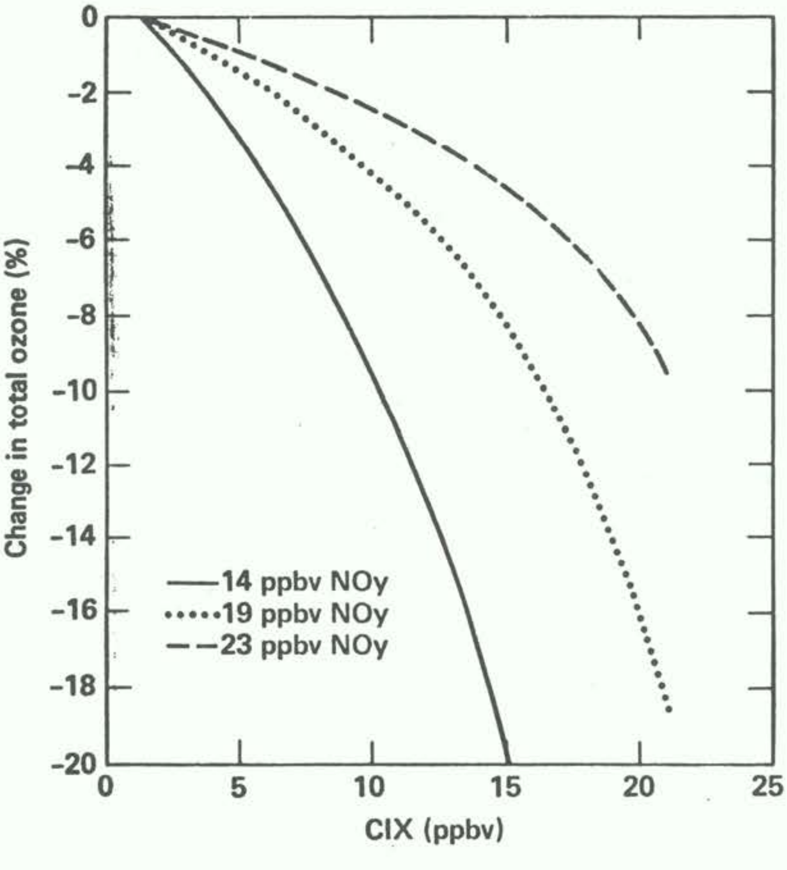


Figure 3.1

Calculated change in total ozone versus ClX as dependent on levels of NO_y

levels of methane and NO_y, is shown in table 2. These hypothetical sensitivity studies show that the level of ClX yielding a large change in ozone, increases with the atmospheric levels of both methane and NO_y.

Table 2 The level of odd chlorine (ClX) in the stratosphere corresponding to a calculated steady-state ozone reduction of 10 per cent, for several levels of methane (CH_4) and total odd nitrogen (NO_y)

CH_4 (Troposphere)	NO_y (Stratosphere)	ClX Level (for O_3 = -10 per cent)
1.6 ppm	14 ppb	10 ppb
1.6 ppm*	19 ppb[a/]	16 ppb
1.6 ppm	23 ppb	22 ppb
4.8 ppm	14 ppb	13 ppb
4.8 ppm	19 ppb	20 ppb
4.8 ppm	23 ppb	26 ppb

a/Approximate levels in the present atmosphere

The modelled rapid decrease in O_3 when ClX exceeds NO_y can be understood quantitatively as a titration of odd nitrogen by chlorine in the lower stratosphere (20-30 km). In the present atmosphere, ozone destruction in this region is thought to be dominated by NO_x-catalysed cycles. When CLX levels increase, NO_y is sequestered in the temporary reservoir $ClONO_2$. After a large fraction of NO_y is thus tied up, saturation occurs and further added chlorine leads to more ClX-catalysed ozone destruction. In these models, the OH concentration increased rapidly at high ClX levels due to slower destruction of OH through reactions like OH + HNO_3. Increased OH pushes the partitioning of ClX species towards the catalytically active forms (Cl + ClO).

As shown in figure 3.2, the modelled response of O_3 to ClX is a monotonic decrease in the upper stratosphere. In the lower stratosphere, a small ClX addition decreases NO_x-catalysed ozone destruction and gives an ozone increase. The positive ozone change in the lower stratosphere changes sign when the chlorine and nitrogen levels are about equal, after which additional ClX gives a large modelled ozone depletion. It should be noted that the greatest modelled decrease for the high ClX scenarios occurs in the lower stratosphere, a region with significant remaining uncertainties because important chemical species, such as most of the temporary reservoirs, are yet unobserved and because the role of transport processes is not as yet well understood.

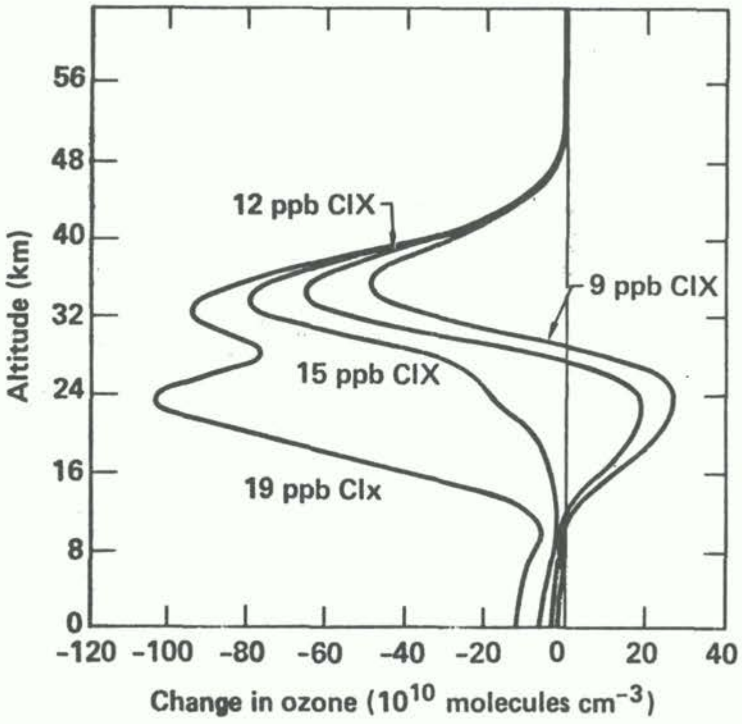


Figure 3.2

Model Calculated response of ozone to levels of ClX at different altitudes

The overall features of the results from 1-D models shown in figures 3.1 and 3.2 have also been seen in 2-D model calculations. An interesting feature in some 2-D models is that the latitudinal gradient in calculated ozone depletion, which is two or three times greater at the poles than at the equator for small chlorine loadings, decreases significantly as the amount of ClX in the model is increased. The global mean ozone change as a function of ClX, obtained in 2-D models, is very similar in shape and magnitude to that found in 1-D models. The sensitivity to NO_y found in 2-D models appears to be similar to that described previously for 1-D models.

Steady-state calculations in various multiple-perturbation studies have led to the conclusion that the single effects described in the individual perturbations add up in a highly non-linear manner.

As an indication of this effect, figure 3.3 shows three different cases (A, B, and C) based on a background atmosphere with twice the present levels of CO_2 and tropospheric NO_x, three times the present CH_4 level, and 1.25 times the present N_2O level. These are selected as representative of the levels that these species might reach in about 100 years' time if present trends continue. The curve in figure 3.3 shows the computed steady-state change in the total-ozone column, if fixed amounts of ClX are introduced into this hypothetical scenario. The same (elevated) levels of CO_2 and CH_4 are used in the background

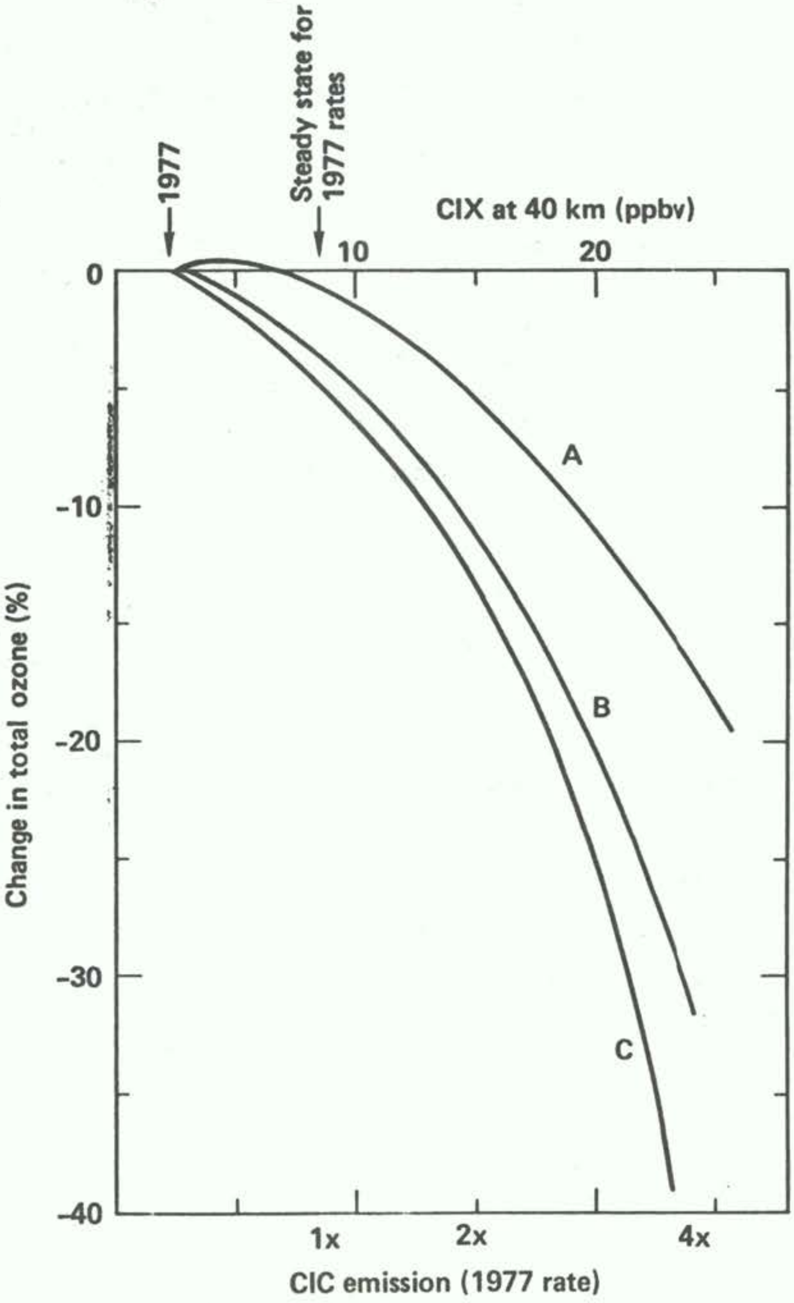


Figure 3.3
The computed steady-state change in the total ozone column with introduction of fixed amounts of ClX in three hypothetical cases (A), (B) and (C) (see text)

atmosphere for scenario B, with present levels of N_2O and NO_x. The difference between scenarios A and B demonstrates the importance of total odd nitrogen on chlorine-catalysed ozone destruction. Scenario C, for comparison, gives the hypothetical case where only CFCs increase but all other source gases remain at the present levels.

Constant CFC emissions at the 1977 rate give a calculated 0.6 per cent total ozone decrease in scenario A, 3.4 per cent in scenario B and 5.8 per cent decreases in scenario C. It is obvious that the non-linear fall-off for high odd-chlorine levels is strongly dependent on the assumptions made for other trace gases, especially on the amount of odd nitrogen available in the stratosphere. For scenarios A and B, the model shows a decrease in ozone around 40 km and an increase in the troposphere. These results point to the fact that realistic predictions can be made only with a time dependent model using the best estimates for the time development of all relevant trace gases.

2. Time-dependent multiple scenarios

Attempts to model the time-dependent combined effects of all potential perturbations should provide an improved understanding of the coupling between the different trace gases for the best estimates of possible future source gas scenarios. Only through such studies can we get an indication of what measurements would be necessary to detect and test the predicted effect on ozone.

As mentioned in the section on measured ozone trends, model calculations which take into account the changing concentrations of all the source gases have been performed to study the trends in ozone and temperature from 1970 to 1980. These models calculate a 0.4 per cent increase in the total column ozone which results from a decrease in the ozone from 32-40 km ranging from 2-4 per cent and an increase in lower stratospheric and tropospheric ozone.

Recent 1-D and 2-D model studies (see for instance, figures 4.1 and 4.2) suggest that future ozone changes associated with CFCs may be drastically altered when other perturbing effects are included. As seen in figure 4.1, the magnitude and sign of the calculated effect on total ozone is strongly dependent on which scenarios are assumed for CFCs, CO_2, CH_4, and other relevant gases.

Recent model calculations (see figure 4.1) suggest that little overall change in total ozone (less than 1 per cent) would be expected in the next few decades for the combined source gas effect unless significant sustained growth in CFC emissions were to occur. Over this time period, the effects of projected CO_2 and CH_4 concentration increases would be expected to counterbalance the calculated decrease in ozone due to CFCs alone.

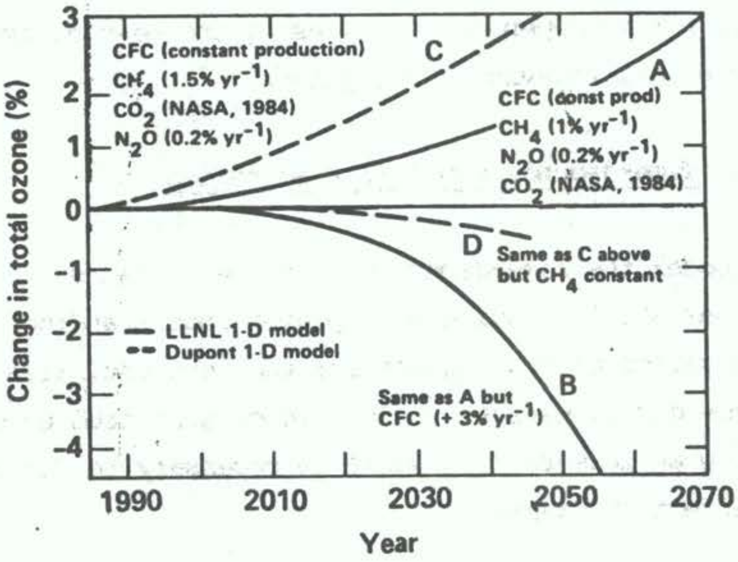
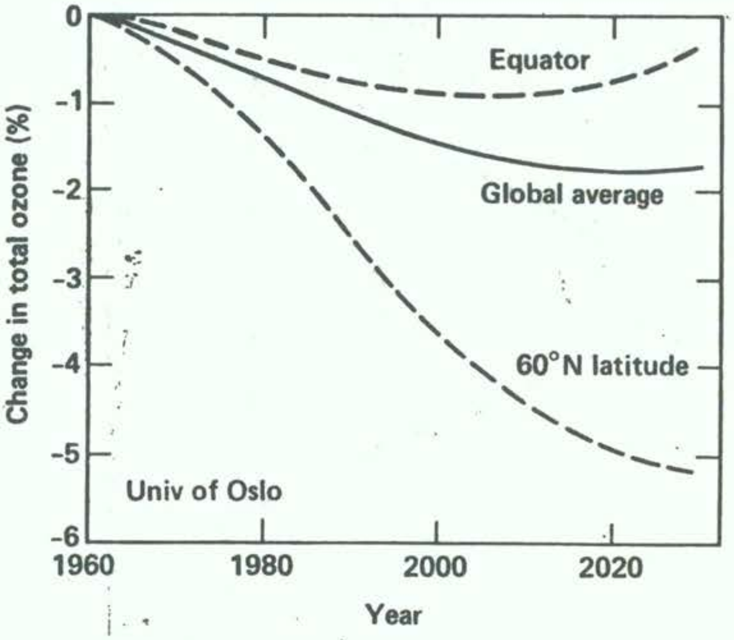


Figure 4.1 Time-dependent changes in total ozone for various assumed trace-gase future scenarios. Results are shown for several different 1-D modelling groups. Estimated growth in NO_x emissions from aircraft of 14 per cent/year until 1990, and constant emissions thereafter, are included in scenatios C and D, but are not included in scenarios A, C, and D.

The calculated effects over long periods are sensitive to assumed source gas scenarios. For example, scenario A of constant CFC emissions with increasing CO_2, CH_4 and N_2O as shown in figure 4.1 gives an increase in total ozone of 1.8 per cent in the year 2050 (relative to the present day), whereas, if a sustained 3 per cent per year growth in CFC emissions is assumed (a factor of 6.8 growth in emission by 2050), with otherwise the same scenarios, the result is a decrease in total ozone of 3.5 per cent in 2050. The results in scenario B of figure 4.1 suggest that the non-linear relationship between changes in ozone and odd-chlorine levels will eventually be reached if the sustained growth in CFC emissions is not less than 3 per cent per annum.

Results from a recent 2-D model calculation including scenarios for CFC-11, CFC-12, CH_3CCl_3 as well as CH_4 and N_2O (but not CO_2), are shown in figure 4.2. These results suggest that significant variations with latitude and season may be expected in the combined effects on total ozone.



Release rate increases

CH_4 : 0.7% per year
N_2O : 0.2% per year
CFC-11, CFC-12, CH_3CCl_3 : 3% per year 1980-2000, constant release after 2000
CO_2 : not included

Figure 4.2

2-D model calculation of change in total ozone with scenarios for CFC-11, CFC-12, CH_3CCl_2, CH_4 and N_2O

Even in those model calculations showing little change in total ozone calculated for combined future source-gas scenarios, there are significant changes being predicted in the altitude distribution of ozone, with large decreases above 30 km and increases or small decreases below. Calculated increases in tropospheric ozone are extremely sensitive to the assumed scenarios for CH_4, CO, and NO_x perturbations, but not to the ClX scenarios. Typical 1-D model results are shown in figures 4.3 (a) and (b) based on cases A and B from figure 4.1. Large percentage decreases in ozone are calculated above 30 km; for example, scenario A (constant CFC emission at 1977 rates, increasing CO_2, CH_4 and N_2O at 0.5 per cent, 1 per cent and 0.2 per cent per year respectively) calculates about a 14 per cent decrease in ozone at 40 km over the next two decades. These decreases are accompanied by corresponding increases at lower altitudes.

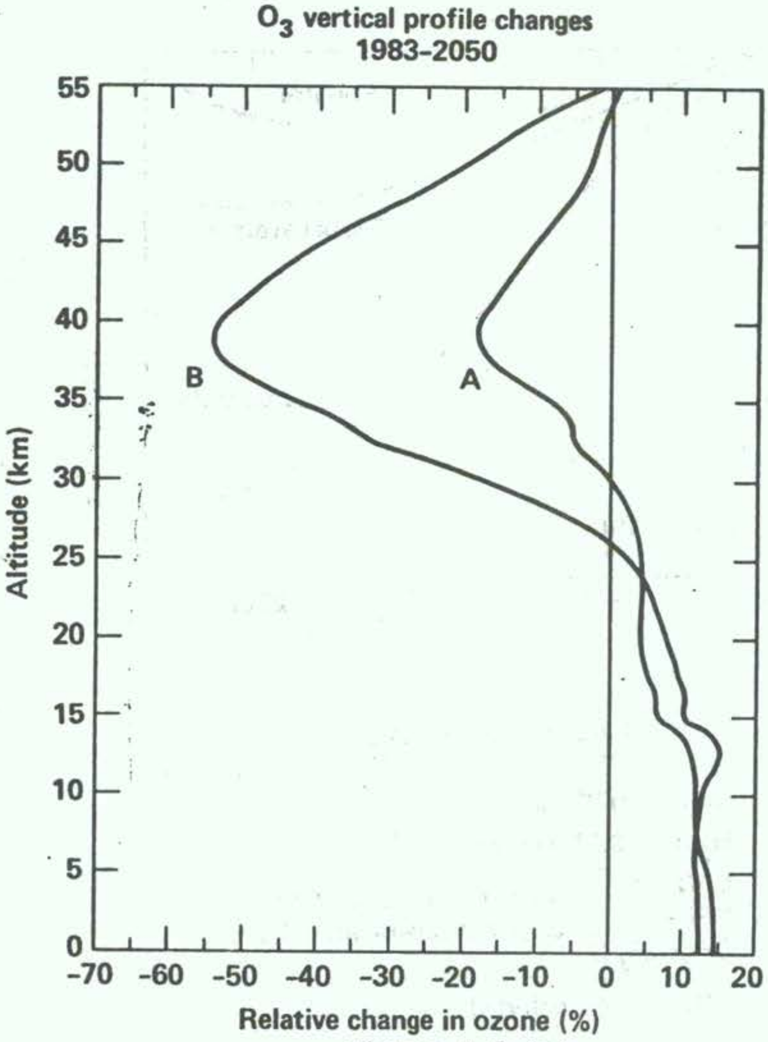


Figure 4.3 (a)

1-D model calculation of relative change in ozone (1983-2050) with altitude based on cases (A) and (B) in Figure 4.1

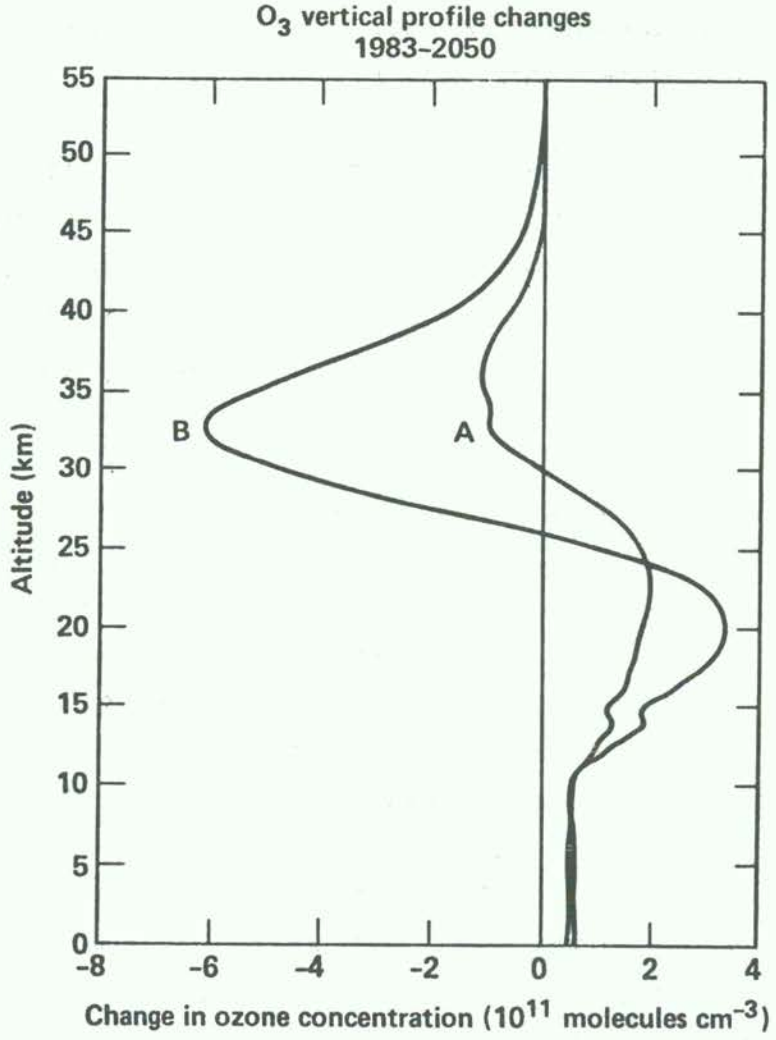


Figure 4.3 (b)
1-D model calculation of change in ozone concentrations (1983-2050) with altitude based on cases (A) and (B) in Figure 4.1

Similar effects on the vertical ozone distribution are also found with 2-D models, but with significant latitudinal and seasonal variations in the magnitude of ozone change at any given altitude. These predicted changes in the ozone distribution have potentially significant radiative and climatic impliactions that require further analysis.

3. Uncertainties and sensitivities

In the current predictions of ozone change, major areas of remaining uncertainty are:

(a) The trace gas scenarios;

(b) Photochemical processes and rate coefficients; and

(c) Radiative - dynamical interraction.

Future scenarios for the combinations of trace gases must be used with caution. At present, forecasts of future concentrations except for CO_2, are based primarily on historical trends rather than on detailed analyses of expected changes in sources and sinks. Unfortunately, the budgets of several important gases (e.g. methane, nitrous oxide and carbon monoxide) are not well understood.

Although uncertainties in chemical-rate constants are being reduced as new laboratory measurements become available, the possibility of significant variations in the predicted ozone depletion from new chemistry or changes in rate constants still remains. As an example, if a very fast reaction coefficient were established for the reaction $HCl + ClONO_2 \rightarrow Cl + HNO_3$ then model calculations would show significantly increased estimates of ozone depletion from chlorine perturbation.

Uncertainties in product distributions are also important. For example, if HCl is produced, significantly in the reaction of ClO with OH, both the calculated levels of ClO_x and the influence of chlorine on ozone would be significantly reduced.

Additional uncertainty, not easily quantified, is associated with the models used to predict ozone change. For example, many predictions are based on 1-D models, which attempt to include the average effects of transport, but which do not represent the detailed mechanisms of atmospheric transport processes. Many of the 1-D and 2-D calculations have not taken into account the effects of temperature feedbacks, and none include radiative-dynamical feedbacks.

4. Effects of source gases and ozone on climate

There are two distinct ways in which trace gases can affect climate:

(a) Directly, through infra-red absorption and emission. Several of the source gases discussed above (e.g. CO_2, CH_4, N_2O, CFCs) have strong absorption bands in the 7-13 μm spectral wavelength region, the "atmospheric window". These gases thus enhance the greenhouse effect and could contribute to global surface warming;

(b) Indirectly, by changing the ozone or water vapour distributions. Ozone, water vapour and carbon dioxide provide most of the infra-red opacity of the atmosphere, and absorption of ultraviolet radiation by ozone is the primary radiative heating source in the stratosphere. Changes in the vertical ozone distribution will modify the temperature profile. If the tropopause temperature changes, there may be a corresponding change in stratospheric water vapour. Since methane oxidization is thought to be a major source of stratospheric water vapour, increased CH_4 could yield elevated H_2O levels in the upper stratosphere.

The climatic effects of the source gases have been most extensively studied with one-dimensional models. The limitations of a one-dimensional model are well recognized, but few assessments of source-gas changes have been performed using higher-dimensional models. The effects on tropospheric climate are then characterized by a single number: the computed surface temperature change. Model results in table 1 above give the computed equilibrium surface temperature changes for selected scenarios (CO_2, CH_4, CFCs, N_2O). In all these cases, the modelled tropospheric temperature change is predominantly due to direct infra-red absorption and emission.

The infra-red effectiveness of a given amount of ozone in the troposphere is about ten times as large as in the stratosphere. Doubling of tropospheric ozone is predicted to increase the surface temperature by about one half a degree (K). Of the source gases discussed in this report, CH_4 has the largest calculated impact on tropospheric ozone; roughly 20 per cent of the computed change in the surface temperature is due to tropospheric ozone changes related to increasing methane.

As discussed in the previous section, model calculations based on reasonable scenarios for the major source gases (CO_2, CH_4, N_2O, NO_x, and CFCs) over the past decade and the next few decades suggest that there may be an ozone concentration decrease in the upper stratosphere and a slightly larger increase in the lower stratosphere and the troposphere. One dimensional coupled model calculations (scenario C in figure 4.1) suggest changes in the temperature profile from the present day until the year 2050 characterized by an increase in the troposphere (+2.5K) and generally larger decreases throughout the stratosphere (8K at 40km, 12K at 50 km). The modelled contribution of the other source gases (CH_4, N_2O, CFCs) to the surface temperature warming during this time is roughly equal to the surface warming due to CO_2. Methane alone gives a modelled surface temperature change about half as large as CO_2.

The influence of these computed changes in ozone and temperature on the dynamics of the stratosphere have not been fully investigated, although general circulation models with a sufficiently complete treatment of stratospheric dynamics to make an assessment are under development. While changes in stratospheric ozone may, in principle, alter tropospheric weather patterns, the few studies of a limited nature that have been made to date suggest that the impact of the changes anticipated in the next few decades would be minimal.

Changes in tropospheric and stratospheric dynamics could influence the stratospheric-ozone and trace gas distributions. The magnitude of this feedback cannot be quantified until sophisticated, fully interactive 3-D chemistry-transport models are developed. It is very important in the development of such models to obtain a better understanding of troposphere-stratosphere exchange processes and to clarify the very complex roles of ozone and other source gases in the climate system.

5. Model interpretation and evaluation

Many types of numerical models can play, and have played important roles in stratospheric research. 1-D models provide a means of exploring photochemical theory without a detailed representation of complex atmospheric transport processes. Similarly, 1-D radiative-convective models remain the most commonly used models for studying the effect of trace species on the atmospheric temperature profile. 1-D chemistry-transport and radiative-convective models have been coupled to investigage the interaction between chemistry and temperature.

One of the largest uncertainties in the development of 2-D (latitude-altitude) models has been the lack of a fundamental understanding of how properly to parametrize the atmospheric dynamical processes responsible for trace species transport. In spite of recent advances in atmospheric dynamics, the quantitative accuracy of 2-D transport treatments currently used in models and the accuracy with which evaluations of future ozone changes can be made have not been established. It will probably take several years before fully coupled 2-D chemical-climate models will be available.

In principle, 3-D models can be made more internally consistent and can include more interactive physical processes than the more parametrized models. Unfortunately, because of the limitations on 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 basic research than towards 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.

While the first - and so far the only - general test of the validity of any photochemical model is how well it reproduces the trace-gas distributions in today's atmosphere, such comparisons are not sufficient to establish the predictive reliability of current 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 calculation, appear to produce results consistent with those from ozone trend analysis. A conclusive comparison between model-predicted and measured trace-gas distributions and ozone variations is limited by several factors:

(a) Although, for several species, satellite data (SAMS, LIMS, SBUV, SAGE, SME) have become available, the overall data base is still not sufficient to permit a full characterization of the spatial and temporal variations in the stratospheric distributions of trace gases. 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 concentration with a certain error range only.

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

With the increasing concern over chemistry and climate coupling, the need for better data (both theoretical and observational) relevant to the lower stratosphere and upper troposphere has 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, and H_2O_2 is also necessary.

Current understanding indicates that photochemistry predominates over all other physical processes in determining the ozone distribution in the upper stratosphere ($>$ 30 km). Consequently, 1-D or 2-D models can be regarded as pure local photochemical models in this region, and there are no problems in accepting their predictions at these altitudes as globally representative. Nevertheless, current models still seem to be unable to reproduce the measured value of ozone in the upper stratosphere, with models underestimating measured ozone concentration at 50 km by 20-30 per cent.

Part of this deficiency could be traced to uncertainties in measured solar-flux intensity, chemical kinetics, reaction rate coefficients, model boundary conditions, transport coefficients, and source-gas distributions. The unqualified 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 can only be evaluated on a most subjective basis at present.

The two major aspects of model predictions - past or near-term trends and long-term ozone change - have different sensitivities to model input parameters. In the analysis of possible trends, a major uncertainty lies in the description of variables governing the temporal evolution of the system, such as transport parameters and solar flux variations. For long-term changes, an additional concern is the uncertainty of the future state of the atmosphere. Recent research in coupled perturbations has contributed a wide appreciation of the degree of complexity of this problem. Increased efforts must be devoted to assessing the most probable coupled scenarios based on evolution in world economic and cultural patterns. A reference set of scenarios would aid in the intercomparison of highly complex chemical and climate model assessments of trace gas influences.

The model results described previously suggest that it may be extremely difficult to detect changes in total ozone due to anthropogenic perturbations in the coming decades. The calculated variations with altitude indicate that changes in the ozone distribution may be more readily detectable, although natural fluctuations need to be better understood. The influences of such phenomena as solar-flux variations, solar-proton events, and volcanic eruptions may affect the detectability of ozone changes due to CFCs and other trace gases.

H. Biological effects

Although current atmospheric scenarios predict a range of both positive and negative ozone changes, biological studies have focused on the effects of an ozone decrease. If a depletion in total atmospheric ozone occurs, solar UV-B irradiance will increase. This will have an effect on man, animals and plants. 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.

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, and 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 more exact simulations of natural and enhanced UV-B radiation will provide better data for the evaluation of the UV-B effects on all biological systems.

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

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 in total ozone, with its attendant increase in solar UV-B radiation, could be significant for them.

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, maize and soya beans, barley, potatoes and beans. Although there are many uncertainties involved in the simulation of enhanced levels of solar UV-B radiation, 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 a simulated 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 more resistant. Although these data result from work primarily simulating high UV-B radiation levels in the presence of relatively low white light, it has also been demonstrated that, in the presence of relatively high levels of white light, enhanced UV-B radiation simulating ozone depletion of 10-12 per cent also has deleterious effects in sensitive plants. Furthermore, these experiments have indicated that plants are particularly sensitive during the early stages of seedling growth and development. However, the extent of damage at high levels of white light is less than at low levels. This relationship was also demonstrated for relatively UV-B insensitive soya bean seedlings.

For wheat, maize, rice and soya beans, information to date suggests that the direct effects of UV-B radiation supplementation (simulating current ozone scenarios) will not result in sizeable reductions in the yield of crop plants in the field. However, following simulation of a UV-B increase associated with a 16 per cent ozone reduction, three of six soya beans cultivars tested did show changes in seed quality (e.g. reduced protein quantity). These results are relevant not only in relation to crop plants, but to natural plant populations as well, because alterations in seed reserves may substantially affect seedling supervisorship. The ultimate consequences of most importance may involve more subtle changes in plant allocation patterns and interactions with other organisms. Changes in the competitive balance of irradiated plant communities have been clearly demonstrated in a wheat/weed community. Moreover, increased incidence of leaf rust in one cultivar of wheat has been shown. These subtle changes may have an indirect effect on crop yield. Furthermore, it has been shown that the effect on growth and photosynthesis of UV-B in combination with other commonly experienced stresses, such as water and mineral deficiency, is greater than the sum of the effects produced by the stresses independently.

The action spectra for some 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. Action spectra taken by monochromatic radiation do not accurately reflect the biological responses in natural light. Data on both plants and animals indicate that monochromatic action spectra lead in some cases to an overestimation and in other cases to an underestimation of the deleterious responses to polychromatic radiation.

Studies on the mechanism by which UV-B radiation acts on photosynthesis in chloroplasts showed that UV-B attacks the photosystem II reaction centres, which are essential for photosynthetic water oxidization. The reaction centres of photosystem I as well as of the photophosphorylation system are quite resistant to UV-B radiation.

Field studies have demonstrated that some higher plants can show acclimatization to supplemental UV-B radiation under field conditions with increased UV-B exposure. These plants synthesize more UV-screening compounds (e.g., flavonoids) and the epidermal transmittance decreases. In some fungi, UV-B radiation photoinduces carotenoids that may also act as screening pigments. However, prolonged UV-B irradiation decreases the capacity for carotenoid biosynthesis.

2. Effects on aquatic organisms

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, larvae, etc.), lives in the top 20 m of ocean waters. There are large uncertainties regarding the natural mortality of aquatic organisms and the role of current levels of UV-B exposure in the mortality rate. Various experiments using exposure levels of UV-B radiation simulating ozone decreases ranging from 5 to 25 per cent have shown damaging effects on fish (larvae and juveniles), shrimp larvae, crab larvae, 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 chlorophyll at UV-B irradiances equivalent to ozone reductions ranging from 5 to 15 per cent. 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. Furthermore, indirect effects of ambient and enhanced UV-B endanger the survival of micro-organisms (Euglena, slime mould, some blue-green algae) by decreasing their motility and by inhibiting phototactic and photophobic responses. This reduces the ability of a population to move into favorable environments to avoid damage which may impair development.

In simulated marine ecosystems enhanced UV-B - simulating a 15 per cent ozone decrease - results in shifts of the community composition and species diversity of phytoplankton and zooplankton communities. It appears as if, in natural marine plant communities, a change in species composition rather than a decrease in net production might be a more likely result of an enhanced UV-B exposure. The decreased species diversity observed in simulated field studies usually is not accompanied by deleterious effects on biomass and chlorophyll accumulation or by deleterious effects on community primary productivity. However, the change in community composition may result in a more unstable ecosystem and may have an influence on higher trophic levels.

Studies on over 60 species of 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 quantitative dose-response curves and action spectra for a variety of aquatic organisms are being determined.

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

Human health is influenced by UV radiation in many ways, for example, by the formation of vitamin D_3, by the occurrence of sunburn, by eye diseases, by immunological changes and photo-allergic reactions, and by skin diseases including cancer of the skin. Skin cancer stands out as one problem that will increase with increased UV-B irradiance. The severity of health and other biological effects of radiation depend on its spectral composition, irradiance and exposure time. UV-B radiation has in many instances, been demonstrated to be more biologically effective than UV-A radiation by several orders of magnitude.

Epidemiological studies have shown that the incidence of non-melanoma skin cancer correlates with exposure to sunlight. While non-melanoma skin cancers occur in people of all skin types, the incidence is highest in light-skinned people. In patients with xeroderma pigmentosum, who have increased susceptibility to skin cancer, here is evidence of reduced repair of DNA damage caused by UV-B. Animal experiments have revealed that UV-B is the most effective wavelength region for carcinogenesis by UV radiation. These data indicate that increased incidence of non-melanoma skin cancer can be expected to result from increased UV-B irradiance.

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, with unchanged exposure habits, for every 1 per cent decrease in total ozone the incidence of basal cell carcinomas will increase by 2 to 4 per cent and the incidence of squamous cell carcinomas by 3 to 8 per cent. Although the incidence of squamous cell carcinoma is only about 20 per cent of the total, it is more invasive and lethal than basal cell carcinoma. While these conditions can usually be treated effectively, they still result in thousands of deaths per year. In the United States, there are approximately 500,000 new cases of non-melanoma skin cancer per year, and the total annual number of deaths, about 5,000, is comparable to the annual total for malignant melanoma. Recent experiments do not confirm earlier studies suggesting that UV-A enhances the carcinogenic effect of UV-B.

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. In some types of melanoma, such as lentigo maligna and melanoma arising in patients with Xeroderma pigmentosum, the relationship with sunlight is relatively clear. In other cases the evidence is circumstantial. The epidemiological and clinical observations deal with exposure to total sunlight and do not, therefore, point to any particular wavelength range in the solar spectrum. Animal experiments indicating the effective wavelength range are not available. In cases where UV-B is involved, a decrease in atmospheric ozone might be expected to increase the incidence of melanomas. The increased incidence of malgnant melanoma in patients with Xeroderma pigmentosum suggest that, at least in these cases, UV-B radiation is involved.

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 reduction in the number 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. 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. The extent of the immunological perturbations caused by exposure of humans to sunlight is not yet known, and the implications of these perturbations for human health are not clear. A primary concern is the possibility that these immunological changes may contribute to the development of malignant melanoma, especially as the immunological changes are caused mainly by the shortest wavelengths in sunlight.

Increased UV-B irradiance might also increase the positive effects of UV-B radiation. 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 and would thus 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 negative effects.

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

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:

(i). Countries and institutions operating ozone measurements should contribute continuously 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;

(ii). Upgrading and intercomparisons of Dobson instruments should be intensified and testing of new instruments and techniques encouraged;

(iii). New observing techniques showing great potential, such as microwave and LIDAR systems, should be further developed and careful intercomparison between new sensors and conventional instruments should be undertaken;

(iv). There is a need for more accurate calculations and for additional laboratory measurements of molecular spectroscopic parameters in the wavelength range of importance for atmospheric sensors;

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

(vi). The determination of absolute ozone absorption coefficients should be completed, and recalculations of all previous vertical ozone distributions taken by Umkehr and satellite arranged to ensure homogeneity of records;

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

(viii). 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;

(ix). 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;

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

(xi). Studies should be made to gain an understanding of sources, sinks and budgets of natural and anthropogenic source gases, such as carbon dioxide, methane, nitrous oxide and other oxides of nitrogen, which may affect ozone, including historical and future trends;

(xii). The attention of all countries and economic organizations not yet reporting production figures for CFCs 11 and 12, as well as for other halocarbons, 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;

(xiii). A call should be made for continued support to and expansion of the four-station Global Atmosphere Gas

Experiment (GAGE), formerly the Atmospheric Lifetime Experiment, which has already provided a five-year record of CFCs, chlorocarbons and nitrous oxide;

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

(xv). Efforts to identify and obtain quantitative data on any additional reactions which may affect stratospheric chemistry should be intensified, with the emphasis placed on reactions involving temporary reservoir species;

(xvi). A continuing emphasis should be placed on the development and the intercomparison of different sensors for the measurement of trace species concentrations in the stratosphere;

(xvii). An increased emphasis should be placed on the simultaneous insitu measurements of the absolute concentrations of photochemically related compounds of the various families;

(xviii). Measurements of the radical species and temporary reservoir species should be made in the stratosphere and upper troposphere, using different techniques;

(xix). There should be increased effort to understand the mechanisms responsible for the exchange of chemical constituents across the tropopause;

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

(xxi). UNEP should urge WMO and its member States to play an active role in studying tropospheric and stratospheric ozone, for the better understanding of climatic changes;

(xxii). Studies of the radiative effect of ozone and other minor species relevant to ozone photochemistry should be promoted for the purpose of detecting climatic impact;

(xxiii). Ozone modification should be studied with realistic time-dependent multiple-perturbation scenarios;

(xxiv). A reference set of scenarios describing past and future source gas trends for use in chemical and climate models should be established, and the intercomparison of models based on such scenarios is strongly recommended;

(xxv). More emphasis should be placed on the coupling of chemistry with radiation and dynamics; it is thus recommended that the further development of multidimensional models with radiative feedback be undertaken;

(xxvi). Research on the appropriate representation of transport processes in 2-D models should be continued;

(xxvii). Models should be continuously validated by means of field data, an increasing emphasis being placed on the use of satellite data;

(xxviii). Simulation of events such as solar-proton events, volcanic eruptions and periodic solar-flux changes is recommended;

(xxix). The sensitivity of model predictions to uncertainties in the kinetic data, transport parameters, assumed source-gas scenarios and photochemical parameters, should be investigated;

(xxx). Efforts should be made to improve knowledge pertaining to:

a. The relationship between exposure to UV-B radiation and human physiological, morphological and immunological responses;

b. The relationship between malignant melanoma and UV radiation from both natural and artificial sources;

c. The effects of UV-B on human cells in culture and on organ cultures of human skin;

d. The action spectrum for the induction of non-melanoma skin cancer by UV radiation;

e. The dependence of the response on dose and dose rate for the various biological effects of UV radiation;

f. The possible interaction of wavelength regions, mainly UV-B and UV-A, and the possible role of photoprotection, photoaugmentation and photorecovery in carcinogenesis by UV radiation;

g. The possible interaction of chemicals, pharmaceuticals and pollutants with UV radiation;

(xxxi). Improved individual and biological dosimeters should be developed;

(xxxii). The biological effects of UV-B on agricultural crops for different geographical locations and under different local growing conditions should be studied.

(xxxiii). Because of the importance of the balance between UV-B and visible radiation in plant assessment studies, UV irradiation under field conditions should be carefully modulated so as to take account of changes in cloud cover and the time of day.

(xxxiv). Research should be focussed on effects correlating to changes in the ozone layer in the range of 0-10 per cent, although work should also continue on effects of the larger decreases, since existing data for the lower ozone depletion scenario are sparse and uncertain;

(xxxv). Studies on aquatic organisms should be extended to the natural water environment in order to gain a knowledge of the effect of solar UV-B radiation on aquatic food productivity;

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

(xxxvii). Photorepair, adaptation, protective mechanisms, and interaction between UV-B stress and other environmental changes should be studied as part of the overall consideration of UV-B effects;

(xxxviii) Studies should be continued and expanded to determine the influence of changes in the 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; and

e. The effects of other stress situations;

(xxxix). Studies on the mechanisms by which UV-B radiation acts on biological molecules, cells, species and ecosystems should continue;

(xl). UNEP should once again urge FAO and its member States to play an active role in studying the biological effects of UV-B radiation and climatic changes on food production;

(xli). UNEP should once again urge WHO and its member States to play an active role in studying the effects of UV-B radiation and climatic change on human health;

(xlii). UNEP should initiate and encourage the co-sponsorship by interested States and organizations of a major symposium at which member States would present detailed scientific reports covering all biological aspects of the ozone perturbation problem;

(xliii). Governments and organizations which are determined to protect man and the environment against adverse effects resulting from modification of the ozone layer and which are also aware of the need for future research, should critically examine the adequacy of their current levels of funding, especially in the area of effects research, in view of the importance of this issue.

(xliv). The resolution of the International Council of Scientific Unions concerning the proposed work on global change should be strongly supported.

SECTION III

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

AUSTRALIA

In Australia, atmospheric monitoring and research programmes are conducted jointly by the Bureau of Meteorology and the Division of Atmospheric Physics of the Commonwealth Scientific and Industrial Research Organisation (CSIRO).

A network of 5 Dobson ozone stations is operated by the Bureau of Meteorology. These are located between latitudes of 27°S and 54°S, at Brisbane, Perth, Melbourne, Hobart and Macquarie Island. All stations make total ozone and Umkehr observations with the Melbourne station also conducting mast ozone sonde measurements. During 1985 it is planned to re-open a tropical total-ozone and Umkehr station at Darwin (latitude 12°S) and another station at Alice Springs (latitude 23°S).

Also planned for mid-1985 is a project on stratospheric aerosols involving the automatic Dobson at Perth supported by a nearby LIDAR and possibly ozone sonde measurements.

At the Baseline Air Pollution Monitoring Station at Cape Grim in Tasmania, the Bureau of Meteorology and the CSIRO Division of Atmospheric Physics jointly conduct several research programmes relevant to the World Plan of Action on the Ozone Layer.

Surface ozone (O_3) measurements have been made at Cape Grim since 1976 in a programme designed to detect any long-term changes in O_3 concentrations in the lower atmosphere. An annual cycle has been identified with a winter minimum and a summer maximum. Long-term trends have yet to be detected. Analysis is underway to determine the meteorological influences on O_3 at Cape Grim. It is planned for late 1985 to install a sensitive chemiluminescent nitrogen oxides (NO_x) detector at Cape Grim to study the reactive gas chemistry of background air.

Studies are underway to determine the influence of biological sources of NO_x (denitrification and nitrification) on the NO_x budget of the remote continental atmosphere. To this end, measurements of NO_x fluxes, at atmospheric NO_x concentrations, have been made over various unfertilized/fertilized areas. Halocarbons (CCl_3F, CCl_2F_2, CH_3CCl_3, CCl_4) and nitrous oxide (N_2O) observational programmes have also been conducted at Cape Grim since 1976. Long-term trends have been detected and modelled using global release data to deduce atmospheric residence times. Conversely halocarbon growth rates at Cape Grim have been used either to calibrate the transport component of a 2-dimensional tracer transport model or, given the known transport fields and atmospheric residence times, to deduce global releases. Since 1978 this programme has formed an integral part of the Atmospheric Lifetime Experiment (ALE), involving scientists from CSIRO, the Oregon Graduate Center, the Massachusetts and Georgia Institutes of Technology and from the UK.

Methane (CH_4) and carbon monoxide (CO) have been studied at Cape Grim and over the south-eastern part of Australia since 1978. A long-term increase has been measured for CH_4 (ca. 1% per year) and significant seasonal cycles in CH_4 and CO quantified. Modelling experiments suggest that the trend in CH_4 is due to expanding industrial and agricultural activities, and the seasonal cycles appear to be responding to calculated seasonal changes in hydroxyl (OH) radical levels.

Carbon dioxide (CO_2) observations commenced at Cape Grim in 1976 and complement a CSIRO programme of CO_2 measurement over South

East Australia that commenced in 1972. Trends, seasonal cycles and vertical gradients have been measured. The data have been used in conjunction with global data from the Scripps Institute of Oceanography and the National Oceanographic and Atmospheric Administration (USA), in a 2-dimensional model, to refine the magnitudes of the known sources and sinks of CO_2, especially the biosphere, that are part of the global carbon cycle.

The CSIRO Division of Atmospheric Physics also conducts research into other areas that are relevant to the World Plan of Action on the Ozone Layer:

(i) Theoretical studies of the dynamics of the stratosphere;

(ii) Measurements of stratospheric constituents over Australia. Measurements of NO, NO_2, HNO_3, O_2, N_2O, CCl_3F, H_2O, CH_4 and aerosols have been made at 23°S and 34°S during the Australian autumn and spring, corresponding with the times of O_3 minimum and maximum in the stratosphere. Such measurements provide important tests of the chemical and dynamical theories of the stratosphere;

(iii) Tropospheric O_3 removal processes. The loss of O_3 from the atmospheric over a variety of natural surfaces has been investigated and O_3 destruction rates deduced;

(iv) Modelling of atmospheric halocarbon distribution.

In conjunction with US scientists, erythemally effective ultraviolet radiation (UV-B) has been measured at Aspendale (Victoria) and Brisbane (Queensland) since 1975. To-date, the data show no significant change in UV-B, the radiation responsible for skin damage, consistent with the observation that no significant change has been observed in total ozone.

CANADA

Participation in the NASA sponsored BIC (Balloon Intercomparison Campaign) was continued in 1984. Participation in the NASA BOIC (Balloon Ozone-sonde Intercomparison Campaign) was continued with BOIC III flights in March, 1984 and data analysis, with results from both campaigns reported at the 1984 Quadrennial Ozone Symposium (Halkidiki, Greece, 3-6 September 1984). Umkehr profiles derived from Brewer ozone spectrophotometer measurements were comparable with the ozone-sonde profiles at BOIC in Texas.

A SMERF (SME rocket flights) rocket was flown in May, 1984 from Churchill for correlative measurements with the SME (Solar Mesospheric Explorer) satellite. Excellent measurements of the molecular oxygen singledelta profile, which gives high altitude ozone from 50 to 100 km, were obtained in conjunction with a close overpass of the SME satellite.

The tunable diode laser project at York University has been dormant for the last year. A successful engineering flight to measure nitrogen dioxide was conducted in August 1983 at Gimli, Manitoba. A scientific flight to measure nitrogen dioxide is tentatively planned for 1985, if technical difficulties can be resolved.

Studies of the volcanic cloud from El Chichón were continued, with ground-based measurements of ozone, sulphur dioxide and aerosol from Mauna Loa observatory using a Brewer ozone spectrophotometer and an AES 4-channel SONOTEK sunphotometer.

Operation of the World Ozone Data Centre was continued with the publication of Ozone Data for the World and the provision upon request of ozone data on magnetic tapes. Operation of the Canadian ozone monitoring network was continued with daily measurements using Dobsons of total ozone at Edmonton, Churchill, Resolute Bay, Goose Bay and Toronto, and weekly ozone-sonde measurements at the first four of these stations.

Brewer measurements of ozone and sulphur dioxide continued to take place at Toronto, and a Brewer was installed at Edmonton, to replace the Dobson, in February, 1984. The prime Brewer ozone calibration standard, consisting of 3 Brewer spectrophotometers each independently calibrated at Hawaii, has been established. This should provide a good standard for total-ozone measurements since it includes Dobson 77, also calibrated independently at Hawaii, as a fourth instrument. This standard, which is independent of any single physical instrument, should be maintained on a permanent basis in contrast to the United States (and WMO) standard world Dobson which is based on a single physical instrument:Dobson 83. The travelling Brewer standard, instrument 17, visited Australia, New Zealand, Federal Republic of Germany, Greece and Belgium in 1984 to check the calibration of instruments at several world ozone monitoring network stations. SCI TEC Ltd. of Saskatoon assisted in this activity, as well as manufacturing the Brewer spectrophotometers.

In the ozone trends area, a considerable depletion of the ozone layer was detected at all stations of the Canadian network. The depletion exceeded 10 per cent in some months and lasted from December, 1982 to the summer of 1983, inclusive. It was also present at Mauna Loa and many other world ozone stations. The Canadian ozone-sonde profiles indicated that the depletion occurred in the 40 to 70 mb region (24 to 18 km). Unpublished studies suggest that the lower ozone values may be due to the combined effects of the El Chichón volcanic injection (especially chlorine) and the El Niño atmospheric warming event in 1982-83. It is believed that understanding of this major natural ozone depletion is essential to the realistic prediction of anthropogenic depletions of the ozone layer.

A new super sunphotometer has been developed and was flown with the Canadian astronaut on the Space Shuttle in early October. It was used to make solar-radiation measurements which will be interpreted in terms of high-altitude ozone, aerosol, water vapour and nitrogen dioxide profiles in the stratosphere, in a fashion similar to the SAGE (Stratospheric Aerosol Gas Experiment) on the ERBS satellite launched on the same shuttle flight.

DENMARK

Risoe National Laboratory has, under a contract from the Nordic Council of Ministers, completed and reported studies of the kinetics of hydroxyl radicals with ethane and a series of chlorine -and fluorine-substituted methanes.

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

FEDERAL REPUBLIC OF GERMANY

Ongoing and planned activities

The research activities have continued with special emphasis on field measurements of trace constituents of the atmosphere, intercomparison of measurement methods and devices and increasing the accuracy of the results.

The Federal Republic of Germany took part in the international MAP/GLOBUS campaign of 1983, which comprised ground-based, airplane, ozone-sonde, balloon-borne, rocket and satellite measurements focusing on ozone and related components. In the period from 1 September to 12 October 1983, about 200 experiments and soundings were carried out. Part of the results to be reported at this meeting are based on that campaign. The general data evaluation, however, is still under way.

In June 1984, the Federal Minister for Research and Technology organized, in conjunction with NASA, WMO and FAA, a workshop "Current issues in our understanding of the stratosphere and the future of the ozone layer" at Fieldafing near Munich. The aim was to evaluate the current state of knowledge in stratospheric chemistry and dynamics, to present new research results and to discuss deficiencies and research needs. The results obtained will be useful for the topic of this Bulletin.

Ozone observations

The general pattern of changes in the ozone profile during the long-term balloon borne ozone soundings of the Hohenpeissenberg Meteorological Observatory can be seen from figure 5. It is evident that there is an increase in tropospheric and a decrease in stratospheric ozone. The increase in tropospheric ozone is in good agreement with other long-term monitoring results in central Europe, for example, from Belgium or from the German Democratic Republic.

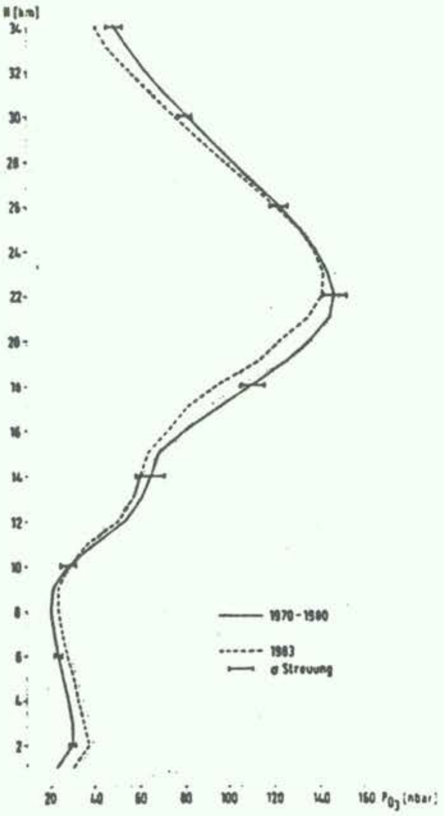


Figure 5 Mean ozone profiles
MOHp for 1983 and for 1970-1980

Although the ozone profiles are of only limited spatial representativity, the measurement results tend to support, at least qualitatively, those of the model calculations.

Temperature in the middle stratosphere

Model calculations predict a temperature decrease in the stratosphere as a consequence of CO_2 increase. The evaluation of satellite measurements by the Free University of Berlin indicates such a trend for the 30 - 90 N Latitude region during the 1970s. This trend can be interpreted as a tentative first result supporting model predictions. Since the early 1980s, a warming has been spreading from the equatorial region towards the north and can be attributed to volcanic eruptions.

Vertical profiles of source gases

The MPI for Aeronomy has recorded vertical profiles of a variety of halogenated hydrocarbons by balloon-borne grab sampling and subsequent laboratory analysis. As can be seen from figure 6, the fall-off behaviour of the concentration with increasing altitude is largely determined by the chlorine content of the different molecules.

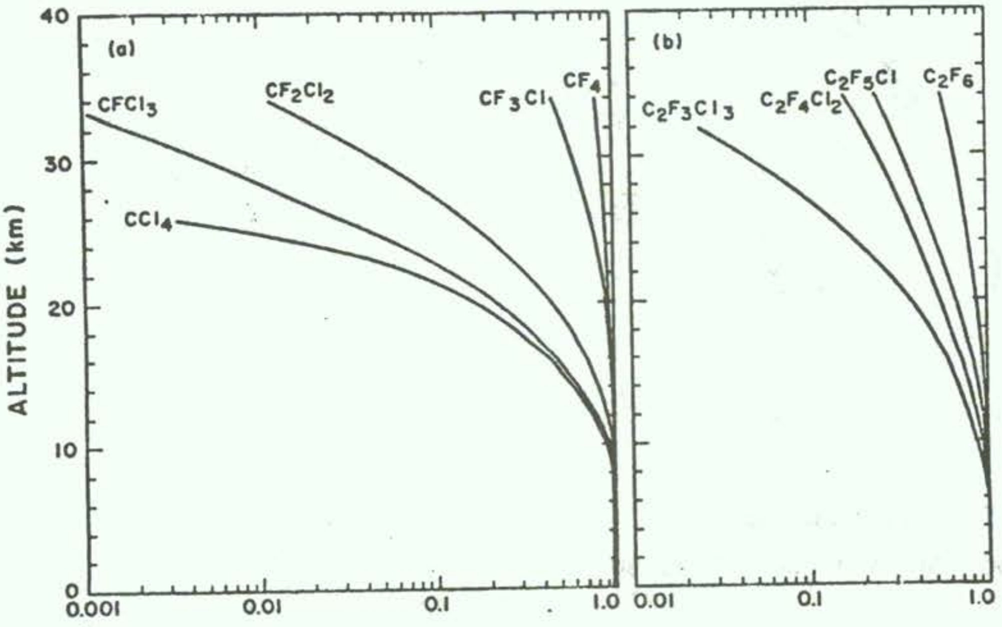


Figure 6 Averaged measured profiles of fully halogenated methanes (a) and ethanes (b) in relative units with respect to the tropospheric abundance

This is due to the fact that the absorption cross-section increases with the number of chlorine atoms attached to a particular carbon atom and consequently, there is a decrease in the altitude at which photolysis occurs. The contribution of different halocarbons to the total amount of odd chlorine thus formed varies with the altitude. The result of a model calculation on these contributions is given in figure 7.

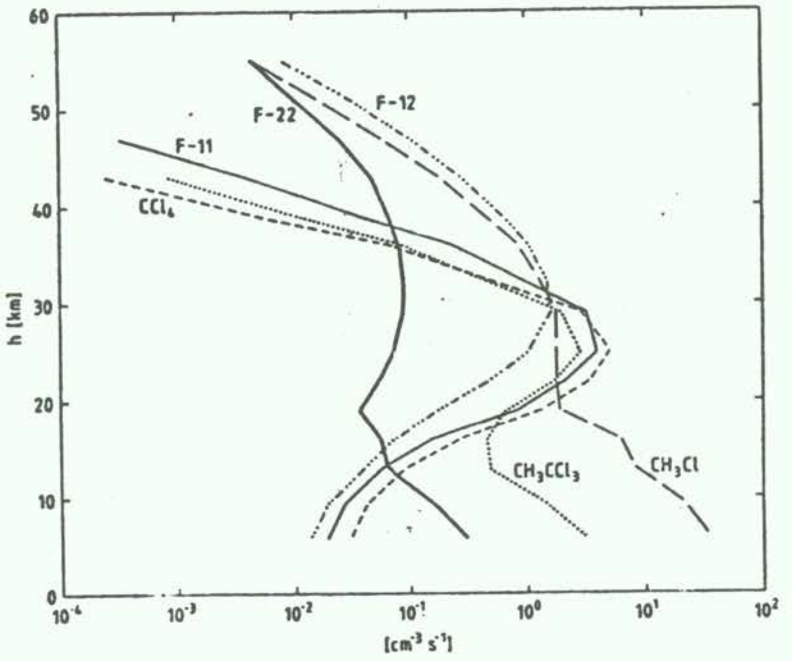


Figure 7 Formation rates of odd-chlorine species (Cl+ClO) from various common halocarbons as a function of altitude calculated by means of a 1-D model using steady-state conditions

It should be pointed out that CFC 22 obviously plays a very important role in altitudes above 40 km, especially with respect to the accelerated increase of global CFC 22 release in recent years.

KFA Jülich continued to investigate the vertical distribution of various source gases including halocarbons. Similar to the results obtained by the MPI for Aeronomy, the observed vertical profiles show a faster fall off with altitude than the calculated ones, as can be seen from figure 8 for $CH_3\,CCl_3$ as an example. These discrepancies may be caused by underestimates of the photochemical destruction rates and/or an inaccuracy in the vertical transport parametrization.

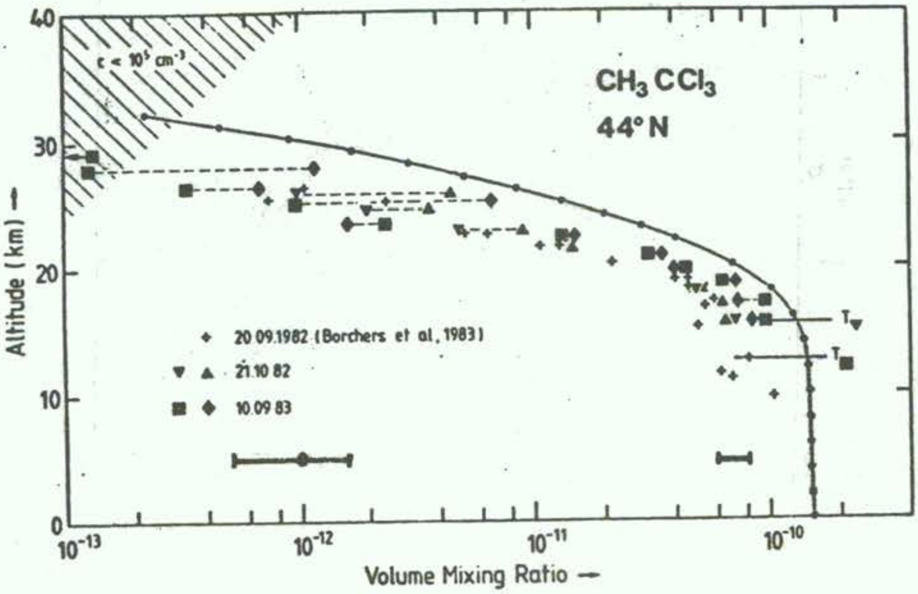


Figure 8

Vertical distribution of CH_3CCl_3 in the stratosphere

The sampling of these measurements is carried out by cryogenic collection so that, together with the compounds under consideration, large quantities of ozone are sampled.

With respect to the accuracy of the result, it is important to know which alterations of the samples can occur during storage pending analysis. A laboratory test under stratospheric conditions showed that the analysis results of CH_4, N_2O, CO_2, $CFCl_3$ and CF_2Cl_2 were not influenced by ozone. In contrast, C_2H_6, C_2H_2, C_3H_8 and $CHCl_3$ were significantly affected in the ppt concentration range. In order to obtain results that are correct within a factor of 2, it is necessary to carry out the analysis within a period of 4 weeks.

The relative variances in stratospheric observations of the long-lived trace gases CH_4, N_2O, CF_2Cl_2, $CFCl_3$ show large differences. These differences are greatly reduced when the local mean standard deviation is normalized to the local vertical gradient. This ratio, called "equivalent displacement height" exhibits a characteristic vertical profile which is very similar for all the long-lived trace gases, as well as for O_3. With the help of this ratio, it is demonstrated that the variances are essentially due to natural causes, i.e., transport. If careful measurements are made, the contribution of experimental uncertainties, is of minor importance.

A new and very promising technique for measuring free radicals has also been developed at the KFA Jülich. The measurements are based on sampling by matrix isolation using a balloon-borne cryosampler, the analysis being subsequently carried out by ESR. Values of stratospheric concentrations of NO_2, HO_2 and NO_3 have been obtained.

Budgets of atmospheric trace gases

Trace gases relevant for stratospheric ozone loss and tropospheric build-up of ozone were monitored in the troposphere. Mixing ratios of CH_4, N_2O, CO and various CFCs were measured as a function of season and latitude. In the case of CH_4, N_2O and NO_x, production and depositing on the ground were studied for different seasons and soil properties. It was found that methane is deposited with a maximum rate in summer, whereas N_2O is produced with a maximum rate in spring. No secular trend in CO could be seen. Odd nitrogen is emitted from the soil and deposited on plants. The deposition rate for NO_2 was found to be between 0.5 and 1.0 cm s^{-1}.

Rate constants and absorption cross-sections

The absorption cross-section for NO_2 has been measured in the wavelength range 200-550 nm. Our values are higher than those measured by Bass et al. in the range 200-280 nm and slightly lower at longer wavelengths. The resulting photo-dissociation coefficients are about 4 per cent lower than the ones calculated from the cross sections tabulated in JPL83. It should, however, be mentioned that correctly wavelength-averaged values from Bass et al. also lead to 2 per cent lower J-values than the single wavelength values given in JPL83. This finding could increase the effectiveness of NO_2 as an ozone sink in photochemical models.

Several kinetic parameters relevant for odd-nitrogen chemistry have been remeasured. Good agreement with previous results has been found for:

$k \ (NO_2+NO_3)$

$k_{eq.} (NO_2 . NO_3/N_2O_5)$

$\sigma \ NO_3$

NO_3 does not react with SO_2, CO or CH_4 but there is some evidence for reaction with Cl.

Construction of a high resolution Michelson interferometer

The University of Munich has in the past, gained experience with balloon-borne infra-red measurements of atmospheric trace constituents. For example, vertical profiles of H_2O and HNO_3 were measured by solar occultation measurements, while profiles of H_2O and CH_4 were deduced from nadir to limb radiance profiles.

A feasibility study has been carried out for the design and operation of a small He-cooled, high-resolution Michelson interferometer (MIPAS).

The measurement requirements, whereby more than 20 trace components are to be observed simultaneously, were deduced from calculated emission spectra.

The spectral range for the emission measurements is 4, 5, to 15 Um, the resolution 0, 1 cm^{-1}, scanning time 1 s, height resolution approximately 3 km.

MIPAS is now under construction; the first measurements will be balloon borne. Later ones will possibly be included in a Space Shuttle mission.

Ozone scenarios

A fully interactive radiative-convective model, including the radiative 0.81 effect of CO_2, H_2O, O_3, CH_4, N_2O, NO_2, $CFCl_3$, CF_2Cl_2 and steady-state chemistry, has been used to calculate changes in ozone and temperature due to an increase of CFCs, N_2O, CH_4, NO_x and CO_2. Our most probable scenario for a time span of 100 years assumes increases of N_2O x 1.25, CH_4 x 3, CO_2 x 2 and tropospheric NO_x x 2 and constant 1977 CFC emission rates. Some high - chlorine scenarios with increased CFC emission rates have also been calculated. We find a change of -0.6 per cent in total ozone for the case with constant CFC emission and of -5.8 per cent for doubled CFC emission. Including the feedback between tropical tropopause temperature and stratospheric water vapour adds another 1.3 per cent decrease. The numbers for various coupled scenarios are given below.

Table 3 The perturbation scenarios, a "*" means the unperturbed value of base case

Case	ClX at 50km altitude (ppb)	N_2O at Surface (ppm)	CH_4 at Surface (ppm)	CO_2 (ppm)	H_2O at 16km altitude (ppm)	NO_x injection at surface (mol/cm s)	Change in 03 column above surface (%)	Surface temperature change (K)
Base	2.3	0.30	1.7	330.	3.5	5.65E 9	0.0	0.00
1	8.6	*	*	*	*	*	-5.0	0.46
2	8.8	*	5.1	*	*	*	-4.7	0.99
3	8.8	*	5.1	660.	*	*	-3.9	2.97
4	8.8	0.375	5.1	660.	*	1.13E10	-0.6	3.15
5	15.3	0.375	5.1	660.	*	1.13E10	-5.8	3.60
6	*	*	5.1	*	*	*	+0.6	0.50
7	15.3	0.375	5.1	660.	6.3	1.13E10	-7.1	3.80
8	14.8	*	*	*	*	*	-12.7	0.81

Validation of photochemical models

The budget of stratospheric odd oxygen has been used to validate the model description of stratospheric chemistry with data from satellite and balloon measurements. This evaluation points to a discrepancy with extra odd-oxygen production below and extra odd-oxygen loss above 30 km. The distribution of odd nitrogen, which supplies the main odd-oxygen sink between 25 and 40 km, can be derived from measured N_2O distributions independently of any parameterization of transport. This approach gives us odd-nitrogen concentrations in reasonable agreement with the field data below 30 km, but much higher values above. These results point to major deficiencies in our understanding of stratospheric odd-nitrogen and odd-oxygen chemistry, if we accept the uncertainties proposed for current photochemical parameters and trace-gas measurements.

Effects

Some results of research on biological effects of increased UV radiation in the Federal Republic of Germany:

1. Aquatic organisms and micro-organisms

Variable UV tolerance has been shown for different aquatic organisms, depending on their environment. Those organisms exposed to less UV in their environment (planktonic daphnia, the stone coral Favia pallida) have less tolerance than organisms environmentally exposed to higher UV levels (daphnia in mountain pools, the coral Platygyra sinensis). With the exception of two copepods, all cladoceres which have been investigated have shown the phenomenon of photoreactivation. This could explain why UV-B tolerance is considerably greater with the addition of light of 400-430 nm than with the irradiation using UV-B alone.

In marine diatoms, UV-B doses equivalent to ambient solar UV-B levels during summer reduce biomass production, protein and pigment content, whereas free amino-acid pools increase. The pattern of amino-acids varied under UV-B conditions. Biosynthesis of photosynthetic products and amino-acids monitored as ^{14}C and ^{15}N incorporation was significantly affected by UV-B stress. Impact of UV-B radiation on marine diatoms was found to be species-dependent (12 species were tested).

Indirect effects of UV may drastically endanger the survival of populations of micro-organisms. Studies done with Euglena, the slime mould Dictyostelium, and the blue-green algae Phormidium indicate that UV-B decreases both the number of motile organisms in a population and the average speed of individuals, thus reducing the ability of a population to move into favourable environments, impairs development and inhibits phototaxic and photophobic responses.

The kinetics of liquid-holding recovery in yeast after UV exposure were shown to be wavelength-dependent. Recovery was absent with 303 and 313 nm radiation. Studies on budding and division delay showed that 254 nm radiation induces division delays which are considerably greater than those for budding. This difference was not found with 313 nm budding, suggesting a general distortion in the sequence of cellular events.

Irradiation of the mycelia of the fungi Fusarium aquaeductum and Neurospora crassa with UV-B as well as with UV-A/blue light caused photoinduction of carotenogenesis. However prolonged UV-B irradiation reduces biosynthetic capacity of carotenoid synthesis, monitored as ^{35}S-methionine uptake. These reductions were restored during subsequent darkness.

Studies on the archaebacterium Halobacterium Halobium have shown that the photophosphorylation functions with 280 nm radiation as well as under white light, although at a greatly reduced quantum efficiency.

2. Higher Plants

Growth in both cucumber and radish seedlings was shown to be successively reduced by a gradual increase in UV-B. In the cucumber seedlings, the reduced growth was due to lower absolute growth rates at higher UV-B levels. Cell division in cotyledons decreased in relation to UV-B intensity. Even moderate enhancements of UV-B radiation, such as would follow a 12 per cent depletion of ozone in the stratosphere, caused significant reductions in the growth of UV-B-sensitive cucumber seedlings.

Furthermore, it has been shown that UV-B in combination with other stresses, for example water stress, produces an effect greater than the sum of the effects produced by the stresses independently.

Cucumber and radish seedlings grown under water stress and enhanced UV-B (approximating to a 12 per cent reduction in ozone) showed increased deleterious effects on growth parameters compared with plants under water or UV stress alone. Cucumber seedlings were more sensitive to UV-B than radish seedlings, perhaps due to the lower levels of screening pigments.

UV-B-dependent formation of UV-B-screening pigments (flavonoids and anthocyanins) has been shown to occur in the leaf epidermis of various plants.

Furthermore, enhanced UV-B radiation caused an increase of about 25 per cent in total cuticular wax on barley, bean, and cucumber leaves. Aldehydes, a minor wax class of cucumber and barley, increased twofold with enhanced UV-B. Within each wax class, UV-B shifted the composition towards a greater proportion with shorter acyl chain lengths, especially in cucumber wax. It was concluded that increased amounts of epicuticular waxes might function in attenuating enhanced UV-B radiation via reflectance and scattering.

The importance of photorepair of UV-B damage has been demonstrated in bean leaves and mustard cotyledons. These photorepair phenomena have been further characterized and their importance for adaptation to an increased UV-B environment pointed out.

In hyoscyamus plants, photoperiodic flower induction was inhibited by additional UV-B influence rates not causing visible damage to the plants. Translation activity of mRNA isolated from leaves was lower after UV-B irradiation.

3. Photosynthesis

Photosynthetic activity in radish seedlings was shown to be reduced by UV-B, whereas UV-A had no effect. Concentrations of photosynthetic pigments were unaffected, suggesting that UV-B influenced the primary photochemistry of the chloroplasts.

The effects of UV-B irradiation on the primary processes of photosynthesis have been analyzed in isolated spinach chloroplasts by fluorometric, flash polarographic, and spectroscopic methods. It was found that UV-B attacks predominantly the reaction centers of photosystem II, which are essential for photosynthetic water oxidization. The reaction centers of photosystem I, as well as the ATP synthesize complex, are practically insensitive to UV-B radiation.

4. Animal cells

Action spectra of inactivation and mutation induction from UV radiation in Chinese hamster fibroblasts were compared with data obtained using polychromatic radiation. The action spectrum for a given effect had to be multiplied by the emission spectrum of the radiation source in question. Dimer formation could be well predicted, but the lethal and mutagenic effects had been considerably underestimated. It may be that the different components of polychromatic radiation act independently with respect to dimer formation, but synergistically with respect to cellular effects.

ITALY

1. Atmospheric measurement

(i) Ground-based measurements

Italy continues to operate a network of four Dobson spectrophotometers at Vigna di Valle (Roma), Sestola (Modena), Cagliari-Elmas and Brindisi.

Weekly ozonesonde flights started in 1985 at Cagliari-Elmas station to measure the ozone profile with the new Vaisala RS80 ozonesondes.

The group at the Rome Physics Department, in collaboration with the Institute of Atmospheric Physics, has been operating a high sensitivity laser radar system (LIDAR) and has obtained high resolution stratospheric aerosol profiles for the period 1982-1984, which covers the various phases following the eruption of the El Chichón volcano (28 March - 4 April 1982). Two-wavelength observations were also carried out in order to obtain information on aerosol sizes. The set of data is currently being used to establish correlations with fluctations in O_3 levels. LIDAR measurements at present of temperatures are being implemented in the upper stratosphere and mesosphere.

(ii) Stratospheric measurements from a balloon borne platform

A high-resolution Fourier Transform spectrometer was used to measure the stratospheric emission in the far infrared region.

The measurements were carried out in connection with the Balloon Intercomparison Campaign (BIC). The vertical concentration profiles of HF, CHl, H_2O and O_3 derived from these measurement are being critically compared with the results obtained by the other groups participating in this international venture.

Results obtained from previous balloon flights have recently been published.

2. Laboratory measurements

The pure rotational spectrum of several molecules of atmospheric interest were measured in the infra-red region (10-100 cm^{-1}) with a resolution of 0.003 cm^{-1}. Results have been published on O_3, SO_2, NO_2, HNCO, and CH_3OH. The spectra of H_2O_2 and H_2S are now being analysed.

The construction of a second interferometer that will make it possible to obtain spectra in the 10-200 cm^{-1} region with a resolution of about 0.001 cm^{-1} is in progress.

3. Epidemiological studies

An epidemiological study was conducted in the city of Rome and the rate of incidence of malignant melanoma determined retrospectively for the years 1970-1979.

The municipal health structures of the city were involved; the cases were all those of patients who were legally resident in Rome and received a histological diagnosis of melanoma during the period in question; the cases referred only to malignant melanoma of the skin (ICD 172, eighth revision).

The analyses of incidence were based on 500 cases, 237 males and 263 females, collected during the period 1970-1979. The data indicate a positive temporal trend in incidence; the average annual increase being 0.27 cases/year per 100,000.

The data show that, in a Mediterranean country like Italy, the incidence of melanoma presents the same ascending trend as in the case of the other Caucasian countries, whether European or not, the slope of the curves being similar in the two sexes.

The distribution of the primary site of insurgence in the two sexes is closely parallel to that described for all the Caucasian populations, the lower limbs being more affected in females and the trunk in males.

NETHERLANDS

1. In the human health section, the main issue is still the fact that UV-B can induce skin cancer.

An investigation into the relationship between the dose and the effect of UV-carcinogenesis in hairless mice was completed. This provided a more solid basis for calculating how much the incidence of non-melanoma skin cancer would increase in the event of ozone layer depletion. The results to all interests and purposes confirmed the earlier calculations. The results of this study were used to formulate a new programme, on the wavelength-dependence of UV-carcinogenesis. A preliminary result of this study shows that UV-A, UV-B and UV-C are all carcinogenic, but UV-B is more so than UV-A and UV-C.. An experiment with UV-A and UV-B administered at the same time did not show any enhancement by UV-A of the carcinogenic effect of UV-B.

A review is presented on recent scientific investigations on UV-carcinogenesis in many countries, including the Netherlands.

2. A multi-year investigation has been completed on the suitability of dimethylether as a propellant in spray cans (as an alternative to chlorofluorocarbons).

No toxic properties or influences on the environment have been detected that might result in objections to the use of dimethylether.

NORWAY

Studies related to atmospheric ozone are being continued in the Institutes of Physics and Geophysics of the University of Oslo. Studies have also begun at the University of Tromso, through a joint ozone measurement programme with the University of Oslo, and at the Norwegian Institute of Air Research (NILU).

Ozone observations with Dobson instruments, which had previously been made only in Oslo, are now being supplemented by observations at Tromso (70° N latitude) and Svalbard (79° N). The instruments at Tromso and Svalbard became operational in the summer of 1983. These measurements are organized by the Institute of Physics of the University of Oslo. It is also proposed that an optical ozone instrument (DISIBI) be brought to Svalbard this winter for surface-ozone measurements.

The Norwegian Institute of Air Research (NILU) has, over the last two to three years, been engaged in measuring long-lived trace species like chlorinated hydrocarbons (CFC-11, CFC-12, CH_3CCl_3, CCl_4) and other hydrocarbons in the Arctic region. Model studies of the transport of such species are carried out in collaboration with the Institute of Geophysics of the University of Oslo.

Two-dimensional model studies of atmospheric ozone chemistry and ozone-perturbation studies are continuing at the Institute of Geophysics of the University of Oslo.

A diabatic model with rather complete ozone chemistry for the stratosphere has been completed and is used for ozone perturbation studies. The model gives strong latitudinal gradients in ozone depletion due to CFC and N_2O increases with the strongest depletion at high latitudes, particularly in spring. Increased releases of methane, on the other hand, which increase total ozone, have the strongest effect at low latitudes. A combined scenario with increased fluxes of CFC, N_2, and CH_4 amplifies, therefore, the latitudinal variation in ozone depletion found in studies with single scenarios.

Two-dimensional studies of tropospheric ozone changes due to the release of pollutants, give ozone increases of the order of 0.5-1.0 per cent per year at mid and high latitudes in the troposphere of the Northern Hemisphere. If such an increase continues into the next century, it will be of importance for the total ozone at these latitudes.

SWEDEN

1. Research

The Swedish Meteorological and Hydrological Institute in Norrköping is using a Brewer spectrophotometer to measure UV-B and is continuing to operate a long-term programme to measure variations in the intensity of UV-radiation.

At the Institute of Physiological Botanics of the University of Lund, studies are being conducted on the influences of UV-B on biological and chemical processes in plants.

2. Publications

Since 1978, the Nordic "ozone-contact group", in its programme of monitoring international research related to ozone, has published reports aimed at disseminating scientific knowledge to be used for the guidance of Nordic measures, both national and international, for the protection of the ozone layer. The latest report from this group was published in June 1984 (Rapport til Embetsmannskomiteren fra Kontaktgruppen for Forskning om beskyttelse av ozonelagret; EK-M 13/84).

SWITZERLAND

Influence of El Chichón on the ozone layer

In 1983, the lowest annual mean values of total ozone were observed at Arosa, Switzerland (Laboratory of Atmospheric Physics, ETH, LAPETH, Zürich) where almost 60 years of such measurements are now available (this is in agreement with observations in many other parts of the Northern Hemisphere). The simultaneous soundings at Payerne (Swiss Meteorological Institute and LAPETH) showed that the main deficit occurred just at and below the level of the ozone maximum, at an altitude where the Quasi-Biennial Oscillation is best shown by the ozone data, and this means that the ozone transport from the tropical source region goes predominantly into that layer. Comparisons with the LIDAR data from Garmisch-Partenkirchen showed that the dust veil produced by the El Chichón eruption reached its peak intensity over Central Europe at the time of the maximum ozone deficiency (winter 1982/83) and was at practically the same height. There is little doubt that the all-time ozone minimum of 1983 is connected with that volcanic eruption, and a number of possible links have been suggested.

Ozone transport

Further research carried out at LAPETH on the January 1979 extreme ozone maxima in the middle stratosphere over Payerne, Switzerland, using LIMS ozone data from the Nimbus 7 satellite, showed that the maximum can be explained by the trajectory method when isentropic analysis using the LIMS geopotential height field, was used. This confirms the internal consistency of the LIMS products. The corresponding results were less satisfactory at lower levels, where observational errors became larger.

Intercomparison between the Umkehr and microwave techniques

The agreement between the Umkehr measurements at Arosa (LAPETH) and the microwave measurements of the vertical ozone distribution carried out at Berne (Institute for Applied Physics) in the winter of 1981/82, was quite satisfactory, once a new text of laboratory measurements concerning the microwave ozone line had been applied in the data reduction. A second comparison, which is planned to last a full year, started in 1984.

Microwave measurements

In connection with the WINE-Programme, the Institute for Applied Physics of the University of Berne, in collaboration with the Max-Planck Institute for Aeronomy at Lindau, Federal Republic of Germany, performed an aeroplane experiment for measuring ozone and water vapour in the middle stratosphere during the polar night north of the Arctic Circle.

The same group at Bern is organizing, in collaboration with the Max-Planck Institute at Lindau, Federal Republic of Germany, and the Naval Research Laboratories at Washington, D.C., a microwave limb-sounding experiment for measuring P, T, O_3, H_2 and ClO at altitudes between 15 and 90 km to be flown on the spacelab in the NASA Earth Observation Mission (EOS).

Troposphere ozone

The further elaboration of the field experiment data obtained in 1982 by LAPETH and the group for Energy and Environment of the Swiss Institute for Reactor Research, showed that, below the crest level of the hills surrounding the Reuss valley to the south-west of Zurich, the surprisingly high night-time ozone destruction was due to an extent of about 80 per cent to dry deposition on the ground because circulation patterns characteristic of the hilly terrain strongly increase this loss as compared with those associated with flat terrain. It was also found that the ground influence on ozone, temperature and humidity reached at least twice the crest level. A second field programme was run in summer 1984 in order to obtain improved information on these night interactions, and also on the extent of the horizontal spread of ozone smog. The data is now being processed.

UNITED STATES OF AMERICA

The United States of America has a comprehensive programme of research, monitoring and technology development for the study of atmospheric ozone. The goals of the programme are:

1. To improve our scientific understanding of the physical and chemical processes which control the concentration of atmospheric ozone;

2. To assess quantitatively possible perturbations to the ozone layer caused by natural phenomena and by man's activities; and

3. To assess the consequences of a change in either the total column content or the vertical distribution of ozone on weather and climate, human health, and terrestrial and aquatic ecosystems.

Panels of expert scientists in each of the scientific disciplines related to stratospheric ozone modification and potential biological and climatic effects have conducted an assessment of the state of knowledge on this complex subject. The report, Causes and Effects of Changes in Stratospheric Ozone: Update 1983, published March 1984, is available from the United States National Academy Press, Washington, D.C.

ATMOSPHERIC SCIENCE RESEARCH AND MONITORING

I. Current programme

The atmospheric research programme is a comprehensive balanced programme of field measurements (insitu and remote-sensing techniques using ground-based platforms, aircraft, and balloon and rocket platforms), laboratory studies (kinetics, photochemistry, spectroscopy and the development of calibration standards), theory 1-D, 2-D and 3-D models), data analysis (including large satellite data sets), Space Shuttle experiments, satellite systems, technology development and advanced satellite definition studies addressing the key areas of atmospheric research.

The programme has the following specific objectives:

1. To understand and quantify the flux strengths and mechanisms for the transport of source gases in the HO_x (H_2O), NO_x (N_2O) ClO_x ($CFCl_3$), CF_2Cl_2, CCl_4, CH_3Cl, CH_3CCl_3, etc), carbon (CH_4, CO_2, CO, NMHC) and sulphur (SO_2, CS_2, COS, DMS, etc) families from the troposphere to the stratosphere;

2. To understand the formation and destruction processes of tropospheric ozone;

3. To understand the chemical transformation processes within the ozone layer, i.e. the coupling between the different chemical families and the partitioning between radical, reservoir and sink species within each family;

4. To understand upper atmospheric dynamics and transport;

5. To obtain global climatologies and trends of ozone (column content and vertical distribution) and key hydrogen, nitrogen and chlorine species in the upper atmosphere;

6. To acquire a quantitative understanding of the seasonal and long-term changes in quantities such as incoming solar flux (wavelength resolved) and atmospheric temperature;

7. To determine the interaction mechanisms among the radiation, chemistry and dynamics of the upper atmosphere;

8. To develop improved photochemical models; and

9. To develop a fully interactive general circulation model (GCM).

II. Recent accomplishments

Total-ozone monitoring. Ground-based and satellite measurements indicate a 5-7 per cent decrease in total ozone (Angell-Korshover technique) in North America, Europe and Asia in late 1982, resulting in record low (since 1958) total-ozone value in North America and the north temperate zone in early 1983. For the Northern Hemisphere, the decrease seems to be about 3 per cent. Total-ozone value appeared to be returning to normal later in 1983. Umkehr and ozone-sonde-derived estimates of layer-mean ozone in the north temperate zone indicate that this decrease in total ozone was mostly due to large (10-15 per cent) ozone decreases in the low stratosphere, though the contribution of the high stratosphere thereto is not easily determined, because of the bias, introduced into Umkehr observations by the stratospheric dust from El Chichón. It is concluded that the decrease in total ozone in late 1982 was more likely due to anomalies in atmospheric circulation than to anomalies in the photochemistry of the high stratosphere.

A. Field measurements

The major recent accomplishments include:

(a) Continued expansion of the atmospheric data base for the concentrations of key stratospheric species in all chemical families;

(b) Successful demonstration of several balloon-borne techniques, including: LIDAR measurements of OH and O_3; far-infra-red FTIR measurements of OH; improved resonance fluorescence measurements of atoms and radicals; the reel up/reel down mechanism for repeated insitu measurements from a single flight; an insitu laser-induced fluorescence system for OH and HO_2; and an insitu infra-red sampling system for NO, NO_2 and H_2O and H_2O species;

(c) Completion of the design, fabrication and laboratory testing of several balloon-borne instruments, including: a high-speed interferometer (2-16 microns, 0.005 cm^{-1} resolution); an improved microwave limb-sounder for ClO and O_3; and an improved total chlorine/bromine sampling system;

(d) The completion of three series of international trace constituents balloon intercomparison flights, the results of which are being evaluated;

> (i) Two campaigns each were used with four insitu and three remote sensing instruments, to measure water vapour;
>
> (ii) In two separate campaigns, 13 and 17 remote sensing instruments (including grating spectrometers, radiometers, and Fourier Transform interferometers) were used to measure a wide variety of atmospheric constituents (HCl, HF, HNO_3, NO_2, NO, O_3, H_2O, CH_4, OH, etc.). These sensors utilized the visible, infrared, far infra-red and microwave regions of the electromagnetic spectrum in both the absorption and emission mode; and

(iii) In three campaigns several research instruments and sondes were used to measure O_3.

(e) Microwave measurements of ClO (including diurnal behaviour) and HO_2 using ground-based microwave techniques;

(f) Continued monitoring of the increases in the tropospheric concentrations of CH_4, CO, N_2O, CFC-11, CFC-12, CCl_4 and CH_3CCl_3 (see also Figures 9-14, pages 122-127);

(g) Continued collection of global data sets of O_3 (column content and vertical distribution), H_2O, CH_4, N_2O and temperature, through the continued operation of the SBUV/TOMS and SAMS instruments on the Nimbus 7 satellite;

(h) Redesigning and testing of the ROCOZ (rocket ozone) system, resulting in improved precision and reliability;

(i) Carrying out a mid-latitude stratosphere-troposphere multi-aircraft experiment to observe a major folding event;

(j) Undertaking Automated Umkehr Ozone Profiling. Work that began in 1982 to automate six Dobson spectrophotometers for Umkehr observations was completed in 1984. This project was funded by the EPA, the Chemical Manufacturers Association, NOAA, and WMO. Five automated Dobson sites were operational in 1984; Perth, Australia; Haute Provence, France; and Boulder, Poker Flat and Mauna Loa, United States of America; and

(k) Continued monitoring of the global stratospheric temperatures via the NOAA operational satellite system and the ground-based balloon-sondes and rocket-sondes.

B. Laboratory studies

The major recent accomplishments include:

(a) Continued overall improvement in the kinetics and photochemical data base;

(b) Obtaining key new HO_x rate constant data (i.e. for the $HO+HO_2$, $O+HO_2$, $H+HO_2$, HI_2+HO_2, $OH+HNO_3$, $OH+HO_2NO_2$, and HO_2+NO_2+M reactions), which improve our understanding of the lower stratosphere;

(c) Minor modifications to the $O+ClO$ and $OH+HCl$ rate constants to represent their values more accurately;

(d) Obtaining new data on O_2 and O_3 absorption cross-sections;

(e) Improved understanding of the reactivity of $ClONO_2$ and of the photo-dissociation mechanism of $ClONO_2$;

(f) Obtaining refined spectroscopic data for the interpretation of atmospheric field-measurements data; and

(g) Development of new instruments, namely: a rapid response dual-beam UV-absorption instrument for balloon-borne measurements of atmospheric ozone.

C. Theoretical studies

The major recent accomplishments include:

(a) The utilization of one- and two- dimensional photochemical models so that there is now an increased awareness of the non-linear coupling in the chemical system, i.e. multiple solutions, O_3 loss as a function of ClX (both at low and high levels of ClX), the response of O_3 to the simultaneous increase in the atmospheric concentrations of CFCs, CH_4, N_2, and CO_2 (multiple-scenario perturbations); and

(b) Significant inital progress in coupling chemistry in a non-interactive manner into a 3-D model. Progress has also been made in the development of general circulation models (GCM) which include detailed treatment of radiative-dynamical -chemical coupling. (See also Figure 15, page 128).

D. Satellite data analysis

The major recent accomplishments include:

(a) Completion of the final processing of Nimbus-7 (LIMS and SAGE and DMSP satellite data) and archiving of the data at the NSSDC. This provides global data sets for temperature, O_3, H_2O, HNO_3, N_2O, NO_2, CH_4 and aerosols;

(b) Selection of a large number of research groups to interpret upper atmospheric data from the Nimbus-4, 6, 7, SAGE and DMSP satellites;

(c) Detection and tracking by SME and SBUV/TOMS and Nimbus-7 of aerosol and sulphur dioxide clouds emitted by El Chichon;

(d) Continued analysis of Nimbus-4 BUV and Nimbus-7 SBUV/TOMS data for possible trends in O_3;

(e) Using SME, which is providing excellent data on solar flux and O_3;

(f) Using satellite data to study stratospheric warming and its consequent effects on ozone distributions; and

(g) Using SME and Nimbus-7 data to determine the time-dependence of NO_2 increases as air parcels emerge from the polar night. This work supports the explanation that the polar NO_y reservoir responsible for the Noxon cliff is N_2O_5.

E. UV-B radiation simulation

A solar UV-B radiation computer-developed almanac was completed. The almanac contains data on solar UV-B radiation fluxes at the earth's surface for combinations of radiation wavelengths, total-column ozone, latitude, season, and time of day. The almanac's intended users are researchers, such as biologists studying health, terrestrial or aquatic effects of UV-B radiation, who need to simulate the solar UV-B radiation fluxes as they correlate to various amounts of total-column ozone change at their laboratory locations.

III. Future programme

The balanced research programme of field measurements, laboratory studies, theoretical studies and data interpretation will continue at the same level in the near future. Specific thrusts will include:

(a) Continuation of the balanced programme of insitu and remote measurements of atmospheric constituents from balloon-borne platforms with an increased emphasis on using multi-sensor platforms so as to perform intercomparisons and to obtain comprehensive data sets;

(b) Studies of the chemical composition of the lower stratosphere, with increased efforts to measure the reservoir species ($ClONO_2$, HO_2O_2, N_2O_5, etc);

(c) Accurate assessment of the budget and partitioning of NO_x;

(d) An enhanced ground-based programme to measure tropospheric source gas concentrations;

(e) Flux studies of source-gases from key ecosystems;

(f) Application of LIDAR to stratospheric ozone determination;

(g) A series of experiments in the tropics and extra-tropics with multiple instrumented aircraft to gain an understanding of stratospheric/tropospheric exchange mechanisms;

(h) Utilization of MST radar systems to study the dynamical processes in the stratosphere;

(i) A second SAGE, to measure global distribution of aerosols, O_3 and NO_2, will be launched in 1984;

(j) The high resolution infra-red interferometer (ATMOS) will be flown in the Space Shuttle in 1984/1985;

(k) Passive and active remote sensor development for future satellite (e.g. the proposed Upper Atmosphere Research Satellite programme) and Space Shuttle applications;

(l) Development of a Solar Back-Scattered Ultraviolet Radiation (SBUV) instrument for flight on a Space Shuttle to calibrate satellite SBUV instruments;

(m) Increased emphasis on analysis and interpretation of existing satellite data sets;

(n) Enhanced development of 2-D models for assessment studies;

(o) Pursuit of multiple approaches to the interactive 3-dimensional modelling of coupled chemical, radiative, and dynamic processes;

(p) Improved data interpretation and comparison with model results for data from major balloon and aircraft measurement campaigns;

(q) The Solar Back-Scattered Ultraviolet Ozone Monitor (SBUV) operational programme will instrument the next United States polar orbiter in an afternoon polar orbit. This will provide near-global coverage; and

(r) A ground-based programme of regular Dobson and automated Umkehr Dobson measurements, together with a three-station balloon-based sampling programme, will be operated for a satellite ground truth programme.

HEALTH EFFECTS RESEARCH

The United States Government supports and conducts laboratory and clinical research into the effects of UV light on health. These effects include sunburn, eye diseases, skin diseases, and skin cancer. Health effects and their severity depend upon radiation wavelength and intensity, exposure time, and host and environmental factors.

This report describes research activities leading to increased understanding of the predisposing conditions and molecular events that lead to UV light-induced irritations and diseases.

Research highlights include the following items:

Epidemiological studies are providing new estimates of skin cancer risks which are adjusted for ethnicity, skin complexion, exposure to ionizing radiation, coal tar, and pre-existing skin conditions.

Beta-carotene modifies the effects of UV-radiation which is a possible risk factor for melanoma, and topical retinoids can cause regression on melanoma metastases. Administration of certain carotenoid pigments causes a delay in the development of tumours induced by UV-B animal models.

Diet may play a role in modifying UV-induced cancer. Current studies hope to determine if dietary fat enhances photocarcinogenesis and to ascertain whether UV and diet may predispose the host to other environmental carcinogens.

Studies of UV-induced DNA damage are focusing on mechanisms associated with excision and repair of such lesions. Such mechanisms, or the lack thereof, will influence the integrity of the DNA and the resulting ability of treated cells to survive.

UV-induced tumours express multiple tumour-associated antigens which can selectively activate the regulatory or effector pathways of immune response. Monoclonal antibodies are being developed to identify the different tumour antigens on individual UV-induced tumours.

Primary neoplasms that have been induced experimentally by UV light are immunologically rejected when transplanted to normal syngenetic recipients but are capable of progressive growth when transplanted in animals exposed to UV light. These results are presumably due to effects on the immunologic system which is mediated by UV light.

The action spectrum of UV-B is being studied as an aetiologic factor that causes antigen-specific unresponsiveness in mouse skin. Antigen presentation to T-lymphocytes may be impaired following exposure to UV-B doses similar to those experienced by humans during recreational activities.

Normal human melanocytes are being maintained in tissue culture to investigate the role of the UV action spectrum in causing melanogenesis and mutagenesis. In vivo studies focus on the effects of UV plus a photosensitizer (PUVA) to study the effects on the melanogenic process since PUVA is used to treat a variety of skin disorders such as psoriasis and vitiligo. In addition, UV plus a carcinogen is a system used to study the origin of melanomas.

Toxic oxygen metabolites including superoxide anion, hydrogen peroxide (H_2O_2) hydroxyl radical and singlet oxygen are triggering agents in cataractogenesis. Protection is afforded by various enzyme systems (catalase, superoxide dismutase (SOD), glutathione peroxidase) of lens and other eye tissues. Experimentally induced cataractogenesis has shown a rise in the H_2O_2 levels and decreases in catalase and SOD. Antioxidants will be used to prevent or arrest cataracts in animal models.

Changes in the three dimensional structure of lens protein can cause a disruption of the molecular organization of the lens causing opacity (cataract). During aging and cataractogenesis, the lens protein undergoes various changes including aggregation and pigmentation. Such modifications of proteins are being investigated using UV as a possible factor in causing changes of lens protein and the formation of senile cataract.

PHOTOBIOLOGY RESEARCH PROGRAMME

I Current programme

Studies continued on the effects of enhanced UV-B radiation both in the laboratory and in the field under otherwise natural growing conditions on crops, and on aquatic organisms.

The effects of enhanced UV-B radiation on the growth and productivity of six field-grown soya bean cultivars were studied. Control plants received ambient levels of UV-B radiation while experimental plants received daily doses equivalent to that expected on the summer solstice under clear sky conditions with a 16 per cent and 25 per cent ozone depletion at the site of the experiment (39°N latitude). Plants were harvested at several reproductive growth stages.

The effects of UV-B radiation on soya bean growth were dependent upon the developmental stage of the plant. This developmental change in response to UV-B radiation may be attributed to acclimatization.

A major concern are the potential effects of UV-B radiation on seed yield. The data indicated that seed yield on a quantitative basis was relatively unaffected by UV-B radiation in all six cultivars tested. However, three of the cultivars did show changes in seed quality (e.g. reduced protein content). These results are relevant not only in relation to crop plants, but to natural plant populations as well, for alterations in seed reserves may substantially affect seedling supervisorship.

Host-pathogen interaction(s) (plant diseases) was a parameter that first affected wheat under enhanced UV-B conditions. The interaction was host-pathogen specific. Thus, though wheat yield was not directly affected by UV-B radiation, the wheat rust increase had the effect of decreasing the effective yield.

Recent research has also centered on: (1) the development of action spectra for damage to photosynthesis of higher plant leaves, (2) field experiments to determine the capacity of higher plants to acclimatize to more intense UV-B radiation, and (3) to determine the changes in competitive balance between plants subjected to higher UV irradiance in the field. The action spectrum for broad bean Vicia faba appears to be similar to that of the model plant Rumex patientia. Thus, this indicates a steep action spectrum which would result in a significant radiation amplification factor if ozone reduction ensues. Field studies during the summer of 1983 demonstrated that higher plants could show acclimatization to supplemented UV radiation under field conditions. With modest UV supplements (corresponding to a 9 per cent ozone reduction) the plants synthesized more UV screening compounds and the epidermal transmittance decreased. The importance of a balance between UV-B and visible radiation in plant assessment studies is generally recognized. Therefore, carefully modulated UV-irradiation under field conditions (to account for changes in cloud cover and time of day) is particularly important for realistic simulations of ozone reductions.

Information to date does not suggest that UV radiation supplementation (simulating current ozone scenarios) can result in sizeable reductions in plant productivity. The ultimate consequences of most importance may include more subtle changes in plant allocation patterns and interactions with other organisms. Changes in the competitive balance of species have been clearly demonstrated.

Numerous investigators have measured a depression in marine phytoplankton community structure following exposure to enhanced levels of UV-B radiation, There is a decrease in species diversity following exposure to enhanced levels of UV-B radiation. It appears as if, in natural plant communities, a change in species composition rather than a decrease in net production might be a more likely result of a decreased ozone layer. There are several implications of an alteration in the community structure of diatom assemblages. Marine diatoms are an important carbon source for invertebrate grazers and detritus feeders. The decreased species diversity observed in studies simulating natural conditions is usually not accompanied by deleterious effects on biomass and chlorophyll accumulation or by deleterious effects on community primary productivity.

Experiments have been performed with marine animals (larval shrimp and adult euphausids) comparing survival at various UV-B doses and dose-rates combined with different levels of near-UV and visible irradiance. Results suggest that photorepair to UV damage does occur in larval shrimp and adult euphausids and that this photorepair reaches a maximum at relatively low visible light intensities. Thereofore, previous experimental results, using much less visible irradiance than is naturally present, are likely valid with respect to photorepair potentials. Research confirmed previously determined tolerance limits for shrimp larvae and adult euphausids. Additional experiments demonstrated the apparent inability of euphausids directly to detect and avoid harmful levels of UV-B irradiance. Experiments will continue to determine the UV-B dose/dose-rate response of a large marine copepod. This work complements earlier studies on very important smaller copepods. The smaller copepods tolerated considerably less UV-B radiation, with thresholds, depending on species, close to those currently experienced in the upper one metre, where these copepods are very abundant.

The dye laser is currently being used to produce UV-B action spectra for four eukaryotic micro-organisms, a yeast, an alga, and two protozoans. Repair through photoreactivation has been tested in the two protozoans. Genetic inhibition of repair appeared important throughout the range tested, but photoreactivation seemed to have a much reduced significance at 310 and 315 nm. It was noted that efficiency of inactivation at 310 nm and longer wavelengths was less than would be predicted from the shape of the DNA absorption curve, suggesting that repair at those wavelengths might be more efficient than for shorter components. With this system, sunlight lethality is not subject to post irradiation photoreversal. It is possible that other repair systems also work better following long-wave UV-B exposure, or the anomaly could imply that the quantum yield for lesions may decrease at wavelengths greater than 310 nm. One possible implication of these results is that ozone depletion could produce biological effects greater than those predicted on the basis of the assumption that action spectra precisely parallel DNA absorption spectra.

II Future research

The photobiological research programme will concentrate on effects correlating to ozone decreases of about 5 per cent. Existing data in this ozone depletion region are sparse and uncertain. The photorepair mechanisms and effects, as well as amelioration and adaptability capabilities, will also be studied in this region. The interaction between UV-B stress and other environmental changes (e.g. increased atmospheric CO_2, water stress) will be investigated.

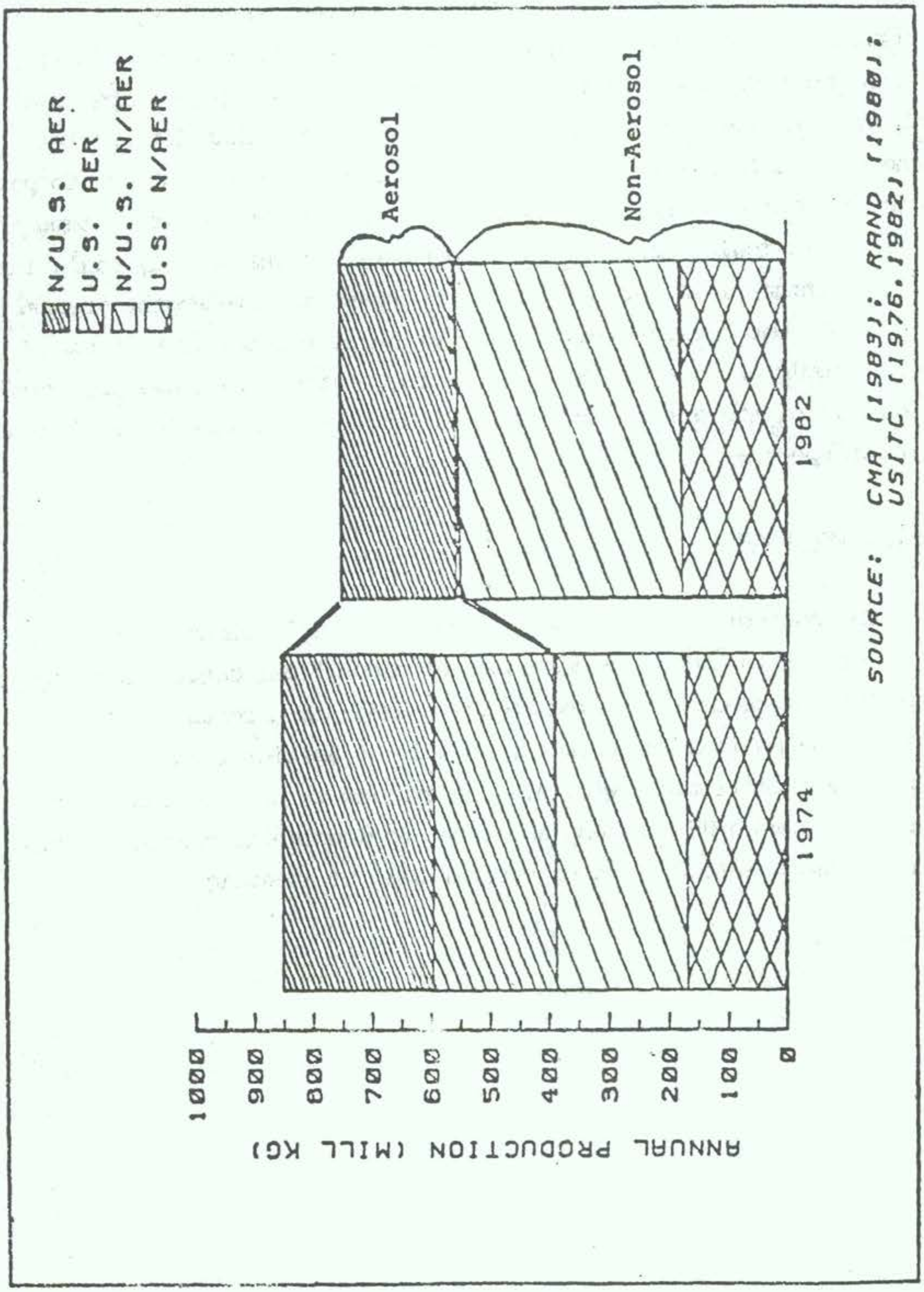
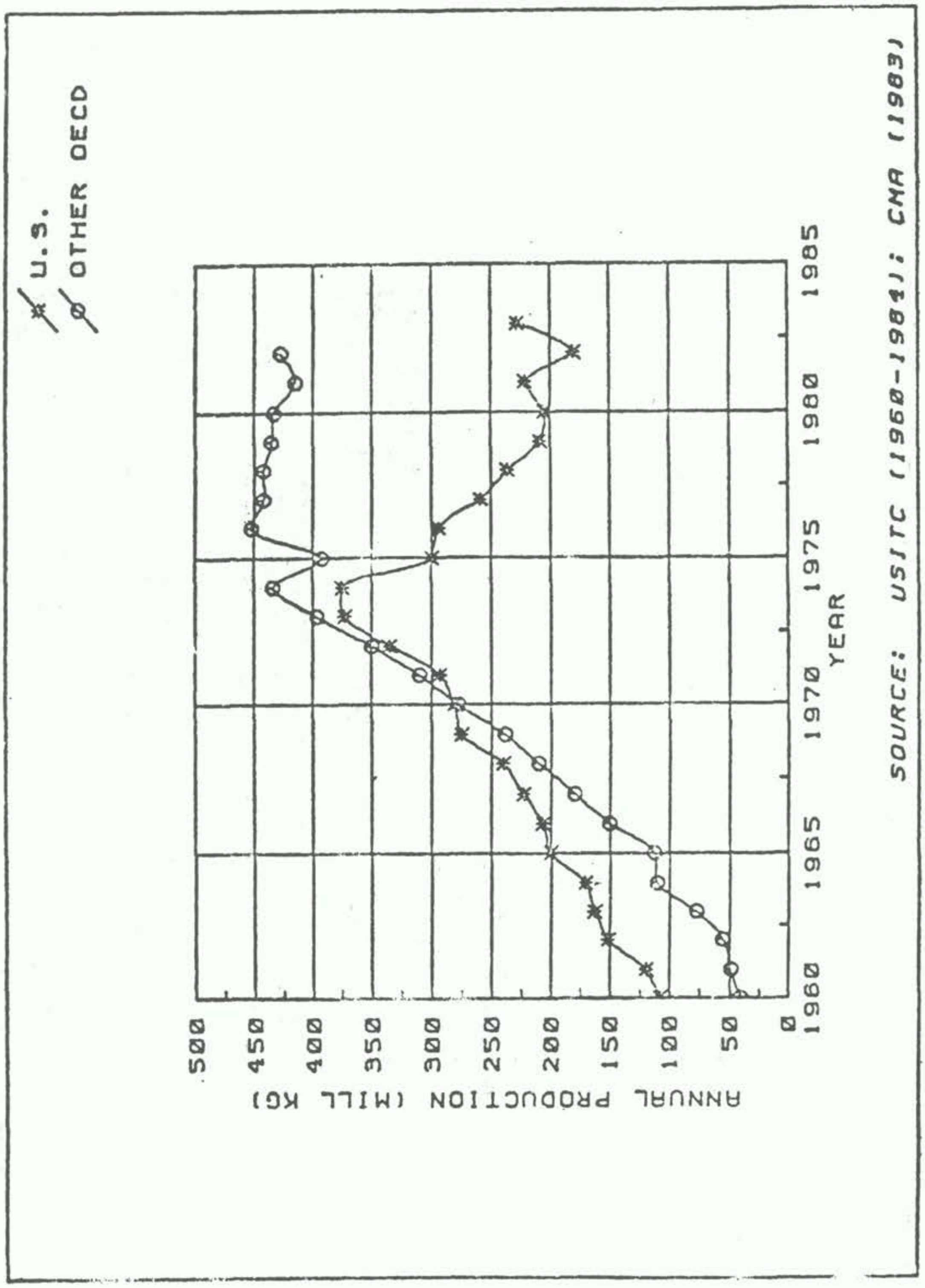


Figure 9

Changing composition of world CFC use



SOURCE: USITC (1960-1984); CMA (1983)

Figure 10
CFC 11 and 12 production: U.S. and other OECD Nations

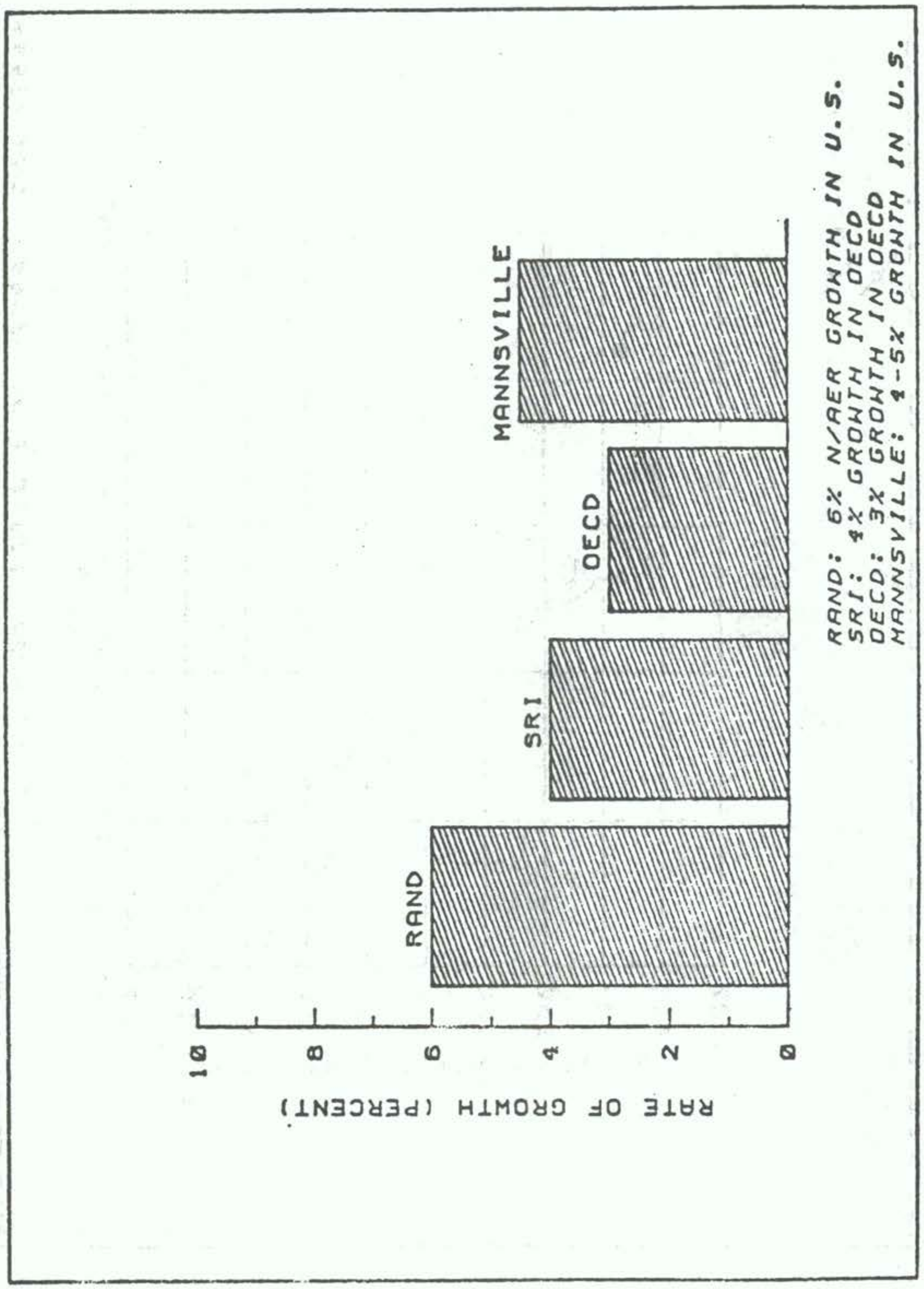


Figure 11

Published estimates of future CFC production

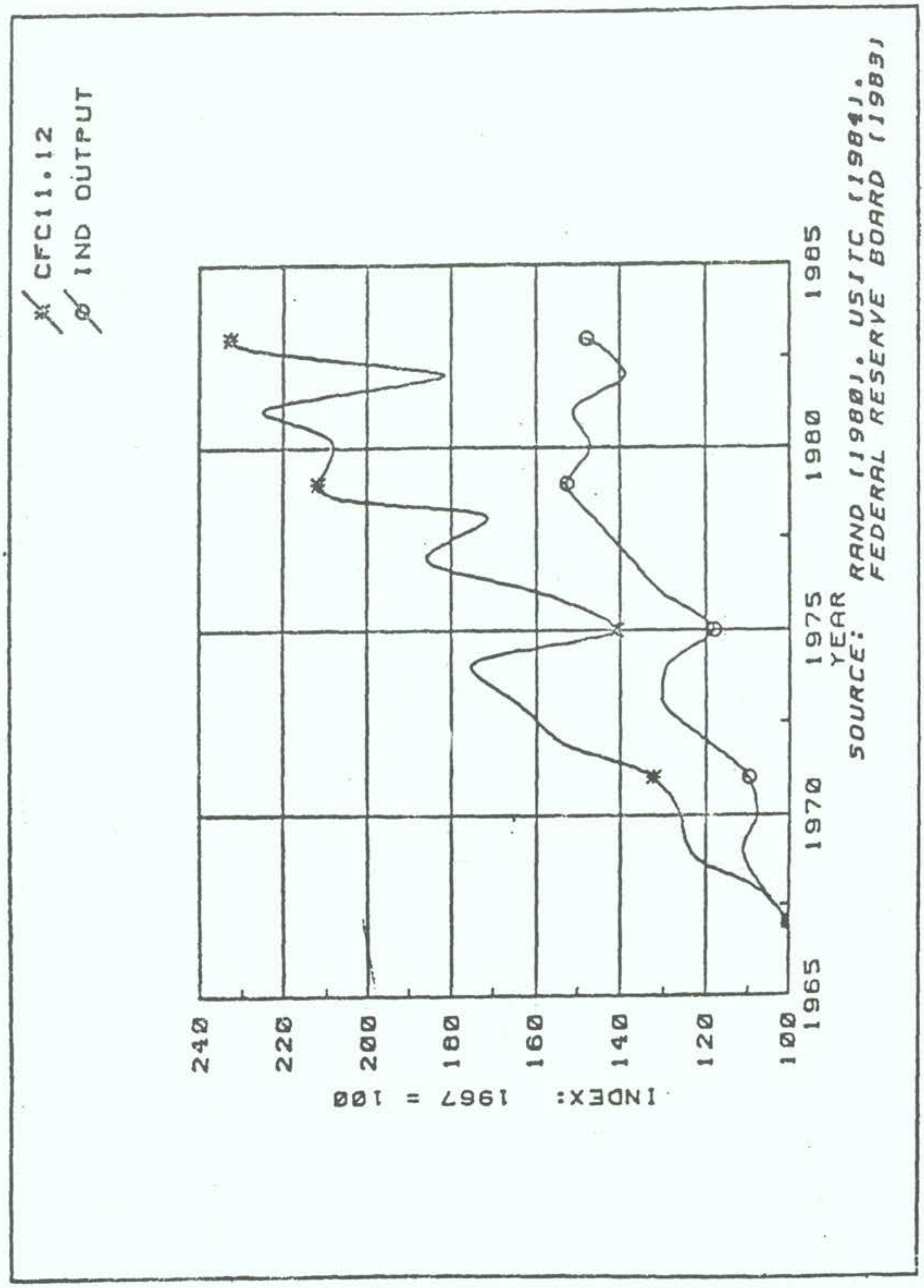


Figure 12

U.S. - Non-aerosol CFC production versus total industrial output

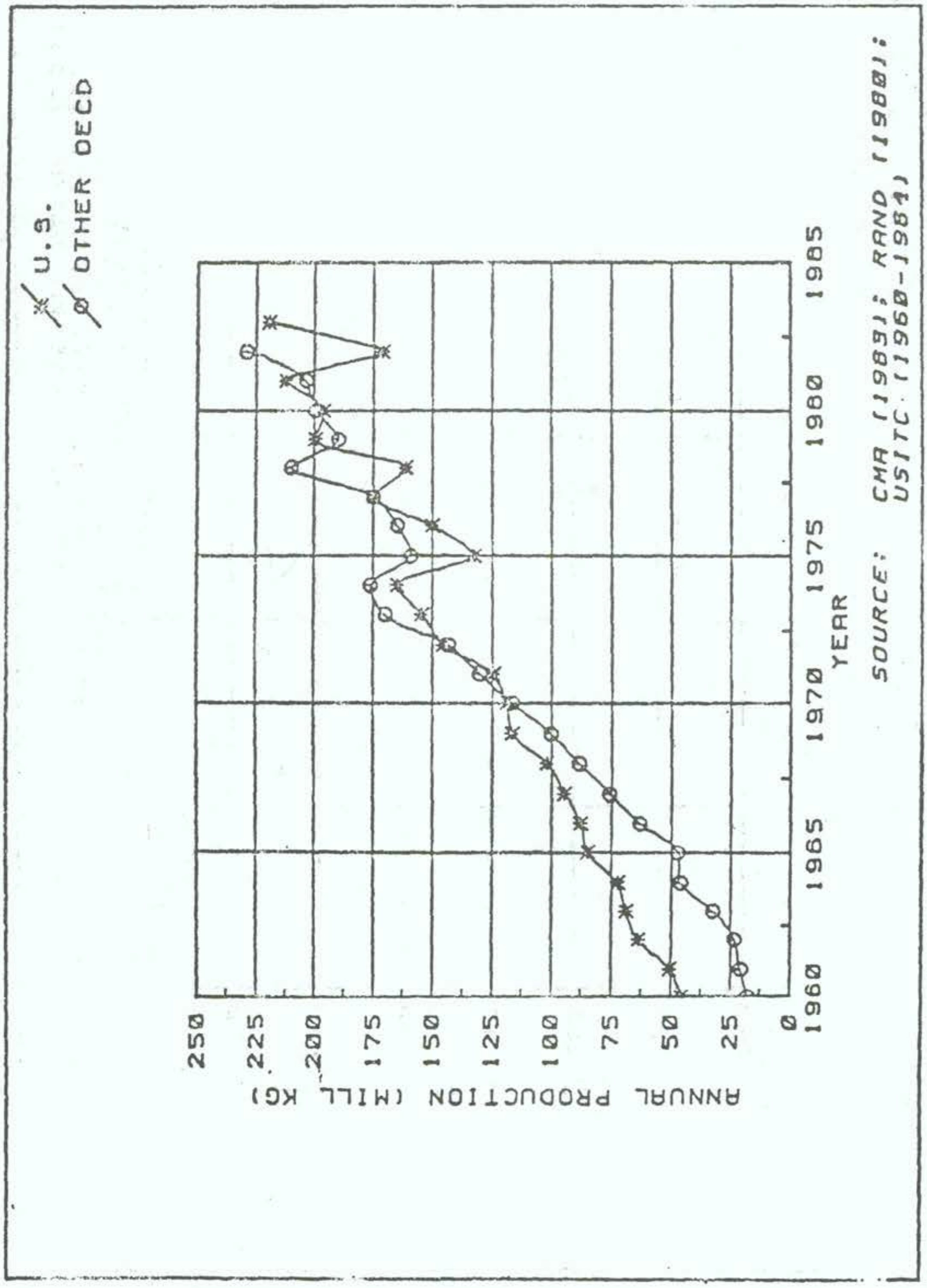


Figure 13

CFC 11 and 12 Non-aerosol use. U.S. and other OECD Nations

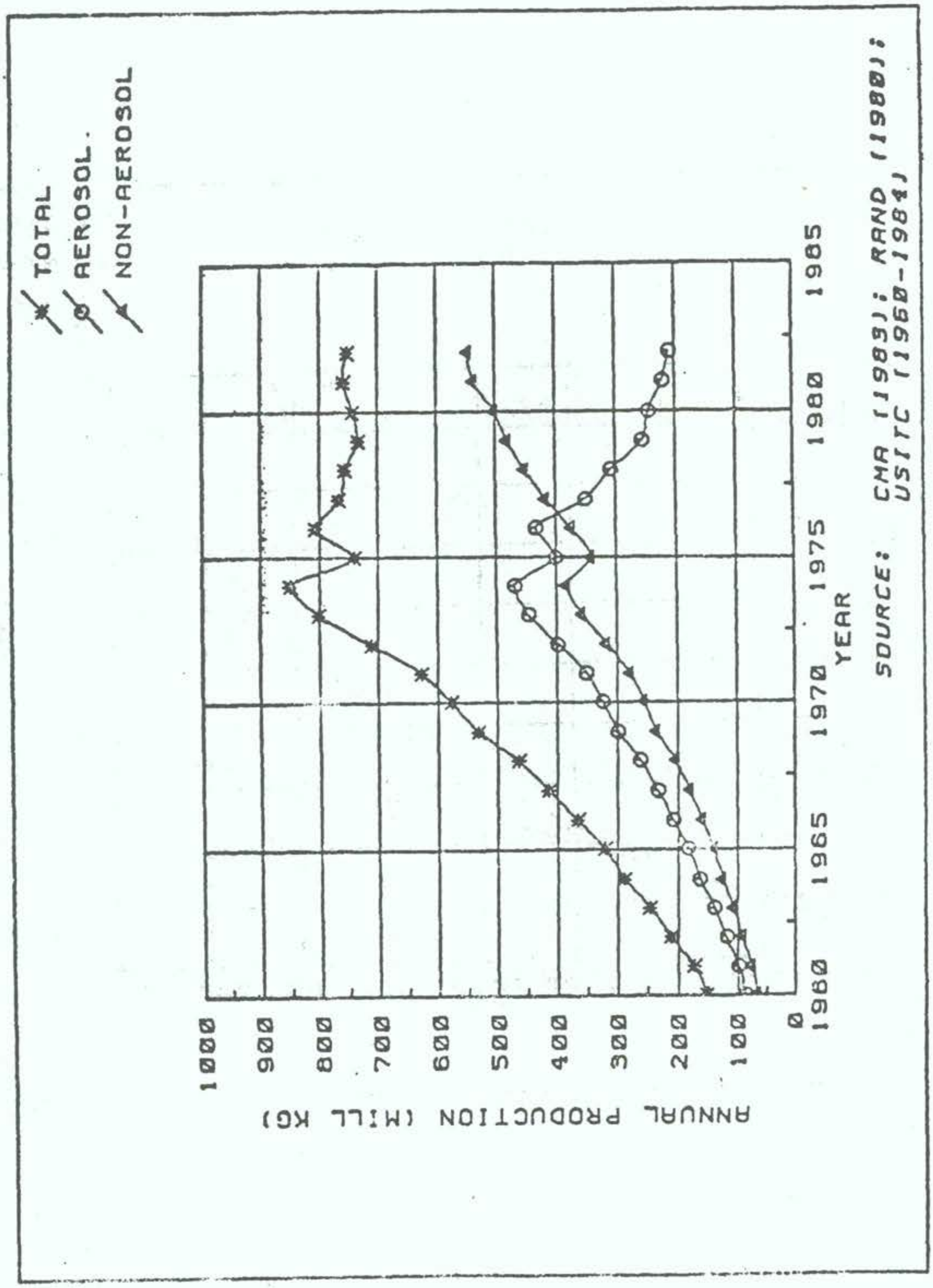


Figure 14

CFC 11 and CFC 12 : World production

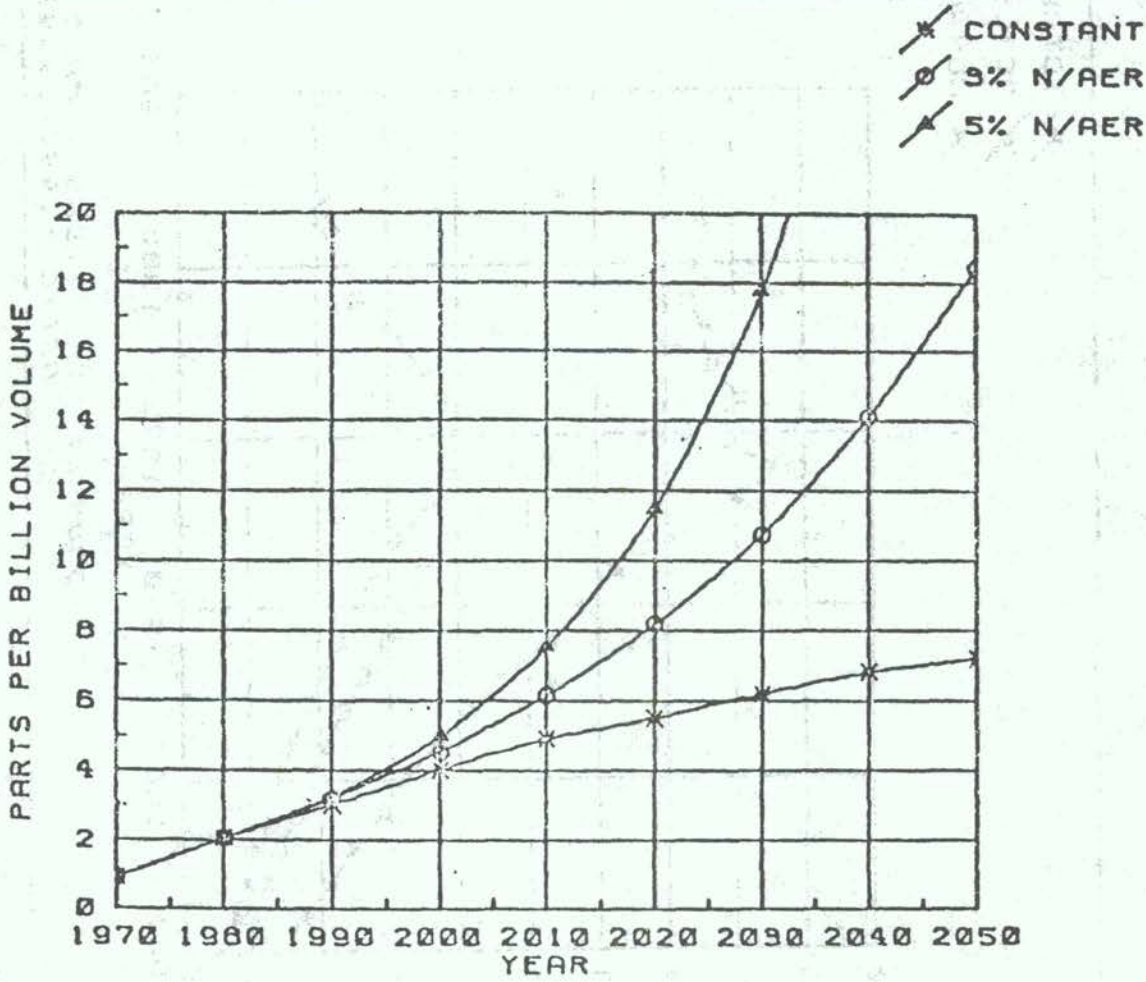


Figure 15

Atmospheric ClX assuming various growth rates for CFCs, CCl_4 and CH_3CCl_3

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

Introduction

Since the sixth session of CCOL, the United Kingdom has continued its research programme into the ozone layer and the effects of man-made perturbations. The work is funded by government departments, the Science and Engineering Research Council and the Chemical Manufacturers Association. Some activities are carried out in collaboration with NASA. The programme can be conveniently reported under three headings: atmospheric measurements, laboratory kinetic studies, and stratospheric modelling.

1. Atmospheric measurements

(i) Ground-based measurements

The Meteorological Office has continued the measurement of columnar ozone abundance by Dobson instruments at several stations.

The British Antarctic Survey has continued ozone observations at Faraday and Halley stations using Dobson spectrophotometers. At Faraday, a detailed comparison of Instrument No.73 with its replacement, No.31, will take place during the austral summer of 1984/85. At Halley, Instrument No. 123 is now operating satisfactorily at the new station. Instrument No.103 has been recovered from Grytviken where it was abandoned during the Falkland Islands war. Damage appears to be only slight, but the instrument will be thoroughly cleaned and overhauled before reuse. The reduction to a common standard of ozone data for the decade 1973-1983, is well advanced.

(ii) Aircraft measurements

Aircraft measurements were made by the Meteorological Office around polar front jet streams near the British Isles in April 1983; the calculation of ozone fluxes associated with a developing jet is in hand, with spectral analysis to examine characteristic length scales. Large horizontal variations in ozone were found above the jet core, on its cyclonic side and below it. There was little variability on scales less than 10 km.

Further aircraft profiles of trace gases in a cut-off low near the British Isles in April 1983 have been analysed, in collaboration with Harwell. The data have been combined with meteorological analyses and interpreted to show that extrusion of stratospheric air into the troposphere accelerates the oxidization of light hydrocarbons, via enhanced OH concentration.

(iii) Balloon-borne measurements

The major effort of the Upper Atmosphere Group of the National Physical Laboratory (NPL) has been in its continued involvement in the Balloon Intercomparison Campaign (BIC). This international campaign was conceived to:

(a) Determine the accuracy and precision of measurements of minor stratospheric constituents using remote sensing techniques; and

(b) Provide a validated data set with which to test photochemical models of the stratosphere.

The measurement phases of the campaign took place during autumn 1982 (BIC I) and spring 1983 (BIC II). NPL monitored O_3, HNO_3, NO_2, H_2O, CH_4, N_2O, CHC-11 and CFC-12 using a cooled grating spectrometer which measured atmospheric thermal emission spectra; the data reduction was carried out during the last 18 months.

Summarized below are some of the preliminary conclusions from BIC, as presented at the Quadrennial Ozone Symposium, Greece, in September 1984.

Ozone

In general, agreement between all techniques (absorption/emission, mid IR - microwave) is within the quoted errors. Typical differences are of the order of 15 per cent below 37 km.

Agreement between the insitu techniques (Atmospheric Environment Service Ozone Sondes and NASA-JSC UV phtometer) is between 5 - 10 per cent below 36 km.

HNO_3

The HNO_3 profiles obtained using emission spectroscopy in the 11.33 micron band agree within the quoted errors. The occultation measurements of ONERA, France, made using the Q-branch of the 7.5 micron band, diverge from the others below 27 km, though other occultation measurements of the column amount are generally in agreement with the column amount measured by the emission techniques. The BIC I and II HNO_3 profiles are very similar.

The BIC occultation measurements in the visible and IR are in good agreement. Although the intercomparison is somewhat limited, the emission measurements of NPL support the occultation measurements, whereas the emission measurements of the Oxford PMR indicate much lower concentration.

HCl

The concentrations of HCl measured using near IR absorption spectroscopy are in good agreement with those measured using IR emission spectroscopy, however the concentrations obtained from observations in the far infra-red spectral region are lower.

The final BIC results and conclusions are likely to be published during 1985.

For the future, NPL is planning to develop a balloon borne diode laser spectrometer to make measurements of stratospheric composition. It hopes shortly to buy a commercial laboratory diode laser spectrometer to assess the problems associated with flying such a system from a balloon, and also to carry out some laboratory spectroscopy in support of stratospheric measurements. The group will investigate the feasibility of using diode laser spectroscopy to measure species such as N_2O_5 and $ClONO_2$ which have eluded positive identification by conventional spectroscopic techniques.

NPL is also collaborating with the University of Oregon to make improvements to its existing cooled grating spectrometer with the aim of significantly increasing its sensitivity, especially to the NO_x family of gases.

Mr. Julian Nott is planning a round-the-world flight in a helium-filled balloon flying in the Southern sub-equatorial jet stream. The Meteorological Office is preparing instruments to measure ozone, water vapour, temperature and pressure from an instrument package which can be lowered down to 1 km below the balloon. This will provide valuable information on gaseous exchange between the stratosphere and troposphere in the region of the jet.

(iv) Satellite measurements

Analysis of satellite data from the LIMS and SAMS experiments carried out by Rutherford Appleton Laboratory (RAL) has been used to derive global fields of important radicals and to make modes checks on present photochemical theory. Two independent derivations have been carried out. Assuming HNO_3 and NO_2, which are measured by LIMS, to be in photochemical steady state, OH can be derived. This is called the ratio method. OH can also be calculated from its sources (H_2O, CH_4) and sinks (HO_2, HNO_3, HNO_4). Measurements for some of these species exist; for the others photochemical steady-state arguments can be made.

These two methods produce OH fields which are in excellent agreement in low latitudes. In higher latitudes, where the satellite observations are made at high zenith angles, present photochemical theory suggests that the two methods should diverge with the ratio method predicting much less OH. This is precisely what is found in the derivations. The encouraging results indicate no obvious problems with present photochemical theory.

At Oxford University, development continues of the Improved Stratospheric and Mesospheric Sounder (ISAMS) for the Upper Atmosphere Research Satellite. This instrument measures temperature and abundances of minor constituents (CO, CH_4, H_2O, N_2O, NO, NO_2, N_2O_5, HNO_3, CF_2Cl_2, O_3) from 15 km upwards to an altitude of from 60 to 120 km depending on species. The launch is scheduled for 1989.

A small instrument dedicated to the measurement of water vapour in the region of the mesopause (60 to 100 km of altitude) is also being developed for the first flight of the European Retrievable Carrier in 1987.

Oxford University is participating in the NASA 'ATMOS' project, which involves placing a high resolution interferometer on the Space Shuttle for the transmission spectroscopy of trace constituents during solar occultation. The first flight is on Spacelab 3 in January 1985.

In 1977, NPL, in collaboration with RAL and Oxford University, carried out a feasibility study on a cooled infra-red radiometer (CIR) for Spacelab. The project was not developed beyond that stage due to escalating launch costs. However, with the possible opportunity of flying such an instrument on EUREKA (a reusable ESA space platform) the groups are re-evaluating the CIR instrument to see if it can, in its present form or with some redesign, still provide a valuable contribution to the study of stratospheric composition and dynamics.

2. Laboratory measurements

(i) Spectroscopy

Work on spectroscopy in support of stratospheric measurements has continued at Rutherford Appleton Laboratory using a high-resolution interferomenter. O_3, CO_2, NO_2, HCl and CH_4 have all been studied. A long-path White Cell, allowing study of the weak spectral features typically seen in atmospheric limb paths, has been successfully developed for use in conjunction with the high-resolution interferometer. Paths of up to 256m are currently being used, and will be extended in the near future to about 1 km.

At Cambridge University, the measurement and analysis of the infra-red spectra of important atmospheric species such as SO_3 and CH_3Cl are being carried out at very high resolution ($0.005cm^{-1}$). Preliminary results were published in Chem. Phys. Letters 102, 135 (1983).

(ii) Chemical kinetics

Cambridge University has developed a laboratory method for studying reactions of HO_2 which avoids interference by hydrates of HO_2 and is used at total pressures corresponding to those in the lower stratosphere. It is based on flash photolysis combined with infra-red diode-laser spectroscopy. Measurements of the rate of recombination of HO_2 radicals have been published (J.C.S. Faraday II, 78, 1469 (1982); Chem. Phys. Letters 103, 167 (1983)). This work is important and constitutes an attempt to verify our understanding of hydrogen radical chemistry by measurements of HO_2 and H_2O_2 in the stratosphere.

Because of the importance of the pressure dependences formed for reactions of hydrogen radicals, this work is being extended by applying the highly sensitive but difficult technique of mid-infra-red laser magnetic resonance spectroscopy to study atmospheric reactions of HO_2 with NO, NO_2 etc. in the pressure range 10-50 Torr.

At Harwell, the kinetics of the reaction of ClO with NO_2 have been studied using Ultraviolet and Infra-Red Diode Laser Spectroscopy coupled to a photochemical modulation technique, and using chlorine dioxide as a precursor for ClO radicals. The overall reaction stoichiometry has been shown to be represented by:

$$2OClO + 2NO_2 \longrightarrow 2ClONO_2 + O_2$$

over a wide range of conditions. The rate coefficient k for the reaction

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$

has been determined and the value at low OClO concentration agrees well with the data given in the body of literature for this reaction. At high OClO, k apparently declines. Possible causes for this have been suggested.

The reaction of Cl with HO_2 has also been studied at Harwell, using modulated photolysis of mixtures of Cl_2-H_2-O_2-N_2 at 350 nm in a quartz reaction cell. Measurements of HO_2 and ClO were made using UV absorption at 220 nm and 277.3 nm respectively. Analysis of the results using computer simulation has provided provisional values for the rate constants for the two reaction channels:

$$Cl + HO_2 \xrightarrow{k_1} HCl + O_2$$

$$\xrightarrow{k_2} ClO + OH$$

3. Stratospheric modelling

The Harwell 1-D model has been updated to include revised photolysis rate coefficients for a number of species following recent changes in calculated solar irradiance in the range 195 nm to 220 nm. Calculated profiles for halocarbon species, including minor CFCs and chlorocarbons such as methyl chloroform and carbon tetrachloride, have been compared with experimental data obtained in joint Lindau/Harwell stratospheric balloon campaigns reported previously. The eddy diffusion coefficients were adjusted to fit the observed and predicted concentration profiles for CFC-11. These same coefficients then enabled excellent agreement to be obtained between measured and calculated concentration profiles for the other five species considered, without further adjustment. The new eddy diffusion coefficients profile resembles that of Froidevaux and Jung but differs in respect of the elevation and magnitude of the minimum value, which is placed at 22 km rather than 16 km and has a value ($1 \times 10^3 cm^2 s^{-1}$) only half that of Froidevaux and Jung's minimum. The ability to represent well the profile of six separate species gives high credibility to the use of this new profile in 1-D model calculations. The agreement of the model value with observed CFC 11 and CFC 12 profiles resolves a long standing discrepancy. The calculated atmospheric lifetimes for CFC 11 and CCl_4 (74 and 59 years respectively) agree well with those calculated from ALE data, though there is disagreement in the case of CFC 12 and to a lesser extent as regards CH_3CCl_3. The magnitude of calculated ozone depletion at steady state is not much affected by the new profile, though the time required to reach steady state is increased and there would be a corresponding increase in the time required for response to reduction in releases of CFCs and other halocarbons.

The British Antarctic Survey has analysed the results from a new stratospheric ozone computer model. Particular attention is being paid to the accurate simulation of photolysis rates, taking due account of the effects of multiple scattering and ground reflection, together with the sphericity of the Earth's atmosphere. This is important at high latitudes, where twilight illumination is of long duration. A full revision of rate constants and photolysis cross-sections has been undertaken, in line with the latest recommendations by the NASA Panel for Data Evaluation. Examination of the boundary conditions used in the earlier work has shown that, although appropriate enough for the period then studied, they would give misleading results for a simulation of the polar night. A new algorithm for these boundary conditions has been formulated and is being tested.

Work has continued at Rutherford Appleton Laboratory, in collaboration with the Department of Atmospheric Physics of Oxford University, using a hierarchy of numerical models. Detailed studies of SAMS satellite data for CH_4 and N_2 have been carried out using a two dimensional model. Many of the observed features are reproduced. An interesting feature of the data is the "double peak" in low latitudes when, on a given pressure surface, maxima of N_2O and CH_4 are found in the subtropics with a local minimum at the equator. Recent model experiments suggest that this feature is related to the semi annual oscillation of the equatorial winds.

A diurnal photochemical model has been used to investigate data from a variety of balloon experiments, including the Balloon Intercomparison Campaign (BIC). The diurnal variation of NO and NO_2 appears to be well reproduced. There was some extremely interesting behaviour in the low stratosphere, following the eruption of the El Chichon volcano.

At Oxford University, the current focus is on extension of an existing modelling scheme from two to three dimensions, including an advanced treatment of radiation and photochemistry. In addition, atmospheric modelling is being undertaken to provide the theoretical complement to the experimental programme, and to provide a framework within which planning and analysis of the experiments can be carried out.

A new system for comparing photochemical calculations of stratospheric composition with observations, free of the global scale averaging assumptions inherent in 1-D and 2-D models, has been developed at the Meteorological Office. Trajectories are calculated on isentropic surfaces, with a radiative transfer scheme included so that air parcel motion across these surfaces may be calculated via the radiative heating rate and the thermodynamic equation. A typical parcel size is 5 great circle degrees longitude x 5 great circle degrees latitude x 2 km vertical, and it may be tracked for 4 to 10 days depending upon meteorological conditions. A full photochemical scheme has been integrated along a selection of trajectories during periods of disturbed and zonal flow in February and March 1979, in collaboration with Rutherford Appleton Laboratory. Good agreement has been obtained with temporal variations in ozone and nitrogen dioxide observations made by the LIMS instrument on Nimbus 7, when the model calculation is initialized with LIMS O_3, NO_2, HNO_3 and H_2O and SAMS CH_4 observations.

Exchange of air between the stratosphere and troposphere has been investigated by three-dimensional trajectory analysis of general circulation model data. The results highlight the role of the subtropical jet stream systems as mixing agencies for stratospheric and tropospheric air in the model.

A numerical model of the stratosphere and mesosphere, based on the primitive equations, has been adapted to run on the Meteorological Office Cyber computer and has variable resolution both in the horizontal and in the vertical. Simulations of observed stratospheric sudden warnings have been conducted using observed fields of geopotential height as a forcing applied at the lower boundary of the model, and the principal aspects of the observed events have been successfully reproduced. Idealised experiments have also been carried out to study the effect on the stratosphere of localized developments in the troposphere, such as the growth of blocking anticyclones. Downstream Rossby wave-trains are produced extending well up into the stratosphere, where changes in the circulation occur which resemble those seen during sudden warmings. In particular, the phenomenon of planetary wave breaking has been simulated. Studies to improve the representation of radiative processes in the model and to parametrize the effect of gravity wave breaking in the mesosphere are being made in collaboration with the Department of Atmospheric Physics of Oxford University.

Analyses of the stratospheric circulation up to 1 mb are being made routinely at the Meteorological Office using data from Stratospheric Sounding Units (SSUs) on board NOAA satellites. The data are used for diagnostic studies and a climatology based on the six years of available data is being prepared. Emphasis is being placed on interhemispheric and seasonal differences and connections with the tropospheric circulation and its seasonal cycle. The data are also used to intialize integrations with the stratosphere-mesosphere model. Over twenty institutions in the United Kingdom and elsewhere are sent SSU data both for research purposes and to support scientific campaigns.

As a prelude to the UARS project at the end of the decade, preliminary experiments have been made to feed SSU data into the numerical model during the course of an integration in order to improve the quality of the analytical data, e.g. by obtaining winds not dependent on the geostrophic approximation. The aim is to develop an assimilation scheme to incorporate into an analysis of the circulation the data obtained from the UARS and from SSU in contemporaneous orbit.

UNION OF SOVIET SOCIALIST REPUBLICS

The M-124 filter ozone meter has been designed in the USSR to determine the total ozone content of the Earth's atmosphere, in direct sunlight or diffused light, from a section of the sky at the zenith, at a network of ozone-measurement stations (figure 16).

When the angular altitude of the sun is more than 10°, the M-124 ozone meter measures in relative units the stream of aggregate ultraviolet radiation from the sun or from a section of the sky at the zenith in three spectral ranges, isolated by three light filters, with subsequent recalculation of the values of the streams in the first two ranges of the total ozone content of the atmosphere.

The total ozone content is determined on an ozone nomogram on the basis of the ratio of ultraviolet radiation isolated by the first and second light filters and of the sun's altitude.

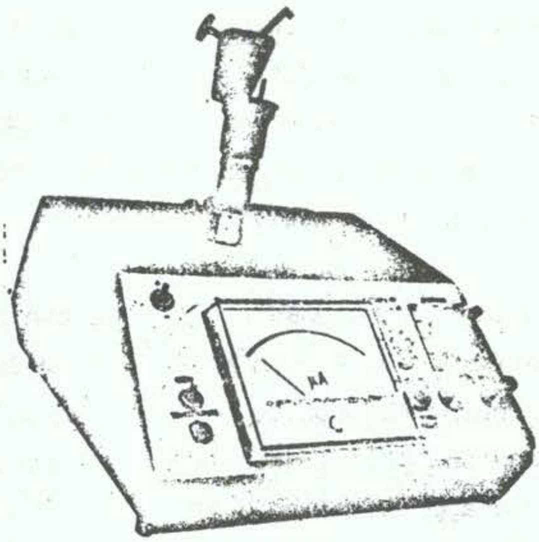


Figure 16

The M-124 filter ozone meter designed in the USSR

A Soviet-made apparatus similar to the M-124 ozone meter has the M-83 universal ozone meter, which is no longer being produced. In contrast to the M-83, the new M-124 uses one light receiver, sealed light filters and a direct current amplifier with a 140UD8 microcircuit; an electrothermometer replaces the mercury thermometer, the altitude/azimuthal device has been considerably simplified, and the overall dimensions and weight of the apparatus have been substantially reduced.

There are no foreign equivalents to this apparatus.

Certificate of copyright No. 892395 has been issued for the M-124 ozone meter.

The economic effect of the introduction of the apparatus is 1.46 thousand roubles a year.

Principle of operation and brief description of the M-124 ozone meter

The design of the ozone meter is shown in the diagram. (Fig.17)

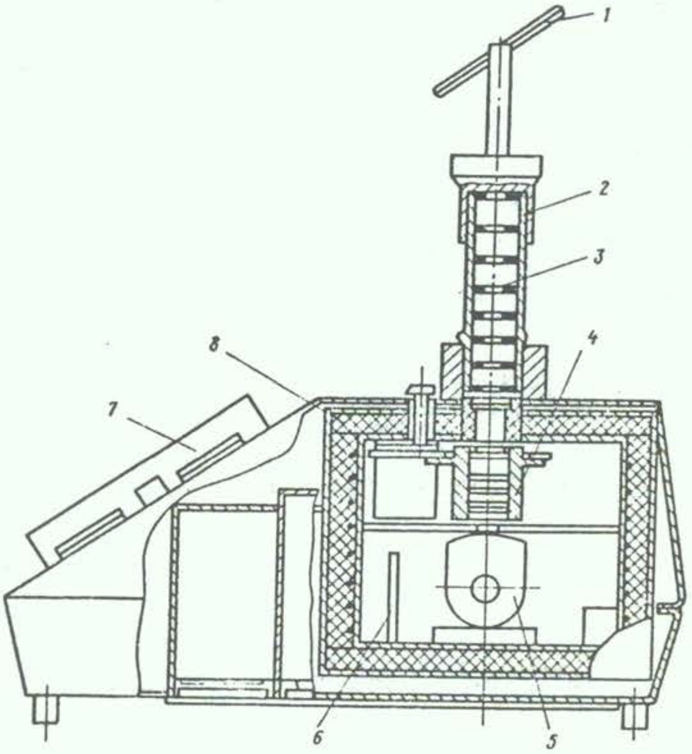


Figure 17
The design of the M-124 ozone meter

The direct light from the sun is directed by the reflector 1 into the viewing tube 2. The viewing tube, together with the diaphragms 3, limits the direct-light flow within a critical angle of entry of 3.5 ± 0.5° and prevent diffused light from falling on the light filters 4 and the light receiver 5.

When the total ozone content is being determined in diffused light from a section of the sky at the zenith, the reflector 1 is not used, and another viewing tube with a critical angle of entry of $6.5 \pm 0.5^{\circ}$ is used.

In either case, the light falls on to one of the light filters 4 mounted in its path, which display the required spectral characteristics of a photometer, and then on to the light receiver 5 which, in the M-124 ozone meter, is the F-14 GOST 20338-74 photoelectric cell.

From the light receiver, an electrical signal proportional to the quantity of light passes to the amplifier 6, and then to the microamperemeter 7.

In order to reduce outside interference and increase the accuracy of measurement, the light filters, the light receiver and the amplifier are located within the passive thermostat 8, in which the temperature is measured by the electrothermometer.

Specifications

Range of determination of total ozone content from ozone nomograms	0.16 - o.60 atm-cm
Error in determination of total ozone content	not more than 8 per cent
Time in which apparatus is ready for operation	not more than 5 min
Time required to switch light filters	not more than 1 s
Number of ranges of sensitivity of the amplifier	11
Independent and separate power supplies:	
For the photoelectric cell	Battery 100PMTsG-U-50 ch TU16-529.297-75

For the amplifier	6 dry cells type 3336 GOST 2583-79
Maximum power requirement of the ozone meter	not more than 1W
Overall dimensions:	
With the viewing tube and reflector	275 x 270 x 300 mm
Without the viewing tube and reflector	275 x 270 x 160 mm
Weight	5.5 kg

Full set supplied

Image converter	1
Reflector	1
Viewing tube for measurements from direct sunlight	1
Viewing tube for measurements from diffused light	1
Cover	1
Case	1

Developed by: A.I. Voeikova Principal Geophysical Observatory, 194018, Leningrad, Ul. Karbysheva, 7, Central Design Office for Construction of Hydrometeorological Apparatus, 249020, Obninsk, Kaluzhaskoy Oblast, Ul. Koroleva, 6.
Prepared by : Central Design Office for Construction of Hydrometeorological Apparatus

EUROPEAN ECONOMIC COMMUNITY

The Commission of the European Communities (CEC) has continued to carry out its activities in supporting Ozone research in the framework of its Research programmes, Environmental Protection and Climatology.

Numerous research contracts dealing with the observational and modelling aspects of the stratosphere and, in particular its influence on climate, will terminate with the end of the above mentioned programmes on 31 December 1985. Based upon the research work of these contracts, a working party "STRATOSPHERE" was established which met for the first time in May 1984 (CEC Rept. "STRATOSPHERE" Ed. A. Ghazi, DG XII/G). With the new research and development programme, Environment and Climatology, foreseen to begin in January 1986, the support for stratospheric research will be continued (subject to their approval by the Council). CEC has also co-sponsored the Quadrennial Ozone Symposium held in Greece in September 1984 and has undertaken the publication of proceedings.

WORLD METEOROLOGICAL ORGANIZATION

Since its lead designation for parts of the UNEP World Plan of Action on the Ozone Layer, WMO, in the Global Ozone Research and Monitoring Project adopted by the WMO Executive Council at its twenty-eighth session (EC-XXVIII), has pursued the following broad programme:

1. Ozone measurements:
   Ground total ozone measurements
   Vertical-ozone profiles observations
2. Ozone trend studies
3. Ozone photochemistry and anthropogenic influences thereof
4. Ozone as a radiatively active gas and its possible contributions to climate change

This is consistent with WMO Executive Council decisions of EC-XXX and EC-XXXII, which were, inter alia, to:

(a) Improve measurements of total and vertical distributions of ozone as well as of the relevant trace species;

(b) Test the chemical and dynamical performance of different ozone models;

(c) Detect trends in the ozone concentration within the so-called photochemical precursor region and in the column;

(d) Study the physical processes and phenomena which would conceivably affect data to be used in assessing ozone trends;

(e) Study the radiative effects of ozone and other minor species (relevant to ozone photochemistry) on stratospheric dynamics and hence on the general circulation.

1. Ozone measurements

Ground-based total ozone measurements:

Dobson instrument No.83 at Boulder, Colorado, USA, has been designated by the WMO Executive Committee as the international primary standard for total ozone measurements. Secondary standards have likewise been designated for the WMO Regional Groupings. This was achieved as a result of Dobson intercomparisons organized by the WMO at Belsk, Arosa, Potsdam and Boulder.

Recalibration of almost one half of the operating Dobson instruments has been accomplished by comparison against the standards. Several instruments have been relocated more favourably and upgraded. In order to increase the precision of the measurements, six selected instruments are being automated (to form an Automated Dobson Network) as a co-operative effort between WMO, and EPA and NOAA in the United States of America. This procedure is also expected to reduce the time currently needed for each observation.

Another type of instrument, a readily portable Brewer spectrophotometer, has been developed by Canada and is being used for quick, diagnostic travelling comparisons. Standard lamps, purchased by WMO, are also being provided to the WMO Regional Associations as an inexpensive means of identifying instruments in need of additional or frequent recalibration.

A new Operations Handbook for ozone observations with a Dobson spectrophotometer has been developed and issued to replace the one published during the International Geophysical Year. An assessment of the performance characteristics of various ozone-observing systems, and a review of the Dobson total-ozone measurements accuracy have been made and the results published.

Both infra-red and ultraviolet radiances have been and are being measured from satellite platforms such as Nimbus 4, Nimbus 6, Nimbus 7, the Tiros N series and the Block 5D series. These can be inverted to yield total-ozone values and some of the data have been archived in centres such as the National Space Science Data Center (NASA) and the National Climate Data Center (NOAA). WMO has arranged for a review of the use of satellites in ozone measurements and this review will include a report on data availability.

Vertical-ozone profile observations:

Realizing that an important aspect of any good observational data set is to have instruments which have been intercompared and whose precisions and accuracies relative to each other are known, WMO has encouraged and actively participated in four intercomparisons of profile-measuring instruments.

There were two intercomparisons of balloon-borne ozone-sondes. Countries using various kinds of sondes, except for India, participated in a campaign at Hohenpeissenberg, Federal Republic of Germany (FRG), in 1978. The Indian sonde was intercompared against the one used by FRG in a second campaign in 1980. Another campaign was conducted in Gap, France, where chemical and optical instruments of both insitu and remote-sensing types (e.g., Umkehr, ECC, Brewer-Mast, LIDAR, Dasibi) were intercompared in 1981.

An intercomparison of rocket-borne ozone-sondes was conducted in 1979 at Wallops Island, Virginia, United States. Chemiluminescent and optical sondes from Australia, Canada, India, Japan and the United States were intercompared. The results are expected to be helpful in delineating possible ozone concentration changes in the precursor region (around 42 km). WMO has also encouraged other campaigns, both national and international, in the context of the Middle Atmosphere Programme.

Two new programmes, at Prague and Sofia, have been initiated for weekly balloon ozone-sonde observations.

With regard to Umkehr observations with Dobson instruments, member countries have been encouraged, in accordance with Executive Council wishes, to increase the frequency and the quality of such observations. In addition, a new multi-wavelength technique, the so-called "Short" Umkehr, which reduces by two thirds the time that had hitherto been required for observations, is being encouraged.

2. Absorption cross sections, stratospheric dust

The difficulties encountered in ozone trend detection have given rise to the realization that the ozone absorption cross-sections adopted in 1968, on the basis of the data then available by the International Ozone Commission (IOC) of IAMAP could be off by a few percentage points. New laboratory measurements, three in the United States and one in France, have recently been performed. With WMO encouragement, the four experimental groups met as an IOC Working Group on Ozone Absorption Cross-Sections and have been comparing their results.

Dr. Robert Hudson (United States) is the Chairman of the Working Group which met just before the recent Quadrennial Ozone Symposium (Halkidiki, Greece, 3-7 September 1984) to finalize discussions on the measured values and their temperature dependences. The relative accuracies of the measurements are the best achievable in a laboratory; but the absolute accuracies show some inexplicable discrepancies. Dr. Hudson had recommended that one set of measurements, that of the National Bureau of Standards in the United States should be adopted for use in satellite ozone-retrieval algorithms. The Ozone Commission has endorsed this recommendation. The question of cross-section values for use in Dobson ozone retrievals is as yet unsettled.

There are other contaminating influences in ozone retrieval: stratospheric aerosols, atmospheric sulphur dioxide (both forming part of volcanic eruptive matter). Concurrent LIDAR aerosol observations, to determine the particulate contribution to observed radiances, will form part of the Automated Dobson Network.

3. Trend analysis

Detection of clearly discernible trends in existing ozone records is still a matter of much ongoing statistical research. This is primarily because ozone exhibits variations of different periodicities, ranging from seasonal to solar-cyclical including the quasi-biennial, and the quality of extant data is inadequate to determine unambiguous secular trends attributable to a given cause. That is the reason why the Executive Council has placed so much emphasis on improving the data-gathering network.

Further, contaminating influences such as volcanic dust and sulphur dioxide impose inaccuracies and it is not clear whether extraterrestrial solar ultraviolet irradiances which exhibit short-term variabilities (although they are assumed to be invariant in Dobson measurements, for example), do not contribute to Dobson data variabilities.

Not only are trends needed in total ozone and ozone densities in the precursor region but also in the upper tropospheric/lower stratospheric concentrations because changes (increases) are possible there as a result of human activities.

Taking all this into account, WMO has completed a review on the sources of errors in the detection of ozone trends.

4. Ozone photochemistry and the anthropogenic influences thereof

In a continuing effort, as requested by the the WMO Executive Council at its thirty-second Session, WMO has participated in a variety of international scientific-evaluation activities with regard to possible human-induced changes to the ozone layer. Basically, this has consisted of Expert Assessment Meetings/Workshops on ozone modelling and stratospheric/tropospheric exchange processes (1977), measurements of rare species relevant to the ozone budget (1977), ozone and stratospheric circulation (1977), two-dimensional ozone models (1980) and rare atmospheric consituents of importance to the ozone layer (1980). In addition, a comprehensive review of the stratospheric properties was carried out, in co-operation with NASA, FAA and NOAA, in the United States in 1981.

It is the current understanding that both anthropogenic NO_x and ClO_x can affect the ozone balance in the atmosphere. The former can contribute to both loss and generation (depending upon the altitude of introduction) while the latter is a loss mechanism. There are still many uncertain factors in calculating the ozone changes that will result from NO_x and ClO_x releases. For assessment purposes, model calculations will have to consider simultaneously all potential perturbations (NO_x, ClO_x and CO_2-induced temperature changes because of the feedback link between temperature and chemistry).

5. Potential climatic impacts

Any alteration to the natural vertical ozone distribution, by redistributing the heat sources and sinks in the atmosphere, can be expected, in principle, to have an effect on the general circulation. Existing studies have shown that, on a per molecule basis, tropospheric redistribution has a potentially greater impact on surface temperature than stratospheric redistribution.

In addition, many source gases such as the chlorofluorocarbons and nitrous oxide have absorption bands in the atmospheric window region, leading to a potential enhancement of the greenhouse effect, if their concentrations in the atmosphere increase.

An exhaustive review of the potential climatic effects of ozone and other minor trace gases has been published by WMO. In addition, in co-operation with the IAMAP Radiation Commission, WMO has planned a series of intercomparisons of radiative codes used in climate prediction models.

6. Exchange of information

Member countries have been urged to supply their ozone data promptly to Atmospheric Environment Service, Toronto, Canada for timely publication in Ozone Data for the World (the "red book").

7. Publications

A list of WMO publications under its Global Ozone Research Monitoring Project is appended (appendix I).

8. Actions completed since the sixth session of CCOL

A set of ozone absorption cross sections, along with their temperature dependence, for the Hartley and Huggins bands has been recommended by the International Ozone Commission for use in satellite ozone retrievals (Halkidiki, September 1984)

The first intercomparison of radiation codes used in climate prediction models, when comparison against line-by-line calculations was made, has been completed (Frascati, August 1984).

Review of Dobson Spectrophotometer and its Accuracy, by Reid E. Basher of the New Zealand Meteorological Service, has been published as

Report No.13 in the WMO Global Ozone Research and Monitoring Project series.

A workshop on Data Requirements for Ozone Modelling and Trends was held at Oxford, United Kingdom, from 10 to 14 October 1983.

WMO Expert Meeting on Tropospheric Ozone, Its Changes and Possible Effect on Climate, was held at Shanghai, China, 22-27 October 1984.

Recalibration of Australian Dobson instruments, with participation (1) of Secondary Standards from Australia, India and Japan and (2) of other Dobsons from Australia and New Zealand, was carried out at Melbourne, Australia, 18 November - 8 December 1984.

Appendix I

PREVIOUS REPORTS PUBLISHED IN CONNECTION WITH THE WMO OZONE 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, December, 1982.

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.

Publications pending:

15. Review of Stratospheric Circulation, by Bojkov, Finger and Murgatroyd.

16. WMO Meeting of Experts on Data Requirements for Ozone Modelling and Trends, Oxford, 10-15 October 1983.

17. Review of Concentrations of Rare Species of Importance to Ozone, by Ramanathan, Singh and Cicerone.

18. Report of Meeting of Experts to Consider the Introduction of New Ozone Absorption Coefficients, Washington, D.C., 14-17 November 1983.

CHEMICAL MANUFACTURERS ASSOCIATION (CMA) - FLUOROCARBON PROGRAM PANEL

1. Modelling

The 2-D model supported in the United States of America by the Fluorocarbon Program Panel (FPP), of the Chemical Manufacturers Association, which is based on Pyle's treatment of wind fields, has been further refined to include radiative-convective and diurnal codes. It can now be used for coupled perturbation calculations on scenarios that include CO_2 growth. An explicit methane oxidization scheme has also been incorporated into the 2-D model to permit study of the effects of increasing methane concentrations on tropospheric ozone. Transport is still highly parametrized, as in other 2-D models, and cannot yet properly simulate the interactions among dynamics, radiation, and chemistry in a perturbed environment.

The advective transport code based on the isentropic formalism of Tung has been developed and successfully tested. Compared to other 2-D models, it allows a simpler parametrization of transport since it involves only the observed temperature field and one small eddy diffusion term (K_{yy}). The transport in the model has been tested with long lived species involving simple chemistry, such as the upward diffusing species N_2O and CFC 11, and the downward diffusing species, HNO_3, with excellent results. Coupling of the complete photochemical code to the advective code is in progress, to permit testing of chemistry and dynamics.

The major improvement to the 1-D photochemical-radiative convective model during the past year is the incorporation of the solar-flux variability model developed by Lean. This semi-empirical model has been shown to simulate well the short-term variability of solar ultraviolet (UV) flux, possibly providing a more realistic method of modelling the long-term ozone trend associated with the 11-year solar cycle. In its first application, the extent to which the variation of solar UV flux can affect the interpretation of the trend in ozone at 40 km was investigated for the period 1962-1982, encompassing two 11-year solar cycles. A series of time-dependent model runs was performed to define the effect on ozone levels of including solar flux variability with and without the inclusion of historic CFC/CO_2 release data. The magnitude of the calculated response of ozone to solar variability over the 11-year cycle is about 5 per cent in the upper stratosphere and is similar to the calculated response of ozone to CFC release in a decade. In the absence of solar modulation, the calculated concentration of ozone shows a monotonically decreasing trend in the modelled stratosphere, due to an increase in total chlorine. Variations in the 10.7 cm solar radio emission have been used as a proxy for solar UV flux. With this proxy, studies suggest that the ozone response to solar variability may affect the interpretation of the ozone trend analyses at 40 km on a decadal time scale. University of Wisconsin statisticians and AER modellers will assess this effect.

Model calculations have been performed to investigate the difference between the observed and calculated column density of NO_2 at high latitudes in winter. Some of the difference may be due to air-parcel transport through the polar vortex as discussed by Solomon and Garcia. The model calculations have assessed the importance of heterogeneous chemistry in the conversion of active odd nitrogen (NO and NO_2) to the more stable reservoir species HNO_3. Given the uncertainties in current knowledge of heterogeneous chemistry in the stratosphere, these reactions warrant further attention.

To enhance the understanding of the relative importance of dynamics and chemistry on the spatial and temporal distribution of ozone, a two-part budget study of model-calculated atmospheric ozone is in progress. The first part is to complete an annual budget analysis (spatial) and the second to complete a seasonal budget analysis (spatial and temporal). Initial results show that most of the ozone is photochemically produced in the tropical lower stratosphere and then transported to high latitudes. The budget analysis shows that the mechanisms by which much of the stratospheric ozone is removed at high latitudes are photochemical processes rather than the downward transport of ozone into the troposphere. This result underscores the importance of NO_x chemistry on stratospheric ozone distribution at high latitudes. Future plans include the study of the seasonal ozone budget in an attempt to understand the processes responsible for the occurrence of the springtime maximum at high latitudes.

The calculated diurnal behaviour of ClO, based on the 2-D model, agrees rather well with the ground-based observations of Soloman, et al., although the model overestimates ClO. Dominant processes responsible for the calculated diurnal variation of ClO at each altitude have been assigned through detailed budget analyses. The large calculated diurnal variation of ClO in the mid-stratosphere (30-40 km) is due mainly to rapid exchange between ClO_x (Cl + CO) and $ClONO_2$, whereas the calculated diurnal variation in the upper stratosphere (40-50 km) is due to exchange between ClO_x and HOCl. In addition, the gradual rise in

ClO observed during the early morning hours appears to rule out the possibility of the formation of isomers of $ClONO_2$ in the three-body reaction of ClO with NO_2.

Calculated profiles of HO_2 appear to be in reasonable agreement with the measurements of de Zafra, et al. No significant conclusion can be drawn, however, because the variability of stratospheric H_2O could affect the interpretation of the HO_2 measurement. The upper limits set by de Zafra, et al., and Chance and Traub, for H_2O_2 are about at the levels calculated with current models.

The most recent NASA evaluation of kinetic and photochemical data contains revised values that affect ozone calculations. The faster rate now recommended for O + HO_2 results in an increase in the calculated concentration of OH in the upper stratosphere. This higher OH concentration leads to a higher calculated ClO concentration in the 40 km region, resulting in better agreement with observation. However, with the new rates, the calculated ozone concentration in the upper stratosphere is smaller than observed. Smaller values of the O_2 cross section are now incorporated into models and lead to smaller calculated scale heights for the trace gases N_2O, HNO_3, and the CFCs in the stratosphere. This smaller O_2 cross section and a faster rate for $ClONO_2$ formation are responsible for the downward revision of the calculated CFC-induced steady state ozone depletion estimates from 6.1 per cent in 1982 to about 3.3 per cent in 1984.

The calculated effect of the slower rate constant for O + ClO suggested by Birks' measurements is to decrease proportionately the steady-state ozone depletion estimates but increase the ClO concentration in the 40 km region. A calculation using the values of the photoabsorption cross-section of HOCl reported by Birks gives photolysis rate values for HOCl about 50 per cent higher at 70 km but 10 per cent lower at 30 km. Because HOCl could be an important reservoir species in modulating the behavior of ClO in the 45 km region, a determination of the HOCl cross-section temperature dependence should have high priority.

Time dependent 2-D calculations to the year 2050, based on continuous emission of CFCs at the 1979 release rate have been completed and give a stratospheric concentration for total chlorine above 50 km of about 6 ppbv. The largest calculated ozone depletion (5 per cent) occurs at high latitudes in the winter with a lower value of about 2 per cent in the summer. The calculated ozone depletion in the equatorial region is about 2 per cent throughout the year. Results of calculations for N_2O or CH_4 emission scenarios also show significant latitudinal gradients with the largest perturbation occurring at the high latitudes. These results indicate the importance of utilizing a 2-D model to analyse the spatial and temporal inhomogeneity of the perturbation estimates. Fully coupled 2-D perturbation calculations are planned.

A study is under way to assess the non-linear response of ozone to high concentrations of stratospheric total chlorine. 1-D and 2-D calculations considering only changing chlorine compound emissions, indicate that at high chlorine values ($>$ 12 ppbv) the concentrations of NO_2, NO, HNO_3, and HO_2NO_2 below 32 km are suppressed, but those of OH and HO_2 are elevated. This creates a perturbed environment in which chlorine becomes a more efficient catalyst for the recombination of odd oxygen. A more detailed assessment of this non-linear effect is in progress to define the role of increased concentrations of CH_4 and N_2O as well as the consideration of changes in stratospheric circulation. Preliminary findings based on coupled perturbation calculations show that the occurrence and magnitude of this effect are highly dependent on the total NO_x concentration assumed for the present-day atmosphere and the growth rates for atmospheric concentrations of N_2O and CH_4. The results support earlier findings that the calculated effect of CFCs on stratospheric ozone is highly dependent on the future growth rates for the concentrations of other trace species.

FPP is also supporting atmospheric modelling projects in Belgium and Japan. The Belgian group has completed a fully diurnal 1-D model and further developed its coupled radiative-convective-chemical model. These models have been used to conduct studies, the results of which support the above conclusions. The Japanese group has developed a 1-D chemistry-transport model.

2. Atmospheric chemistry

The goal of the FPP chemistry programme is to sponsor research that reduces uncertainties in the kinetic and photochemical data base needed to calculate the possible alteration of stratospheric ozone concentrations by CFCs. However, due to advances in understanding the processes that control stratospheric ozone, the emphasis -- but not the goal -- of this programme is changing. Only a few years ago, calculated profiles for species such as OH and ClO were significantly different from the measured profiles. At the same time, significant ozone depletions were calculated at steady state in scenarios assuming constant CFC emissions. Laboratory kineticists then emphasized the need to reduce the uncertainties in reaction rate and photochemical parameters that were important to the understanding of the atmosphere at that time.

Improvements in the values of these parameters have reduced the difference between measured and calculated profiles for most species and concurrently decreased the calculated effect of CFCs on ozone. A major exception to this is the ozone profile itself, for which models underestimate concentrations in the upper stratosphere and overestimate concentrations in the lower stratosphere. Although significant discrepancies remain, the former obvious deficiencies in laboratory kinetic data for the most part are no longer apparent. However, additional reactions with relatively slow rates have not been adequately studied in the laboratory and may need to be incorporated in the models. Such reactions could be significant for model calculations of the atmosphere at steady state for constant CFC production at current rates (i.e., at stratospheric chlorine concentrations four to five fold greater than present levels) but would have little effect on model calculations of the present day atmosphere. The FPP chemistry programme is changing to give more emphasis to the reactions and photochemistry that will be important at chlorine concentrations substantially higher than present day levels.

This change in emphasis is demonstrated by several projects to determine the products of reactions previously studied. In such cases, if a small fraction of the overall reaction leads to alternative products (i.e., a slow rate constant for the reaction leading to the alternative product), there could be a significant difference in model calculations at steady state CFC levels. A recently completed project indicated that as much as 14 per cent of the products of the reaction OH + ClO could be HCl + O_2. Currently, HO_2 + Cl are assumed to be the only products. The products for the OH + ClO reaction will be redetermined using cryogenic matrix isolation followed by infra-red analysis as part of a separate FPP-funded project. Matrix isolation will also be used to study the product distribution of the HO_2 + ClO reaction. As part of another project, the products of NO_3 photolysis will be determined using laser photolysis of the NO_3 and detection of the products by resonance fluorescence.

Recent studies have shown certain reactions are sensitive to the presence of oxygen, indicating the need to investigate the effect of oxygen on stratospheric kinetics. Studies are planned or underway to investigate the possible effects of oxygen on the reaction rates of ClO with other trace species. To date virtually all stratospheric reaction studies have been conducted in inert gas buffers.

Modeling results, referred to in the 1983 CCOL Report indicate that sodium-chlorine interactions could be important in the 35 to 45 km altitude region of the stratosphere. Consequently, the FPP has funded projects to study three of the key reactions:

$$NaOH + HCl \longrightarrow NaCl + H_2O,$$
$$NaO_2 + HCl \longrightarrow NaCl + HO_2, \text{ and}$$
$$NaCl + h\nu \longrightarrow Na + Cl.$$

The results of these studies will help indicate what additional studies of sodium chemistry are needed.

FPP continues to support research to reduce uncertainties in the kinetic and photochemical data base that is already incorporated into the models. The ability to reduce uncertainties results from improvements in laboratory equipment and the experience gained in handling the highly reactive stratospheric species. In some cases, the improvements are the result of more accurate measurements of the temperature and pressure dependences of the reaction rate constants.

The O + ClO reaction is being studied by two FPP-funded research groups. In one of the studies, the oxygen atom concentration is monitored by chemiluminescence (O + NO); in the other, the oxygen atom concentration is measured by resonance fluorescence and ClO is simultaneously monitored by UV absorption. As a result of these and other studies, it is likely that the recommended value for the O + ClO reaction-rate constant will be reduced, resulting in lowered ozone depletion estimates and higher calculated ClO concentrations in the 40 km region, as mentioned in the preceding section.

Recent results from balloon-borne experiments indicate that previous laboratory measurements overestimated the O_2 cross-sections in the Herzberg continuum. A laboratory experiment, using a 6.65 m photoelectric scanning spectrometer to resolve the lines of the Schumann-Runge bands that are superimposed on the Herzberg continuum, confirmed the balloon results in the 193 to 204 nm region. This project will continue, using a 130 m optical path length multiple reflection cell and a 0.3 m scanning monochrometer to measure the cross sections in the 204 to 240 region.

Reactions with OH and HO_2 are important to the partitioning between the active and reservoir species for both chlorine and nitrogen compounds. Consequently, improving the understanding of HO_x chemistry continues to be a major effort within the FPP programme. The pressure and temperature dependences of the OH + HO_2NO_2 reaction are being studied using a 420 - litre reaction chamber and N_2 and air as diluent gases. The OH + HOCl reaction rate constant is being measured using laser-induced resonance fluorescence detection for OH and a newly developed HOCl source. In a flash photolysis-UV absorption experiment, the rate constants for HO_2 + HO_2 and HO_2 + NO_2 + M are being remeasured. A study of the HO_2 + HO_2 reaction using laser magnetic resonance detection has recently been completed.

The kinetic data for NO_x reactions are generally considered reliable; however, there are still some discrepancies between atmospheric measurements and model calculations that indicate a need for further investigations. Although the chemical data base permits calculations of the atmospheric concentrations of the temporary reservoir species containing NO_x, atmospheric measurements to confirm these calculations are lacking. This is of concern since the calculations could be in serious error. The possibility that isomers of HNO_3 may be formed in the OH + NO_2 + M reaction is being investigated. Formation of an isomer with a shorter photolytic lifetime than nitric acid would decrease the model-calculated concentration of HNO_3.

The first direct measurement at low pressure of the rate constant for the reaction:

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M$$

has been completed. Previously, the rate constant had to be calculated from thermodynamic data and the rate constant for the reverse reaction.

The major destruction mechanism for HO_2NO_2 in the stratosphere is assumed to be photolysis by solar radiation in the 300 nm region. A laser absorption experiment with simultaneous infra-red (IR) detection of the HO_2NO_2 concentration designed to measure the cross-sections in the 300 nm region has begun. Results of this experiment are expected to decrease the uncertainty in the model-calculated HO_2NO_2 concentration (and, hence, OH concentration) in the lower stratosphere.

A workshop on stratospheric chemistry has been organized by FPP in October, 1984, in Goettingen, Federal Republic of Germany, to provide a forum for FPP-funded investigators to exchange recent results and discuss future research needs with many other internationally recognized scientists. A report on this workshop will be available from CMA.

3. Atmospheric measurements

The atmospheric measurements programme sponsors research to obtain observational data that test and extend knowledge of atmospheric processes as they relate to the stratospheric ozone layer. The last few years have seen steady progress in atmospheric measurements, and the next few years promise significantly greater advances. The results of major intercomparison campaigns are becoming available, and newly developed or improved instruments are being deployed. There is still a dearth of crucial observations, e.g., of the temporary reservoir species ($ClONO_2$, $HOCl$, HO_2NO_2), and uncertainty as to the quality of key observations, e.g. OH in the lower stratosphere. The FPP programme has concentrated on the development and improvement of instruments for ground-based measurements of trace species, co-funding of major balloon campaigns, tropospheric monitoring of halocarbons, and supporting laboratory work.

A highlight of the FPP activities since the 1983 CCOL Report has been continued observations by a ground-based microwave instrument at Mauna Kea, Hawaii. The diurnal variation of ClO has been measured with a high degree of confidence. Model calculations relate this diurnal change in ClO to the photochemistry of $ClONO_2$ and other chlorine-containing temporary reservoir species. Observations with the same instrument have been made of the altitude profile of HO_2, and model calculations agree well with these observations. Good-quality data have also been obtained for N_2O and O_3.

A latitudinal survey of trace species is planned using a ground-based IR spectroscopic technique which offers a good prospect of measurements of $ClONO_2$. The record of solar spectra at Kitt Peak National Observatory is being analysed for historical trends in trace gases.

The results from the Atmospheric Lifetime Experiment (ALE) have proved to be more far-reaching than the initial programme objective of establishing the atmospheric lifetimes of CFC 11 and 12. The ALE data base from monitoring sites around the world provides a wealth of information on atmospheric processes, e.g., global circulation, tropospheric chemistry, and local pollution. Consequently FPP funding has been continued beyond 1983. The ALE network will be succeeded by the Global Atmospheric Gases Experiment (GAGE), which will add a number of key molecules such as CH_4 and CO. FPP plans to participate in the funding of GAGE, thereby permitting the Barbados station to continue as part of the network.

Another highlight of FPP activities has been the international Balloon Intercomparison Campaign (BIC), a project co-funded with NASA, the Commission of the European Communities, and organizations from seven countries. The campaign is meeting its objective to improve knowledge of the accuracy of individual experimental techniques by permitting measurements of the same trace species in an air mass at a given time. The balloon observations were complemented by ground-based and aircraft-borne measurements, significantly increasing the atmospheric measurements data base. The campaign took place in two phases: September/October, 1982 and June, 1983. Many questions are being answered about the accuracy of instruments and the reality of the variability in the atmospheric measurements. Unfortunately many of the instruments were destroyed in accidents at the end of phase II. FPP is assisting in the funding for instrument reconstruction. Meanwhile, analysis of data from the key far-IR Fourier Transform emission instruments, which offer the best prospect for the measurement of species such as ClO and OH, is being funded. Theoretical work that combines field data and numerical modelling is being supported. The field data include BIC and other balloon data and data from the LIMS and SAMS satellites. This theoretical work is providing valuable insights into the photochemistry of the atmosphere.

Other FPP co-funding of balloon experiments includes flights of the newly-developed reel-down technique, which incorporates an improved instrument for in situ detection of ClO, of an in situ laser instrument for OH and other species, and of a LIDAR OH instrument.

In support of the far-IR Fourier Transform emission instruments that can detect ClO_x and HO_x species, FPP is funding work in several laboratories to measure pressure-broadening coefficients, line positions, and interferences from weak lines of other atmospheric constituents. Quantitative line strength measurements on a feature of the HO_2 spectrum have been funded to assist in the development of a suitable observational method for this key species. A similar project involving HOCl has recently been funded.

Accurate measurements of the temperature dependence of the IR band strengths for CFC 11 and CFC 12 are being funded. These data are needed to assess the significance of the CFCs for the radiative balance of the atmosphere.

In November, 1983, FPP held a workshop on atmospheric spectra in conjunction with the United States National Bureau of Standards. The presentations addressed three areas: atmospheric monitoring, laboratory measurements, and data collection and retrieval.

4. Ozone trend analysis

The FPP-funded groups at Princeton University, the University of Wisconsin, and the University of Chicago have continued their studies of atmospheric ozone measurements for evidence of changes. Based on total column ozone measurements recorded at 36 ground-based Dobson stations, current trend estimates for the period since 1970, with their 95 per cent confidence limits, are (+0.02 ± 0.94) per cent/decade (Wisconsin/Chicago) and (-0.59 ± 1.16) per cent/decade (Princeton). Adjustments have been made for solar variation and shifts from instrument recalibrations. Neither trend is significantly different from a zero trend based on the 95 per cent confidence limits of uncertainty. The uncertainty limits of the observed trend include the current model estimate of about +0.35 per cent/decade during the period 1970-1980 for the coupled effect of chlorocarbons (including CFCs), N_2O, NO_x, CO_2, and CH_4. However, this trend, with its uncertainty limits, does not validate the current model.

Joint studies by FPP-sponsored investigators from the Universities of Wisconsin and Chicago and investigators from NASA, NOAA, and the Canadian AES have focused on Umkehr ozone profile data for 24-48 km (Umkehr layers 5-9). The 1958-80 data from 13 Umkehr stations showed no statistically significant trend near 40 km as indicated in the 1983 CCOL Report. However, an attempt to correct for volcanic aerosol effects has been made using atmospheric transmission data from Mauna Loa, Hawaii. With that correction, the trend result was (-3.0 ± 1.6) %/decade near 40 km. As noted by the National Academy of Sciences in 1984, "These analyses show that the Umkehr network is approaching the ability to detect trends in the upper stratosphere of the magnitude calculated by atmospheric models. However, significant questions regarding the global representation of the network (heavily concentrated in the Northern Hemisphere) and the accuracy of basing the aerosol correction on transmission observations from a single station need to be resolved". The statistically calculated thresholds of ozone trend detection for the Dobson network are ± 1 %/decade for total ozone and ± 1.6 %/decade for ozone at 40 km.

Analyses of Nimbus 4 BUV satellite total ozone data for the period 1970-1977 suggest an instrument drift of -0.5 per cent/year. 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 Umkehr ozone vertical profiles.

Under joint FPP and NASA support, Wisconsin/Chicago, NASA, NOAA, and AES investigators are studying Nimbus 7 SBUV profile ozone data (November, 1978, to September, 1982). The Wisconsin/Chicago team is also studying balloon ozone sonde profile data from 13 geographical locations.

5. Ozone measurements

FPP is keenly interested in work that will lead to improved observation and monitoring of atmospheric ozone. It has provided travel funds to enable Japanese and Indian scientists to take their instruments to an intercomparison of Dobson ozone instruments to be held in Australia. A project jointly funded by EPA, NOAA, and FPP is under way to automate Umkehr ozone monitoring stations in strategic locations around the world. To date, four Umkehr stations in the Northern Hemisphere have been upgraded to take automated, high quality ozone profile measurements at regular intervals (i.e., daily, weather permitting). When the project is completed, there will also be three stations with similar instrumentation in the Southern Hemisphere.

In the Umkehr ozone profile trend analysis, an aerosol correction has been based on the only available observations which are from a single measuring station and may not be globally representative. FPP is providing partial funding for a project to gather and analyse atmospheric transmission data from a number of geographically different sites, in order to study the aerosol effects on stratospheric ozone measurements. Because the correction of the Umkehr technique to compensate for aerosol scattering is very significant and is least accurate in the critical 40-45 km and 15-20 km regions of the atmosphere, the FPP is also encouraging exploratory work which could lead to a new ozone monitoring instrument, e.g. LIDAR.

6. Temperature trend analysis

Calculations of the radiative effect of several trace gases, principally CO_2 but including CFCs, suggest that the techniques of trend analysis could also be applied to historical data of the atmospheric temperature profile. To this end Princeton investigators, with FPP funding, have analysed 1964-1979 weather balloon radiosonde temperature data from 128 stations world-wide at altitude levels ranging between the surface and 24 km. With or without an approximate correction for the temperature change that may have resulted from the Mount Agung volcanic eruption in 1963, a statistically significant cooling pattern of approximately 0.5°C/decade was detected at 24 km. A slight warming (not statistically significant) was seen at or below 11 km. The observed trends are qualitatively in accord with the calculated temperature changes for the fully coupled case in which CO_2, chlorocarbons, N_2O, NO_x, and CH_4 are considered jointly.

7. Production and release of CFC 11 and CFC 12

FPP has continued to collect and report production, sales, and release data for CFC 11 and CFC 12. The latest report, covering production, sales, and releases up to the end of 1983, is expected to be issued in October, 1984, and will be supplied to CCOL. This latest report is confined to data from reporting companies only, estimated as approximately 80-85 per cent of the world total. In previous reports, FPP had attempted to estimate production in the rest of the world by extrapolation from data published for the Union of Soviet Socialist Republics covering the period 1968-1975. The data suggested an 18 percent per annum growth for that period. Use of this 18 percent extrapolation in the absence, of more recent production figures for the USSR, Eastern Europe, or the Peoples Republic of China, however, progressively introduces a large error into estimates of global releases. Since the data base is incomplete, accurate estimates of world-wide releases cannot be made. A description of the changes in the report and the justification for the changes will be incorporated with the most recent calculations.

8. Climate and biological effects

The FPP has funded research with the objective of addressing the effects of CFCs and other atmospheric trace gases on the temperature of the earth's surface. A sensitivity study using a 1-D vertical-radiative-convective model showed that the calculated combined surface warming caused by increases of CFC 11 and CFC 12 from 0 to 2 ppbv each lies in the range of 0.3 - 0.9 K, compared to the 2-4 K range calculated for a doubling of CO_2.

FPP is funding a statistical analysis of the various models that are available of the relationship between changes in solar UV-B and changes in the incidence of non-melanoma skin cancer.

INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS

Resolution

Future action by the International Council of Scientific Unions (ICSU) relevant to the World Plan of Action of the Ozone Layer is contained in the following resolution adopted by the twentieth General Assembly of the International Council of Scientific Unions (ICSU), meeting at Ottawa, Canada (September 23 - 28), which reads: The General Assembly of the International Council of Scientific Unions, Taking into consideration the discussions that have occurred over the past year relating to global change in the interaction between the physical and living world and the ICSU symposium held in Ottawa on 25 September 1984 and expressing its continued support for existing related programmes; invites the Executive Board to establish an ad hoc planning group on global change to review the relevant ongoing activities of bodies in the ICSU family and other organizations, to identify priority subjects for early action and to develop a coherent programme, after analysis of the possible contribution of ICSU Scientific Unions, National Members and specialist bodies, and requests ICSU to provide the necessary resources to enable the planning group to undertake this task; <u>invites</u> National Members of ICSU to support the development of the global change programme and to consider their possible contributions to the programme; and <u>requests</u> the planning group to report to the twenty-first General Assembly in 1986.

SECTION IV

PRODUCTION AND SALES DATA FOR CHLOROFLUOROCARBONS 11 AND 12 UP TO AND INCLUDING 1983 - PROVIDED BY PARTICIPATING COMPANIES REPORTING TO THE CHEMICAL MANUFACTURERS ASSOCIATION

Schedule 1 - Listing of reporting companies

Schedule 2 - A tabulation of the total production of CFC 11 on an annual basis for the period 1931 to 1983 inclusive, from reporting companies

Schedule 3 - A tabulation of the total production of CFC 12 on an annual basis for the period 1931 to 1983 includive, from reporting companies

Schedule 4 - A tabulation of the deviation estimate of total production of CFC 11 and CFC 12 applying the submitted estimate of probable error from reporting companies

Schedule 5 - A tabulation of the total CFC 11 sales by category for years 1976 to 1983 inclusive, from reporting companies

Schedule 6 - A tabulation of the total CFC 12 sales by category for years 1976 to 1983 inclusive, from reporting companies

Schedule 7 - A tabulation of the total CFC 11 and CFC 12 sales by hemisphere for the period 1931 to 1983 inclusive, from reporting companies

Schedule 8 - A tabulation of the total production of CFC 11 and CFC 12 on an annual basis from companies in India and Argentina up to and including 1982

The following schedules of production and consumption have been compiled from the article cited in note 5 (see list of notes given after the schedules);

Schedule 9 - A tabulation of USSR production of CFC 11 and CFC 12 for the years 1968 to 1975 inclusive

Schedule 10 - A tabulation of the total consumption of CFC 11 and CFC 12 in the USSR for the years 1968 to 1975 inclusive

Schedule 1

LIST OF REPORTING COMPANIES

The following is a list of the reporting companies, including any related subsidiaries and/or joint ventures that reported production and release data:

1. Akzo Chemie B.V. (Netherlands)
2. Allied Corporation (United States)
    - (a) Allied Canada Inc. (Canada)
    - (b) Quimobasicos, S.A. (Mexico)
3. Asahi Glass Co., Ltd. (Japan)
4. ATOCHEM, S.A.
   New parent company of the Produits Chimiques Ugine Kuhlmann ((a) Pacific Chemical Industries Pty. Ltd (Australia), (b) Ugimica S.A. (Spain), (c) Produven (Venezuela), CHLOE Chimie (France) and S.I.C.N.G. Thessalonica (Greece)
5. Australian Fluorine Chemical Pty. Ltd. (Australia)
6. Daikin Kogyo Co. Ltd. (Japan)
7. Du Pont Canada, Inc. (Canada)
8. E.I. du Pont de Nemours and Company, Inc. (United States)
    - (a) Du Pont de Nemours (Nederland) N.V.
    - (b) Ducilo S.A. (Argentina)

    (c) Du Pont do Brasil S.A. (Brazil)
    (d) Halocarburos S.A. (Mexico)

9. Essex Chemical Corporation (Racon) (United States)

10. Hoechst AG (Federal Republic of Germany)

    (a) Hoechst Iberica (Spain)
    (b) Hoechst do Brasil Quimica e Farmaceutica S.A.

11. Imperial Chemical Industries PLC (United Kingdom)

    (a) African Explosives and Chemical Industries, Ltd.

12. I.S.C. Chemicals Ltd. (United Kingdom)

13. Kaiser Aluminium and Chemical Corporation (United States)

14. Kali-Chemie Aktiengesellschaft (Federal Republic of Germany)
    (a) Kali-Chemie Iberia SA (Spain)

15. Mitsui Fluorochemicals Co., Ltd. (Japan)

16. Montefluos S.p.A. (formerly Montedison S.p.A.) (Italy)

17. Navin Fluorine Industries (India)

18. Pennwalt Corporation (United States)

19. Showa Denko, K.K. (Japan)

20. Union Carbide Corporation (United States) (Union Carbide ceased production in 1977; sales by Union Carbide have been included by category in this report)

Schedule 2

A tabulation of the total production of CFC 11 on an annual basis for the period 1931 to 1983 inclusive, from reporting companies[a]

Year	Production[b] (Metric tons)	Year	Production[b] (Metric tons)
1931	-	1957	33,929
1932	-	1958	29,529
1933	-	1959	35,562
1934	45	1960	49,714
1935	45	1961	60,464
1936	91	1962	78,106
1937	136	1963	93,304
1938	91	1964	111,085
1939	91	1965	122,833
1940	181	1966	141,022
1941	272	1967	159,756
1942	318	1968	183,116
1943	408	1969	217,271
1944	363	1970	238,136
1945	363	1971	263,175
1946	726	1972	306,856
1947	1,315	1973	349,085
1948	2,994	1974	369,724
1949	4,491	1975	314,068
1950	6,623	1976	339,832
1951	9,072	1977	320,464
1952	13,562	1978	308,852
1953	17,282	1979	289,483
1954	20,911	1980	289,619
1955	26,263	1981	286,943
1956	32,477	1982	271,443[c]
		1983	290,804
		Total production	5,692,298

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[a] See note 1.
[b] See note 2.
[c] See note 6.

Schedule 3

A tabulation of the total production of CFC 12 on an annual basis for the period 1931 to 1983 inclusive from reporting companies[a]

Year	Production[b] (Metric tons)	Year	Production[b] (Metric tons)
1931	544	1957	74,163
1932	136	1958	73,437
1933	318	1959	87,589
1934	680	1960	99,428
1935	998	1961	108,499
1936	1,724	1962	128,095
1937	3,084	1963	146,420
1938	2,812	1964	170,097
1939	3,946	1965	190,056
1940	4,536	1966	216,182
1941	6,260	1967	242,763
1942	5,942	1968	267,484
1943	8,210	1969	297,285
1944	16,738	1970	321,099
1945	20,094	1971	341,556
1946	16,647	1972	379,884
1947	20,140	1973	423,338
1948	24,766	1974	442,798
1949	26,127	1975	380,973
1950	34,564	1976	410,729
1951	36,242	1977	382,833
1952	37,240	1978	372,082
1953	46,493	1979	357,159
1954	49,124	1980	350,219
1955	57,606	1981	351,308
1956	68,674	1982	328,039
		1983	353,359
		Total production	7,790,519

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[a] See note 1.

[b] See note 2.

Schedule 4

A tabulation of the deviation estimate of total production of CFC 11 and CFC 12 applying the submitted estimate of probable error from reporting companies[a/]

(Metric tons)

Chemical	Total Production	Deviation[b/]
CFC-11	5,692,298	60,823
CFC-12	7,790,519	77,013

a/ See note 3.

b/ See note 2.

Schedule 5

A tabulation of the total CFC 11 sales by category for years 1976 to 1983 inclusive, from reporting companies[a/]

(Metric tons)

Year	Refrigeration	Blowing agent closed-cell foam	Blowing agent open-cell foam	Aerosol propellant	All other uses	Total sales
1976	26,898	52,073	44,906	195,000	20,956	339,833
1977	24,721	65,227	52,118	164,609	13,789	320,464
1978	27,216	66,089	53,116	143,517	18,915	308,853
1979	30,481	80,105	51,619	111,584	15,694	289,483
1980	29,030	84,051	53,116	105,098	18,325	289,620
1981	27,669	97,704	50,485	93,985	17,101	286,944
1982	24,325	95,937	45,632	92,442	14,107	271,443
1983	25,691	97,861	54,610	93,607	19,035	290,804
Total	216,031	638,047	405,602	999,842	137,922	2,397,444

[a/] See note 1

Schedule 6

A tabulation of the total CFC 12 sales by category for years 1976 to 1983 inclusive, from reporting companies[a/]

(Metric tons)

Year	Refrigeration	Blowing agent closed-cell foam	Blowing agent open-cell foam	Aerosol propellant	All other uses	Total sales
1976	127,823	6,441	8,528	237,275	30,663	410,730
1977	156,081	10,161	13,064	186,200	17,327	382,833
1978	159,483	18,098	8,482	163,702	22,317	372,082
1979	164,836	18,053	15,014	142,973	16,284	357,160
1980	162,250	23,859	12,292	138,119	13,699	350,219
1981	167,058	21,319	15,830	127,596	19,505	351,308
1982	155,809	22,725	13,608	116,029	19,867	328,038
1983	175,548	26,188	16,170	118,009	17,444	353,359
Total	1,268,888	146,844	102,988	1,229,903	157,106	2,905,729

[a/] See note 1

Schedule 7

A tabulation of the total CFC 11 and CFC 12 sales by hemisphere for the period 1931 to 1983 inclusive from reporting companies[a]

(Metric tons)

	Northern Hemisphere	Southern Hemisphere	Total sales
CFC 11	5,451,220	241,078	5,692,298
CFC 12	7,380,881	409,638	7,790,519

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[a] See note 1.

Schedule 8

A tabulation of the total production of CFC 11 and CFC 12 on an annual basis reported from companies in India and Argentina up to and including 1982[a]

(Metric tons)

Year	Production of CFC 11	Production of CFC 12
1968	45	272
1969	45	318
1970	45	454
1971	91	635
1972	136	862
1973	590	1,270
1974	771	1,678
1975	817	1,678
1976	817	2,540
1977	544	2,177
1978	499	2,132
1979	544	2,087
1980	227	1,089
1981	227	1,089
1982	408	1,406
	5,806	19,687

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[a] See notes 1 and 4

Schedule 9

A tabulation of USSR production of CFC 11 and CFC 12 for the years 1968 to 1975 inclusive[a/]

(Metric tons)

Year	Production of CFC 11	Production of CFC 12
1968	1,400	9,800
1969	2,200	12,200
1970	2,500	13,500
1971	2,900	16,200
1972	3,700	18,500
1973	4,100	20,100
1974	6,200	25,900
1975	7,500	31,700
Total	30,500	147,900

[a/] See note 5

Schedule 10

A tabulation of the total consumption of CFC 11 and CFC 12 in the USSR for the years 1968 to 1975 inclusive[a/]

(Metric tons)

Year	Refrigeration	Foam for Refrigerators	Aerosol Propellants	Other
1968	7,240	-	3,590	300
1969	8,090	-	5,780	500
1970	8,640	-	6,640	850
1971	10,200	20	7,970	930
1972	11,710	30	4,620	1,000
1973	12,390	100	4,950	1,100
1974	16,000	200	13,360	1,480
1975	18,290	300	18,240	1,680
Total	92,560	650	65,150	7,840

[a/] See note 5

Notes to 1983 production and sales data for chlorofluorocarbons CFC 11 and CFC 12

Note 1 - new participant

Beginning in 1983, the production and sales data from Navin Fluorine Industries are included in the report.

Note 2 - production amounts

These amounts exclude any production of a product used as an intermediate for chemical or plastic production.

Note 3 - calculation of deviation

The deviation presented in schedule 4 was computed by the square root of the sum of the squares method. A 95 per cent confidence level was used for this calculation.

Note 4 - Production amounts for India and Argentina

The amounts recorded up to and including 1982 were compiled for the following companies:

(1) Tool Research S.A.

(2) I.R.A., S.A.

(3) Aegis Chemical Industries, Ltd.

(4) Navin Fluroine Industries

Tool Research S.A. and I.R.A., S.A., both located in Argentina, ceased manufacturing in 1979. From 1980 to 1982, therefore, estimates are for India only. Moreover, in 1981, Everest

Refrigerants Ltd. came under new ownership and is now known as Aegis Chemical Industries Ltd. Its production for 1983 has not been estimated.

Note 5 - USSR production amounts

These figures were calculated on the basis of the data in tons given by E.P. Borisenkov and Y.E. Kazakoc, Tr. Gl. Geofiz. Obs. 1980, no. 438, pp. 62-74.

Note 6 - Correction of error

The reported production and sales figures for 1982 have been reduced by 11,191 metric tons to correct an overreporting error.

ABBREVIATIONS

AES - Atmospheric Environment Service of the Department of the Environment (Canada)

ALE - Atmospheric Lifetime Experiment

ATMOS - Atmospheric trace molecules by spectroscopy

BIC - Balloon Intercomparison Campaign

BOIC - Balloon Ozone Sonde Intercomparison Campaign

Brx - Bromine species

BUV - Back-scattered ultraviolet radiation

CCOL - Co-ordinating Committee on the Ozone Layer

CCSS - Comparative and Complementary Stratosphere Study

CFCs - Chlorofluorocarbons

CFC 11 - $CFCl_3$

CFC 12 - CF_2Cl_2

CFC 13 - CF_3Cl

CFC 21 - $CHFCl_2$

CFC 22 - CHF_2Cl

CFC 113 - $C_2F_3Cl_3$

CFC 114 - $C_2F_4Cl_2$

CFC 115 - C_2F_5Cl

CH_4 - Methane

ClX - Chlorine species

ClO_x - Oxides of chlorine

CIR - Cooled infra-red radiometer

CMA - Chemical Manufacturers Association

$cm^3 molecule^{-1} S^{-1}$ - Cubic centimetres per molecule per second

CNRS/SA	-	Centre National de la Recherche Scientifique/Service d'Aéronomie
CO_2	-	Carbon dioxide
CRCCHT	-	Centre de Recherche sur la Chimie de la Combustion et des Hautes Temperatures (France)
DGRST	-	Délégation Générale à la Recherche Scientifique et Technique (France)
DMS	-	Dimethyl sulphide
DMSP	-	Defense Meteorological Satellite Program (United States)
ECE	-	Economic Commission for Europe
EEC	-	European Economic Community
EERM	-	Etablissement d'Etudes et de Recherche Météorologiques (France)
EOS	-	Earth Observation Mission (NASA Spacelab)
ESA	-	European Space Agency
EPA	-	Environmental Protection Agency (United States)
FAA	-	Federal Aviation Administration (United States)
FC	-	Fluorocarbons
FC14	-	CF_4
FC116	-	C_2F_6
FPP	-	Fluorocarbon Program Panel (United States)
FTIR	-	Fourier transformation infra-red
GAGE	-	Global Atmospheric Gases Experiment
GC/MS	-	Gas chromatograph/mass spectrometer
GHz	-	Gigahertz
GOOS	-	Global Ozone Observing System
GSFC	-	Goddard Space Flight Center (United States)

HALOE - Halogen occultation experiment

HIRS - High-resolution infra-red sounder

HO_x - Oxides of hydrogen

HO_2NO_2 - Pernitric acid

HNO_3 - Nitric acid

IAGA - International Association of Geomagnetism and Aeronomy

IAMAP - International Association of Meteorology and Atmospheric Physics

ICSU - International Council of Scientific Unions

IFA/CNR - Institute for Physics of the Atmosphere (Rome)

IGY - International Geophysical Year

IOC - Intergovernment Oceanographic Commission

IR - Infra-red

IRIS - Infra-red interferometer spectrometer

ISAMS - Improved stratospheric and mesospheric sounder

IUGG - International Union of Geodesy and Geophysics

JPL - Jet Propulsion Laboratory

k - rate constant

K - Degree Kelvin

KFA - Institut für Chemie der Kernforschungsanlage (Jülich, Federal Republic of Germany)

km - Kilometre

kt - kiloton (1,000 metric tons)

LAPETH - Laboratory of Atmospheric Physics, Eidgenossische Technische Hochschule (Zurich)

LIDAR - Light detection and ranging laser radar system

LIMS - Limb infra-red monitor of the stratosphere

LIPSP - Laboratoire de Physique Stellaire et Planétaire (France)

LRIR - Limb radiance inversion radiometer

MAP - Middle Atmospheric Programme

MAS - Microwave Atmospheric Sounder

mb - Millibar

$m^{-2}h^{-1}$ - Per square metre per hour

mj - Millijoule

MMS - Molecular modulation spectroscopy

MO - Meteorological Office (United Kingdom)

molecule cm^{-2} - Molecules per square centimetre

molecule cm^{-3} - Molecules per cubic centimetre

MPI - Max Planck Institute for Aeronomy

MST - Mesosphere stratosphere explorer

ug - 10^{-6} gram

um - 10^{-6} metre

NASA - National Aeronautics and Space Administration (United States)

NILU - Norwegian Institute of Air Research

nm - 10^{-9} metre

NO_y - Total odd-nitrogen

NO - Nitric oxide

N_2O - Nitrous oxide

NO_2 - Nitrogen dioxide

N_2O_5 - Nitrogen pentoxide

NO_x - Oxides of nitrogen

NOAA - National Oceanic and Atmospheric Administration (United States)

NOBLE - Nitrogen Oxides Balance Experiment

NPL - National Physical Laboratory (United Kingdom)

OECD - Organisation for Economic Co-operation and Development

OHP - Observatoire de Haute-Provence (France)

ONERA - Office National d'Etudes et de Recherche Aérospatiales (France)

PMR - Pressure-modulated radiometer

ppb - Parts per billion

ppbv - Parts per billion by volume

ppmv - Parts per million by volume

ppt - Parts per trillion

RAF - Radiation amplification factor

RAL - Rutherford Appleton Laboratory (United Kingdom)

SAGE - Stratospheric Aerosol and Gas Experiment

SAMS - Stratospheric and mesospheric sounder

SBUV - Solar back-scattered ultraviolet radiation

SSBUV - Shuttle solar back-scattered ultraviolet radiation

SCOPE - Scientific Committee on Problems of the Environment

SCOSTEP - Scientific Committee on Solar Terrestrial Physics

SIBEX - Submillimetre Infra-red Balloon Experiment

SME - Solar Mesosphere Explorer Satellite

SMERF - Solar Mesosphere Explorer Rocket Flights

SOD - Superoxide dismutase

SO_x - Oxides of sulphur

SSU	-	Stratospheric Sounding Unit
STP	-	Standard temperature and pressure
STRATOZ	-	Radiometric monitoring of stratospheric ozone experiment
t/a	-	Tons per annum
TOC	-	Total ozone content
TOMS	-	Total Ozone Monitoring System
TOVS	-	Tiros operational vertical sounder
UNEP	-	United Nations Environment Programme
UV	-	Ultraviolet radiation
UV-A	-	Ultraviolet radiation between 320 and 400 nm
UV-B	-	Ultraviolet radiation between 280 and 320 nm
UV-C	-	Ultraviolet radiation between 100 and 280 nm
WHO	-	World Health Organization
WMO	-	World Meteorological Organization
WODC	-	World Ozone Data Centre
1-D	-	One-dimensional
2-D	-	Two-dimensional
3-D	-	Three-dimensional