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Summary of Recent Research Results

Contribution

by

Chemical Manufacturers Association

Research Program Directed by the

Chemical Manufacturers Association Fluorocarbon Program Panel

Progress Report

to the UNEP Co-ordinating Committee on the Ozone Layer

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OZONE TREND ANALYSIS

The analyses of ground-based (Dobson) and satellite ozone data for trends by the two separate U.S. statistical groups funded by CMA show that during the period 1970-79 there was an increase in the column ozone concentration which however was not statistically significant. The two studies find an increase of 0.8 and 1.7 percent per decade. Using data from 36 Dobson stations, these groups have quantified the uncertainty in the detection of any long term trend regardless of cause to be $\pm$ 1.3 percent per decade in the first case and $\pm$ 2.0 percent in the second, expressing the uncertainty as 95 percent confidence limits. These numbers represent the combined error from instrument drifts, station-to-station variance, the white noise, and long-term trends that can be revealed by a 22-year data record. This error was previously estimated at $\pm$ 5.4 percent at the Harpers Ferry NASA Workshop (NASA Ref. Publication 1049, Tab 6.13, p. 325, Dec. 1979). The 1981 WMO/NASA Workshop presents an estimated range for this uncertainty of 1.6 percent to 3.8 percent (preliminary draft).

Because the Dobson stations are land-based and concentrated in the Northern Hemisphere, it has been suggested that the trend estimated from the 36 stations may not represent the true global trend. Satellite data from Nimbus IV over the period 1970-77 have been examined, and it has been shown that the difference between the trend derived from the global satellite ozone data and that derived from the satellite ozone data above the 36 stations studied is small. Hence, there is no statistically significant spatial sampling bias according to this analysis.

The sensitivity of the ozone trend analysis results to the effects of nuclear testing in the 1960's has been examined. According to theory, the extent of the depletion of stratospheric ozone due to the injection of large quantities of NO_x into the stratosphere at that time should have reached a maximum of 2-4 percent, followed by recovery to equilibrium levels. The trend estimate and trend precision for ozone change during the 1970's are essentially unaltered by the inclusion of the effects of nuclear testing.

Associated work by two participating member companies of the CMA Fluorocarbon Program Panel have confirmed the above conclusions drawn from the Dobson station column data. In addition, a detailed study of the Dobson station data from Arosa extending over 48 years has been made. This work has produced threshold limits for the detection of an effect due to CFC release of $\pm$ 2-3 percent per decade. This figure can be compared with the 1979 estimates of 5 percent in the NAS report and 5.7 percent in NASA 1049.

Statistical analysis of the 33-48 km Umkehr data from 15 Dobson stations with more than 50 observations, showed a statistically insignificant increase over the period 1970-79. These results suggest that ozone depletion has not occurred in the region of the stratosphere calculated to be most sensitive to CFC effects.

In support of the conclusion that no depletion of ozone has so far occurred, measurements of sunburn units, essentially equivalent to the erythema action spectrum (EAS), at various locations from 1974 to 1979, have shown no increase in intensity. If the amplification factor relating changes in ozone to changes in incident EAS radiation is correct then the changes in sunburn units should be a sensitive indicator of ozone changes.

ATMOSPHERIC MEASUREMENTS

The emphasis of the measurement program has continued to be on ground-based measurements, which produce a large number of measurements of a stratospheric species over a long period of time, rather than the isolated measurements over a few hours from in situ methods. Data on column ClO from measurements made in Massachusetts in 1980 have been published, showing results consistent with Anderson's balloon measurements. The winter measurement program in Massachusetts in 1981 yielded only a few measurements due to the high water vapor levels in the mild winter, but the equipment has been operated successfully at Mt. Hopkins observatory near Tucson, Arizona, for a 4-week period. The data are expected to characterize the atmospheric variability of ClO and the diurnal cycle, as well as yielding an intercomparison with Waters' balloon-borne ClO measurement program.

Tropospheric measurements other than ALE continue (see following section). In a preliminary study, measured values of CFC-21 in the Red Sea and Indian Ocean were considerably elevated over the background 1 ppt level, and it is speculated that this may be the result of decomposition of CFC-11 on sand. An experiment is in progress to test this hypothesis by sampling an air parcel as it enters the desert area and again several hundred kilometers downwind. The samples will be analyzed for CFC-11 and CFC-21 to determine if CFC-11 concentrations are reduced during passage over the desert and if corresponding amounts of CFC-21 are formed.

Further data reduction from the National Physical Laboratory/University of Florence flight from Texas in April 1979, a program to make aircraft-borne ClO measurements, and an international data analysis program between the University of Denver and the University of Reims are in progress. A balloon

flight is planned to determine the concentration of $ClONO_2$ by several techniques simultaneously, and to search for HOCl and HO_2NO_2. An IR measurement balloon is also planned in conjunction with Anderson's reel-down experiment, presently scheduled for spring 1982.

Method development has continued to be given considerable support.

- A UV method for ClO measurement is nearing completion.
- A simple method for measuring methyl chloride in ambient air and in river or sea waters has been completed.
- A new technique for accurately measuring N_2O in the atmosphere using a tunable diode laser has been developed.
- A flow system using Laser Magnetic Resonance detection for measuring the rate constants of important reactions at pressures and temperatures corresponding to those actually present in the stratosphere has been built.
- An evaluation is being made of the application to other species of the ground-based microwave technique now being used successfully and routinely for ClO and for the simultaneous measurement of ClO and O_3.
- Studies are in progress to record the far-infrared laboratory spectra of a number of molecules of interest in current stratospheric chemistry, in particular the spectrum of HOCl. The apparatus can be flown on a balloon for stratospheric measurements.

A study to measure total chlorine in air by passage of the sample through a microwave discharge followed by measurement of chlorine resonance lines showed the sensitivity of the method was not sufficient to permit total chlorine analysis of stratospheric air samples.

ATMOSPHERIC LIFETIME EXPERIMENT (ALE)

Preliminary results from two years' data indicate an atmospheric lifetime for CFC-11 of roughly one half of the currently calculated lifetime (75 years) due to the stratospheric removal process alone. The error bars in the observed lifetime are, however, still large - of the order of 15 years to infinity. Three years of data will provide a much firmer estimate.

Computer models, in contrast to this real world experiment, contain the assumption that there is no destruction of CFC-11 or CFC-12 other than by stratospheric processes. If lifetimes one half of those now assumed are considered, the calculated steady state ozone depletion would be reduced by 50 percent.

The four original ALE monitoring stations have now been in operation for over 36 months and performance continues at a high level. Calibration checks have been completed on the first 30 months data. A fifth station on the Oregon Coast (Northwest USA) has been in operation since March 1980. The data record at this station for CFC-11 has been obtained from parallel equipment since 1979, augmenting the data in the important northern hemisphere temperate zone.

Work using an exponential dilution chamber has been completed to supplement the data on the absolute calibration of the ALE network standards. In addition, a coulometric technique has been used to provide a further absolute calibration value. The three independent calibrations of the reference standards agree with each other to within a few percent.

CFC-11 AND CFC-12 PRODUCTION

Production and release data for CFC-11 and CFC-12 have again been collected from the world CFC manufacturers and the data submitted separately to UNEP. These figures show that world CFC production peaked in 1974 and that the 1980 production was 18.1 percent below the 1974 level.

ATMOSPHERIC CHEMISTRY

The industry program to elucidate stratospheric chemistry centers on species and reactions likely to affect the chlorofluorocarbon/ozone depletion theory, e.g. Cl, ClO, higher chlorine oxides, $ClONO_2$, HOCl, CH, and HO_2, and on reactions that might constitute ozone production cycles. The pressure and temperature dependences and product distributions of important reactions have received increased emphasis recently.

Much of the work is concentrated on examination of the products produced from stratospheric reactions. The disappearance of reactants is well characterized for many of these systems, but a single product path has often been assumed. These studies include:

- $ClO + NO_2$ where isomers of $ClONO_2$ are being sought.
- $Cl + O_3$ where excited singlet O_2 ($^1\Delta_g$, $^1\Sigma^+_g$), which can react with O_3 to produce O atoms, has been observed (although this observation is unlikely to be of great importance in the stratosphere).
- $HO_2 + Cl$ where $HCl + O_2$ is the major product, but $OH + ClO$ is not insignificant.
- $HO_2 + ClO$ where one investigator has set an upper limit of 2 percent for the $HCl + O_3$ branch.

- $OH + ClO$ where the $HOCl + O$ and $HCl + O_2$ minor branches are being sought.

- $Cl + HOCl$.

Reaction rates for $HO_2 + HO_2$, $OH + HO_2NO_2$, $OH + HO_2$, $OH + HNO_3$, and $HO_2 + Cl$ are currently under investigation in the important area of HO_x chemistry. Atmospheric observations, particularly of ClO profiles, indicate that OH concentration in the lower stratosphere is considerably less than has been calculated by the theoretical models. Although agreement is much improved with the latest chemistry, considerable uncertainty still surrounds the OH chemistry in this region. Study of the above important reactions has been undertaken to try to resolve this question.

Sources of odd oxygen are being explored by study of the reactions $Cl + O_3$, $Cl + ClOCl$, $Cl + OClO$, and the photolysis of HOCl, ClOO, and OClOO.

A two-day chemistry workshop was held in March, bringing together a large number of eminent kineticists to discuss the current uncertainties in stratospheric chemistry. A report on this workshop is available from CMA.

MODELING

Emphasis by the two CMA FPP-supported modeling groups is now being placed on 2-D models. Major conclusions from this work are given below. It should be noted that improved knowledge of the chemistry during the last year has considerably reduced the calculated steady-state ozone depletion potential of CFCs. This underlines the uncertainties associated with the model calculations and illustrates the danger of drawing firm conclusions from them.

A present-day (1980) depletion of 0.6 percent is indicated by 1-D model calculations based on historical release of CFCs. Continued emissions at the 1977 production levels are calculated to give 1.2 percent depletion by 1990, increasing to 1.7 percent in the year 2000. Continued release of CFCs gives an ultimate calculated reduction in global average ozone of 6.1 percent at steady state. This compares with 10 percent in the UNEP-CCOL 1980 report and 15 percent in the UNEP-CCOL 1979 report.

These values have been calculated with a slower rate of formation of chlorine nitrate relative to previous recommendations. If the fast formation rate (included within the specified uncertainty in current recommendations) is used, steady state depletions of about 5.0 percent are calculated. The correct rate of formation of chlorine nitrate is still unresolved.

Recent changes in the chemistry used for model calculations mean that there is no longer a prediction of much greater depletion at high latitudes than at low latitudes. Although there is still a somewhat greater depletion at the North Pole than at the equator in current calculations, the difference is now only about 20 percent.

Another shift in the location of ozone depletion has occurred in the vertical dimension. The high depletion formerly calculated in the lower stratosphere has virtually disappeared, so that most ozone depletion is now calculated (as it once was) to occur above 30 kilometers. Both 1-D and 2-D results indicate a net increase in ozone due to chlorine in the lower stratosphere (primarily in tropical regions in the 2-D model).

The chemical reactions have been considered to be the best known and firmest of the model input data, yet surprising and dramatic changes in chemistry have produced significantly lower values and different distributions of ozone depletion than those calculated in 1979. Considerable uncertainty still remains throughout the chemical scheme.

RESEARCH UNDER CONSIDERATION

The CMA program of research in chemistry, modeling, and measurements is continuing through 1982.

Specific new research projects being considered include:

- automation of Dobson stations to facilitate Umkehr measurements.
- cofunding with NASA and other groups of balloon flights for the intercomparison of various techniques for measuring HCl in the stratosphere.
- investigation of the proposed complex of ClO with oxygen, namely $ClO.O_2$.