# International Conference on Problems Related to the Stratosphere

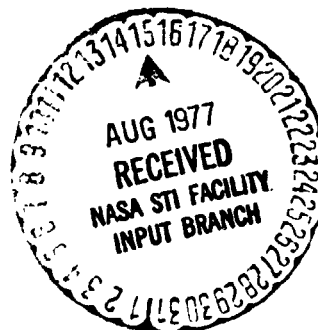Held at Utah State University, Logan, Utah
September 15-17, 1976

National Aeronautics and
Space Administration

**Jet Propulsion Laboratory**
California Institute of Technology
Pasadena, California 91103

# International Conference on Problems Related to the Stratosphere

Held at Utah State University, Logan, Utah
September 15–17, 1976

Edited by
W. Huntress, Jr., and D. Maple

May 15, 1977

# FOREWORD

In the last five years there has been a growing awareness that man's activities can have harmful effects in the stratosphere. To the original source, exhausts of high-flying aircraft, have now been added rocket exhausts, halocarbons, and denitrification of fertilizers. One consequence of the public concern was an instruction to NASA by Congress, as part of the Fiscal Year 1976 Authorization Act, to develop and implement a comprehensive program of research, technology, and monitoring of the phenomena of the upper atmosphere. The aims are to provide an understanding of this region and to maintain its chemical and physical integrity.

The conference summarized in this volume was in effect a "send-off" for NASA's program. The aim was to bring together scientists in a wide range of the relevant disciplines, and politiciars and administrators concerned with the corresponding social problems. Panel discussions and invited papers were organized on scientific and policy issues, with speakers chosen to represent opposing viewpoints. Contributed papers were mainly presented in a poster exposition, though a few were given orally. The discussions were lent a special spice by the release, just a few days earlier, of the reports on the halocarbon issue by the Committee on Impacts of Stratospheric Change of the National Academy of Sciences, and by its Panel on Atmospheric Chemistry.

The Chairman's task was immensely lightened by the hard work of the Executive Secretary, Wesley Huntress, and his secretary, Pamela Fisher. Thanks go also to the international Organizing Committee, especially Carroll Pegler, and to our hosts in Logan, headed by Clayton Clark.

Donald M. Hunten
Conference Chairman

## SPONSORING ORGANIZATIONS

U. S. National Aeronautics and Space Administration

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International Association of Meteorology and Atmospheric Physics

International Association of Geophysics and Aeronomy

American Geophysical Union

American Meteorological Society

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| | |
|---|---|
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## CONFERENCE AGENDA

### POSTER EXPOSITION

A.   Exposition on Models and Theoretical Studies

B.   Exposition on Instruments and Stratospheric Measurements

C.   Exposition on Laboratory Measurements

### ORAL SESSIONS

#### Wednesday Morning, 15 September

Welcoming Remarks

|  |  |
|---|---|
| 8:30 am | Donald Hunten, Conference Chairman |
| 8:40 am | Dean F. Peterson, Vice President for Research, Utah State University |
| 8:50 am | Honorable Frank Moss, U.S. Senator, Utah |
| 9:00 am | James Fletcher, NASA Administrator |

Stratospheric and Laboratory Measurements

Chairman:  Jacques Blamont, University of Paris

#### Invited Papers

9:15 am    "Survey of the Results of the Ozone Symposium in
           Dresden"
                   H. U. Dütsch, Atmospharenphysik ETH, Zurich

10:15 am   "Remote Sensing of Ozone:  Uses and Limitations"
                   B. Conrath, Goddard Space Flight Center

#### Contributed Papers

10:35 am   "The Increase in Total Ozone of the 1960's; Probable
           Cause"
                   H. W. Ellsaesser

10:45 am     Coffee Break

11:00 am     "Measurement of NO to 45 km"
             J. W. Drummond, J. M. Rosen, and D. J. Hoffman

11:10 am     "Spectroscopic Investigations of Atmospheric Chlorine
             Oxide"
             R. W. Carlson

11:20 am     "A Critical Review of $ClO_x$ and $BrO_x$ Rate Constants of
             Atmospheric Importance"
             R. T. Watson

11:30 am     "Rate Constant for Formation of Chlorine Nitrate by
             the Reaction $ClO + NO_2 + M$"
             M. T. Leu, C. L. Lin, and W. B. DeMore

11:40 am     "The Temperature Dependences of the Ultraviolet
             Cross-Sections of $CCl_2F_2$ and $CCl_3F$, and Their
             Stratospheric Significance.
             C. C. Chou, W. S. Smith, H. Vera Ruiz, K. Moe,
             G. Crescenti, M. J. Molina, and F. S. Rowland

11:50 am     "Seasonal and Latitudinal Behavior of Stratospheric
             $NO_2$"
             J. F. Noxon

12:00 pm     "Results of Global Determination of Ozone Distribution
             by Infrared Limb Scanning"
             J. C. Gille

12:10 pm     "Measurements of the Nitrogen Chemistry of the Ozone
             Layer from Project Stratoprobe"
             W. F. J. Evans, J. B. Kerr, and B. A. Ridley

12:20 pm     Lunch


             Wednesday Afternoon, 15 September


Sources for and Atmospheric Budget of $N_2O$ and $NO_x$

    Chairman:  H. Schiff, York University, Ontario, Canada


                      Invited Papers


2:00 pm      "Atmospheric $N_2O$:  Sources, Sinks and Perturbations"
             M. McElroy, Harvard University

2:30 pm      "Biological Production and Utilization of $N_2O$"
             C. C. Delwiche, University of California, Davis

3:00 pm    "Sources of Atmospheric $N_2O$ at the Earth's Surface"
           J. Hahn, Max-Planck Institute fur Chemie

3:30 pm    "Comments on the Atmospheric $N_2O$ Budget"
           S. C. Liu and R. Cicerone

3:50 pm    Coffee Break


Contributed Papers


4:05 pm    "Nitrous Oxide:  Atmospheric Concentrations 1964-1976,
           Industrial Sources and Air-Sea Exchange"
           R. F. Weiss, W. Dowd, and H. Craig

4:15 pm    "Measuring Nitrous Oxide Fluxes Resulting From
           Denitrification in Soil"
           D. E. Ralston, University of California

4:25 pm    "Nitrous Oxide in the Sea"
           T. Yoshinari, McGill University


Panel Discussion


4:35 pm    Panel:  H. Schiff (Chairman), R. Cicerone,
           C. C. Delwiche, J. Hahn, H. Johnston, S. C. Liu,
           M. McElroy, R. Weiss, T. Yoshinari


Thursday Morning, 16 September


Sources for and Atmospheric Budget of Halogens

    Chairman:  J. Friend, Drexel University


Invited Papers


8:30 am    "Stratospheric Chlorine Chemistry"
           F. S. Rowland, University of California, Irvine

9:00 am    "Status of the WSU Interhemispheric Halocarbon and
           Nitrous Oxide Measurements"
           R. Rasmussen, Washington State University

9:30 am    "An Industry View of the Scientific Aspect of the
           Fluorocarbon/Ozone Issue"
           J. P. Jessen, E. I. Du Pont de Nemours

10:00 am    "Deliberations and Findings of the Atmospheric
Chemistry Panel of the National Research Council"
        F. Kaufman, University of Pittsburgh

10:10 am    Coffee Break

Contributed Papers

10:30 am    "The Effect of HCl from Solid Fueled Rocket Engines
On Stratospheric Ozone:  A Two-Dimensional Model
Study"
        W. J. Borucki, R. C. Whitten, V. R. Watson,
        C. A. Riegel, and L. A. Capone

10:40 am    "Effects of Diurnal Variations and Scattering on
Ozone in the Stratosphere for Present-Day and
Predicted Future Chlorine Concentrations"
        R. Kurzeja

10:50 am    "The Rate Constant for $Cl + CH_4$ From 200-500K"
        J. H. Lee, J. V. Michael, W. A. Payne,
        L. J. Stief, and D. A. Whytock

11:00 am    "Microwave Aircraft Measurements of Stratospheric
Molecules"
        J. W. Waters, J. J. Gustincic, R. K. Kakar,
        A. R. Kerr, R. J. Mattauch, H. K. Roscoe, and
        P. N. Swanson

11:10 am    "A Simultaneous Measurement of Cl and ClO Between
45 and 20 km"
        J. G. Anderson, University of Michigan

Panel Discussion

11:20 am    Panel:  F. Kaufman (Chairman), M. Ackerman,
J. Anderson, J. Friend, J. Lovelock, R. McCarthy,
R. Rasmussen, F. S. Rowland, R. Stolarski, S. Wofsy

12:20 pm    Lunch

Thursday Afternoon, 16 September

Science and Public Policy:  Dynamics of Decision Making on the
Stratosphere

Chairman:  C. Bastian, NSF

2:00 pm       Opening remarks, C. Bastian

Invited Speeches

2:10 pm       Environmental Regulatory Issues
                      Wilson K. Talley, Assistant Administrator for
                      Research and Development, U.S. Environmental
                      Protection Agency

2:50 pm       Consumer Protection
                      Commissioner David Pittle, U.S Consumer Product
                      Safety Commission

3:30 pm       Coffee Break

3:45 pm       International Policy Issues
                      Erik Lykke, Director General, Ministry of
                      Environment, Norway

4:25 pm       Fluorocarbon Industries' Research Program
                      Dr. Richard Soulen, Pennwalt Corporation

5:05 pm       Upper Atmospheric Research in the U.S. Federal
              Government
                      Dr. L. R. Greenwood, Deputy Associate
                      Administrator, Office of Space Science, NASA

Friday Morning, 17 September

Science and Public Policy:  Dynamics of Decision Making on the
Stratosphere

Chairman:  C. Bastian, NSF

Invited Speech

8:30 am       "Science and Public Policy"
                      Dr. Russell W. Peterson, Chairman,
                      Council on Environmental Quality

9:10 am       Coffee Break

Panel

9:25 am       Opening remarks by individual panel members:
              C. Bastian (Chairman), NSF

|              |                                   |
|--------------|-----------------------------------|
| J. Brydon:   | Environmental Protection Service of Canada |
| R. Cicerone: | University of Michigan             |
| J. Merritt:  | President, Cosmetic, Toiletry and Fragrance Association, Inc. |
| W. Moomaw:   | U.S. Senate Staff                 |
| R. Reichert: | E. I. duPont                      |
| h. Compton:  | Natural Resources Defense Council |
| W. Sullivan: | N. Y. Times                       |

10:05 am   Guided discussion among panel members, followed by open discussion with audience participation

## Closing Remarks

11:45 am   Dr. Noel W. Hinners, Associate Administrator for Space Science, NASA

12:00 pm   End of Conference

# CONTENTS

## ABSTRACT

On September 15, 16 and 17, 1976, a conference was held in Logan, Utah, U.S.A., on the potential for pollution of the earth's stratosphere by injection of various gases as a result of man's activity on the surface of our planet. The conference was attended by over three hundred participants from countries over the entire globe. Represented were both scientists conducting research into stratospheric problems and policy makers involved in making regulatory decisions on various aspects of the international stratospheric pollution issue.

The conference was focused on four main areas of investigation concerning the potential for reduction of stratospheric ozone: laboratory studies and stratospheric measurements of stratospheric chemistry and constituents, sources for and chemical budget of stratospheric halogen compounds, sources for and chemical budget of stratospheric nitrous oxide, and the dynamics of decision making on regulation of potential pollutants of the stratosphere.

In this volume are included extended abstracts of the scientific sessions of the conference as well as complete transcriptions of the panel discussions on sources for and atmospheric budget of halocarbons and nitrous oxide. It is in these panel discussions that the scientific issues involved are best illustrated.

The political, social and economic issues involving regulation of potential stratospheric pollutants were examined extensively in the final session of the conference by policy makers at the highest levels of U.S. and foreign industry, government and consumer protection agencies. Because of the uniqueness of this type of session in a nominally scientific conference, and because of the importance of the issues involved to the welfare of humanity on this planet, this session is transcribed in its entirety.

The conference as a whole has set the stage for the initial efforts, in the latter part of this decade, to assess the potential damage to the stratospheric ozone layer by man-made pollutants and to examine the necessity for coordination and communication between science and technology, ecological issues, and social-political-economic concerns in order to insure the survivability of our present technological civilization.

Utah State University, Logan, Utah

# SCIENTIFIC PRESENTATIONS:

# SUMMARIES AND PANEL DISCUSSIONS

SECTION I

STRATOSPHERIC AND LABORATORY MEASUREMENTS

## SUMMARY OF THE FINDINGS OF THE DRESDEN SYMPOSIUM
## OF THE INTERNATIONAL OZONE COMMISSION AND ICACGP

### H. U. DÜTSCH

Atmosphärenphysik ETH, Zurich

## A.    MEASUREMENTS

After the strong emphasis on theoretical work during the past decade, (photochemical models, etc.), the importance of adequate (extended and improved) measurements is presently stressed again.  The program recently developed under the auspices of WMO, and to be run with support from UNEP, was discussed and approved at the Dresden meeting. It consists of a special observational effort (3-4 years), followed by a monitoring program (for detecting trends) and is to be paralleled by modeling and other theoretical efforts.  The special observational effort has to provide an improved basis for modeling and should allow researchers to prove or disprove theoretical results.

## 1.    Total ozone

A combination of a ground-based network with a satellite system is needed in order to supervise fluctuations and trends in the ozone layer. A 1% detection limit (if it is feasible at all) can only be obtained on this basis.

In order to improve the ground-based network (which has higher accuracy than satellite observations but cannot reach full global coverage), intercomparison between primary and secondary (regional) standards is planned, to be followed by regional comparisons.  At the same time the development of a future replacement for the Dobson spectrophotometer must be continued.

An improved version of the BUV method with almost real-time data reduction will be used on Nimbus G and should later become operational on TIROS N; it is supplemented by the IR method carried by Air Force satellites.

## 2.    Vertical distribution

Optimum information can be obtained by combining electrochemical sondes with satellite observations (BUV and possibly IR limb scanning technique).

Results from extended sounding series (up to 10 years) show in mid latitudes a pronounced 26 months' oscillation at the level of the ozone maximum (Attmannspacher, London and Dütsch).  It was further shown (De Muer) that transient eddies produce a considerable (poleward) ozone transport only in the lower stratosphere.  This means that such eddies provide only a minor part of the stratospheric ozone flux.

Comparison between Cunnold's 3-D model and the observations of the vertical distribution in winter 1970-1971 by the BUV technique on Nimbus IV showed some general agreement but also considerable differences, especially at high latitudes, which may have several reasons: observations in only one winter, with a strong stratospheric warming, incomplete photochemistry in the 3-D model and/or inaccuracy of the BUV-observations near the terminator.

## 3. Tropospheric ozone

The tropospheric ozone budget was discussed in considerable detail. Danielsen and Mohnen as well as Reiter showed direct observational evidence of downward ozone flux through the tropopause and tried to estimate its magnitude. Fabian, from world-wide observations at the ground and some airplane measurements in the upper troposphere, and Dütsch and Wyss from observations of the daily variation at a mountain station and in the lowest 100 m in lower country, concluded that transport and destruction at the ground and not in-situ photochemistry are responsible for the observed day-night difference; however it cannot yet be concluded that there is not a smaller photochemical contribution to the budget itself. Observations presented by Anlauf et al., Fricke and Georgii, van Doop and Guicherit made it clear, on the other hand, that there is a photochemically produced daily variation over relatively large polluted areas.

## 4. Anthropogenic influences

The extended discussion of the chlorine photochemistry (Crutzen, Rowland, Molina, Glasgow) will not be reported here as it is one of the main subjects of the Logan meeting itself.

Duewer et al. stressed the still considerable uncertainty of the effects of anthropogenic $NO_x$ on the ozone distribution, especially because of inaccurate knowledge of some reaction rates - mainly of OH + $HO_2$ but also of $HO_2$ + $O_3$ and some others. Goldsmith determined the $NO_x$ production of nuclear weapons using an entrainment model and pointed out that the 1962 production equalled that of 1200 Concordes, and no clearcut effect on atmospheric ozone was detectable.

## 5. Lack of discussion on the consequences of ozone depletion

Except for the presentation of measurement of the erythemal UV as a function of ozone ($\Delta$UV roughly 2% for 1% change in total ozone) by Komhry et al., no discussion of the consequences of anthropogenically produced ozone depletion took place - neither biological consequences nor the possibility of induced climatic change. Obviously there is still a very considerable ignorance in both fields and much more multidisciplinary research is needed.

6.    Other trace substances

The discussion of this matter was incomplete at the Dresden
meeting (especially with respect to $NO_x$), and since part of the present
conference is dealing directly with it, will not be reported here except
in connection with the evaluation of models.


B.    MODELS

The distribution of most trace substances in the stratosphere is
produced by combined action of photochemistry and transport. Depending
on what aspects are predominantly studied, 1-, 2- and 3-D models are
used. Chang discussed the merits and weaknesses of each of them. As
shown by Table 1, 1-D models are useless when dynamical problems are
studied, while 3-D models are impractical in connection with refined
photochemical research. 2-D models are of special advantage when all
aspects mentioned in Table 1 are to be studied simultaneously with equal
emphasis; only intermediate accuracy can, however, be expected.

Observations of the vertical distribution of the semistable trace
substances in the stratosphere, shown by Ehhalt, were thought to reason-
ably fit a 1-D model. There are, however, still notable deviations be-
tween the observed and the calculated profiles for some of the substances
($N_2O$, $CCL_2F_2$), pointing to the importance of the two dimensionality.


Table 1.  Relative degrees of complexity

|  | 1-D | 2-D | 3-D |
|---|---|---|---|
| Photochemical | xx | x | x |
| kinetics | xx | x | |
| Chemical | xx | x | x |
| coupling | xx | x | |
| Radiation | x | x | xx |
| feedback | x | x | xx |
| Dynamics | x | x | xx |
| | | x | xx |
| Dynamical- | | x | xx |
| chemical | x | x | xx |
| feedback | | | |

The use of two-dimensional models suffers from the fact that
the mean meridional circulation, and especially the mixing tensor used
in the parameterization of large-scale exchange, is badly known; values
derived for the latter from heat flux considerations obviously do not
apply to the transport of trace substances.  Thus each of the various
2-D models presented (Brasseur and Bertin, Harwood and Pyle, Vupputuri)
used different assumptions on circulation and exchange parameters.
By coupling the observed variation with season of the 2-D (latitude
and height) ozone field with photochemical theory, Dütsch and Baumann
computed the ozone flux divergence.  Between 10 and 30 km the highest
convergence was found in winter over mid-latitudes, being about 3 times
the observed increase, thus indicating stronger fluxes than anticipated.

Crutzen, using the BUV data, showed the pronounced effect of a
strong solar proton event at high geomagnetic latitudes and could also
demonstrate, comparing the further observed world-wide development
with computations using a 2-D model, that the high-altitude meridional
transport effects of the model were too large; i.e., he could point out
a specific possibility of testing such models.

# REMOTE SENSING OF OZONE: USES AND LIMITATIONS

Barney J. Conrath

Goddard Space Flight Center
Greenbelt, Maryland

## A. NADIR-VIEWING INFRARED REMOTE SENSING

Measurements in the 1042 $cm^{-1}$ ozone band of thermally emitted radiation have been used to obtain atmospheric ozone information. In order to obtain ozone estimates it is necessary to have information on the temperature of the atmosphere and of the lower boundary (cloud and ground) as well as radiance measurements within the ozone absorption band. However, this is not a serious limitation provided simultaneous measurements within the 667 $cm^{-1}$ $CO_2$ absorption band and the "window" region adjacent to the 1042 $cm^{-1}$ $O_3$ band are available. A more severe limitation is the weakness of the ozone band, which results in the existence of only one piece of information on ozone from measurements within the band. Unfortunately, this single piece of information involves both the total amount of ozone in an atmospheric column and its vertical distribution. Thus, in order to obtain an estimate of the total column abundance, it is necessary to introduce additional information.

In deriving total ozone from measurements obtained with the infrared interferometer spectrometer (IRIS) flown on Nimbus 3, Prabhakara et al. (1970) invoked the known statistical properties of ozone to obtain a unique solution. Deviations from a statistical mean profile were represented by a single characteristic pattern obtained from ensembles of in situ ozone profile measurements. In reducing similar data from the Nimbus 4 IRIS experiment, Prabhakara et al. (1976) used a different approach. A linear relationship between the total column abundance and the pressure level of the center of mass of the ozone vertical distribution was assumed in order to obtain a unique solution.

The accuracy of the measurements is not easy to assess. The approach taken by Prabhakara et al. (1976) was to make comparisons with near-simultaneous Dobson spectrometer measurements. Comparisons with a single station (Arosa) show a relatively good correlation on a day-to-day basis, but the two sets of measurements tend to drift apart as the ozone amount decreases late in the year, with the IRIS values higher than the Dobson measurements. It appears likely that the cause of the discrepancy lies, at least in part, in the assumed relationship between total ozone and the center of gravity.

## B. LIMB-VIEWING INFRARED REMOTE SENSING

Some of the problems encountered in the nadir-viewing mode can be alleviated by observing tangentially through the limb at the horizon. Either the thermally emitted atmospheric radiation can be observed

or the sun can be used as a source and transmission measurements made. Although the latter method has the advantage of high signal-to-noise ratio, it is extremely limited in coverage from satellite orbit. Therefore, the emission measurement approach appears to be the more attractive.

The limb-viewing geometry permits emission measurements in the 1042 cm$^{-1}$ ozone band to be made for relatively long atmospheric paths against a cold space background. The vertical resolution achievable is determined by the vertical dimension of the instrumental field of view. In order to achieve good vertical resolution, detectors with low noise equivalent power are needed. However, the requirements appear to lie well within the state of the art for cooled detectors. Measurements of this type have been obtained with the limb radiance infrared radiometer (LRIR) of Gille and his co-workers carried on Nimbus 6. Ozone profiles with good vertical resolution from the lower to the upper stratosphere have been recovered, and preliminary results from the experiment appear to be encouraging.

## C.    BACKSCATTERED ULTRAVIOLET REMOTE SENSING

The concept of obtaining ozone information from measurements of backscattered ultraviolet radiance was first suggested by Singer (1956). Since that time a considerable amount of work has gone into the development of theoretical methods, and data have been acquired from satellite-borne instruments of varying degrees of sophistication. The most extensive set of data thus far acquired is that of Heath. A backscattered ultraviolet spectrometer (BUV) carried on Nimbus 4 has obtained data on a glob 1 basis for approximately six years and is still in operation on a limited basis.

The extraction of ozone information from backscattered radiance measurements is in principle a straightforward process. The incident solar radiation is scattered back to the satellite sensor from various levels within the atmosphere and from the lower boundary surface. In addition, if the measurement is made within an ozone absorption band, the radiation is attenuated by absorption along the total path. To a first approximation, the majority of the radiation is backscattered from an effective scattering layer. If the distribution of scatterers (atmospheric molecules and aerosols) is assumed known, then a measurement of the ratio of the backscattered radiance to the incident solar flux permits the attenuation due to ozone absorption to be inferred. From a knowledge of the ozone absorption coefficient, the total ozone above the effective scattering layer can then be obtained. For an estimate of the total ozone, the effective scattering layering should be located in the troposphere. To obtain profile information, measurements at several different wavelengths are required, corresponding to scattering layers covering a range of heights in the stratosphere. The problem of extracting ozone information divides naturally into two distinct problems: retrieval of high-level profiles and retrieval of total column abundance. Each area will be considered separately below.

## 1.    Upper-Level Profile

The information content of nadir-viewing BUV measurements is limited both by the nature of the radiative transfer process and by the random error which will always be present in the measurements.  The radiance at a given wavelength is sensitive to ozone not at a single atmospheric level but over a considerable height range; this relative sensitivity is given quantitatively by the so-called contribution f: c-tions (Mateer, 1972).  Because of their considerable widt: and overlap from one spectral interval to the next, it is necessary to resort to a differentiation process to isolate information on ozone within a given atmospheric layer.  Hence, there is a strong sensitivity to random noise in the data (see Figure 1).  For radiance measurement errors of 1% (typical, for example, of the Nimbus 4 BUV), the upper-level mixing ratio profile can b. retrieved with a formal rms error of 10% and a vertical resolution of slightly better than one pressure scale height can be achieved.  The vertical range covered by such measurements is about 0.5 to 10 mb.  The 10-mb limit results from the restriction of the analysis to single scattering.  To extend the retrieval below the ozone maximum requires the inclusion of multiple scattering in the analysis.  This problem has been studied by Yarger (1970) who concludes that the intrinsic information contained in the measurements on this part of the profile is small.  The lower-level profile can probably be better estimated through statistical correlation with the total ozone column abundance (Sellers and Yarger, 1969).

In addition to the postulate of single scattering, other assumptions which have generally been made in retrieving topside ozone profiles include molecular scattering, horizontal homogeneity, and a plane-parallel atmosphere.  The assumptions of horizontal homogeneity and plane-parallel atmosphere do not appear to be serious limitations.  For instruments such as the Nimbus 4 BUV in which the field of view is slightly offset between measurements at successive wavelengths, the profile is representative of spatially averaged conditions, with the upper part of the profile representative of an area slightly different from the lower part.  For large solar zenith and/or viewing angles, the plane-parallel approximation breaks down; however, this is not a fundamental limitation, as more nearly exact geometry can be used as required.

The assumption of molecular scattering constitutes a more serious limitation.  The presence of stratospheric aerosols can provide additional attenuation, and high-level dust layers can result in significant scattering contributions which can have appreciable effects on high-level retrievals.  Elliott (1971) and Cunnold et al. (1973) have studied some aspects of the problem and have provided evidence that dust can have a significant effect.  More detailed sensitivity tests are currently being conducted.
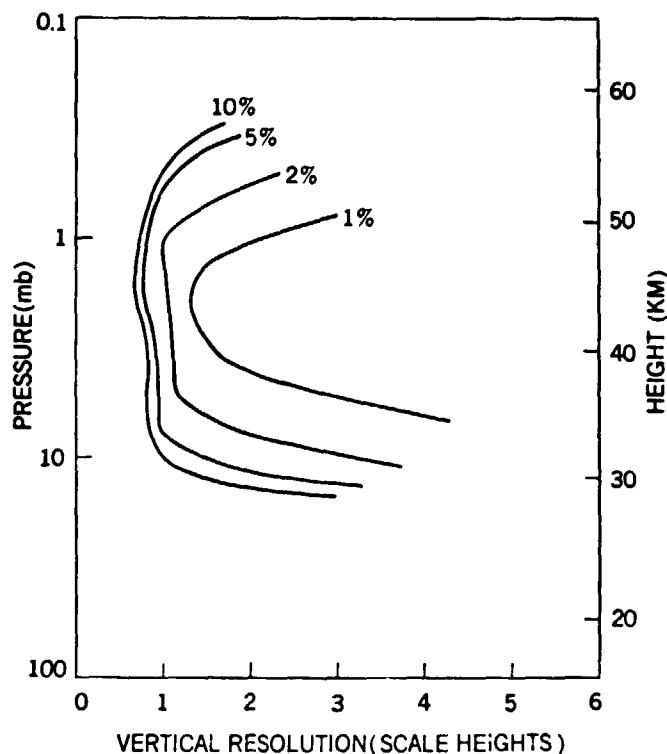
Figure 1.  Vertical resolution of ozone profiles
retrieved from nadir-viewing backscattered
ultraviolet measurements.  The labels on
the curves indicate the formal rms profile
errors due to a 1% measurement error.

## 2.    Retrieval of Total Ozone Column Abundance

Retrieval of ozone column abundance does not require a mathe-
matical inversion procedure in the usual sense.  The technique utilizes
measurements in one or more spectral intervals in the long-wavelength
wing of the Hartley-Huggins band, chosen so the effective scattering
levels are in the troposphere.  The most extensive published study of
the method is that of Dave and Mateer (1967).  Because of the necessity
of performing time-consuming multiple scattering calculations, a table
lookup method has generally been employed.  The basic measurement
required is the ratio of the backscattered radiance to the top of the
atmosphere for a single wavelength.  In practice the ratio of radiances
at two wavelengths is used in an attempt to achieve first-order cancela-
tion of certain neglected physical effects.  In general, the radiance
will depend on the total ozone, the pressure of the effective lower
boundary, the reflectivity of the effective lower boundary and, to a
smaller extent, the relative vertical ozone distribution.  An effective
lower-boundary reflectance is estimated using a measured radiance in an
absorption-free spectral region adjacent to the Hartley-Huggins band.
The dependence on vertical distribution is accounted for in a statistical
sense through the use of average profiles in the precalculated lookup

tables; these profiles are based on ensembles of in situ measurements divided according to the geographic location and season. For existing experiments, no provision exists for the direct determination of lower-boundary effective pressure. Estimates of ozone are made for pressures of 400 and 1000 mb, and an interpolation is made based on the measured albedo in a spectral region outside the absorption band.

Dave and Mateer (1967) have studied the sensitivity of ozone estimates to instrument noise and errors in lower-boundary reflectivity and pressure. A 1% error in the measurement of the ratio of back-scattered radiance to incident solar flux is found to propogate into an ~1% ozone error. The major sources of error are associated with the necessity of modeling the lower boundary. Because of the wavelength dependence of the reflective properties of natural surfaces, clouds, and aerosols, the reflectance measured outside the absorption band must be extrapolated to wavelength within the band. Since an error of 0.5 in reflectance is found to propagate typically into ozone errors of ~3%, this can be a significant source of error. Uncertainties due to lower-boundary pressure errors are found to be of the same order. Detailed estimates of sensitivity to other factors such as aerosols and non-Lambertian and non-homogeneous lower boundaries have not yet been made; however, some efforts are currently underway to address these problems (R.S. Freaser, private communication, 1976). It should be noted also that comparisons between total ozone estimates from the Nimbus 4 BUV and ground-based Dobson measurements have been made. Mateer et al. (1971) analyzed a heterogeneous sample of 320 near-coincident measure-ments and found the satellite values to be smaller than the Dobson values for low total ozone and larger than the Dobson values for high total ozone. The standard error of estimate was found to be ~6%. Similar measurements are currently being made for individual stations as a function of time, but results are not yet available.

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# THE INCREASE IN TOTAL OZONE OF THE 1960's: PROBABLE CAUSE

Hugh W. Ellsaesser

Lawrence Livermore Laboratory, University of California
Livermore, California

The upward trend in total $O_3$ in the northern hemisphere might be or has been attributed to any of the following:

(1)  Recovery from the nuclear tests of 1952 to 1962 (Johnston et al., 1973). This explanation has been questioned by almost all other investigators, the strongest counter-argument being that the total $O_3$ rose to higher mean levels in 1970 than ever previously observed.

(2)  The presumed 50% increase in stratospheric water vapor based on Mastenbrook's (1971) series of observations of Washington, D. C., from 1964 to 1970. Several studies (Crutzen, 1972; Duewer et al., 1976) have now indicated that an increase in $H_2O$ would, at least in the lower stratosphere, inhibit the $NO_x$ destruction of $O_3$ more than it would enhance the $HO_x$ destruction, thus leading to a net increase in $O_3$. Such an explanation would appear to call for similar increases in $O_3$ in the southern hemisphere. However, this objection may not be valid, and increased stratospheric humidity may play a partial role (see below).

(3)  Suggestions are already surfacing that the decrease in $O_3$ since 1970 may be due to a continuing direct variation with the sunspot decline following the most recent sunspot maximum of 1969 (Angell and Korshover, 1976). For this explanation to be persuasive we first need an explanation of why $O_3$ increased over the solar cycle from the all-time sunspot maximum of 1957 to the much lower sunspot maximum of 1969.

(4)  A change in general circulation. Those proposing such explanations (e.g., Komhyr et al. 1971; Crutzen, 1972; Christie, 1973) have tended to be non-specific as to what changes have occurred, since we are lacking in understanding in this area.

Empirical deduction seems to indicate that a weakening of the Hadley circulation and consequently of the exchange of air between the troposphere and the stratosphere would lead to an increase in stratospheric $O_3$. This conclusion rests strongly on the opinion prevailing prior to the unveiling of the $NO_x$ catalytic cycle that the troposphere was the major sink for stratospheric $O_3$. Current theory is remarkably consistent in showing that in the extratropical lower stratosphere, $O_3$ concentrations are in excess of those predicted by photochemical equilibrium. A slowdown in tropospheric-stratospheric exchange would appear to allow more time for $O_3$ in this region to decay to the photochemical equilibrium concentrations. But that effect may well be overpowered

by other effects. A slowdown in tropospheric-stratospheric exchange also reduces the upward rate of transfer of $N_2O$ to the 25-30 km level, where it is oxidized to NO by $O('D)$ and allows more time on the way up for the $N_2O$ to be photodissociated, producing $N_2$ rather than NO. And secondly, since the Hadley cell is driven by tropical convection which in turn maintains upward pressure on the tropical tropopause, any weakening can be expected to allow a lowering and warming of the tropical tropopause. This in turn would allow a higher mixing ratio of $H_2O$ through the cold trap of the tropical tropopause.

Thus a weakening of the Hadley circulation slowing tropospheric-stratospheric exchange has at least three consequences, all of which appear to lead to increases in the stratospheric reservoir of $O_3$:

(1) It reduces the rate of transfer of $O_3$ from the storage region of the lower stratosphere to the underlying well-mixed troposphere and the surface boundary layer, which destroys ozone (i.e., it reduces the tropopause value of $Kz$ of the 1-D model). This should result both in a reduction in the tropospheric concentration and surface destruction rate of $O_3$ and an increase in total $O_3$ in the storage reservoir of the lower stratosphere.

(2) It slows the upward flux of $N_2O$, thus allowing more time for photodissociation and reducing the fraction that is oxidized by $O('D)$ to form NO. It also presumably allows more time for operation of the unknown tropospheric sink, thus assuring that an even smaller fraction survives to produce NO in the stratosphere.

(3) It allows a lowering and warming of the tropical tropopause, which in turn allows a higher $H_2O$ mixing ratio to pass the tropical tropopause cold trap and to increase the humidity of the stratosphere. This in turn ties up a larger fraction of stratospheric $NO_y$ as $HNO_3$, reducing the fraction capable of attacking $O_3$ catalytically.

There remains the nagging problem that the pre-1970 increase in total $O_3$ appears to have been a phenomenon only of the northern hemisphere while the Hadley cell is usually regarded as a global phenomenon. This is not necessarily an insurmountable problem. It is known that the northern hemisphere (winter) Hadley cell is twice as strong as the southern hemisphere (summer) cell (Reed and Vlcek, 1969) (almost 10 times as strong (Dutsch 2nd CIAP, P10)) and that the tropical tropopauses of both hemispheres vary in unison on an annual cycle, i.e., highest and coldest in January and February (pushed up by the northern hemisphere Hadley cell) and lowest and warmest in July and August, when the weak southern hemisphere Hadley cell is operative (Smith, 1963). This seems to indicate that the Hadley circulation and its control of the tropical tropopause and tropospheric-stratospheric exchange is strongly asymmetric, due presumably to both the distribution of land and sea and the eccentricity of the Earth's orbit; the former amplifying the latitudinal temperature gradients to strengthen the northern hemisphere Hadley cell and the latter causing the received solar flux in

January to exceed that of July by nearly 7%, again strengthening the northern hemisphere cell.

Thus, restriction to the northern hemisphere becomes an additional argument supporting a relationship between the pre-1970 increase in $O_3$ an the tropospheric-stratospheric exchange rate since the latter and the nuclear test hypothesis are the only ones proposed which would lead to a hemispheric as opposed to a global phenomenon.

Finally, it is necessary to establish that there was a progressive weakening of the Hadley circulation and a slowdown in tropospheric-stratospheric exchange for approximately a decade prior to 1970-1971. This is attested to by the following evidence.

(1) Angell and Korshover (1974) found a 5-7 mb/decade increase in tropical tropopause pressure which appeared to have begun about 1957. Associated with it was a warming of the tropical tropopause at Singapore and Gan of approximately 1°C/decade, which they suggested might be related to the increase in $H_2O$ mixing ratio in the lower stratosphere observed by Mastenbrook (1971) over Washington, D. C., between 1964 and 1970.

(2) Measurements of Junge layer stratospheric aerosols by both airborne collectors and remote sensing reported a minimum and virtual disappearance of the layer in mid-1971 (Fox et. al., 1973, p. 7799). While the major thinning of the layer from 1963 to this time has been related to Mt. Agung and subsequent volcanic eruptions, the 1971 levels represented a significant decline over the pre-Agung values reported by Junge and Friend. This is even more apparent after application to the pre-Agung data of the 5- to 6-fold correction for impactor collection efficiency which now appears appropriate (Cadle and Grams, 1975). Since gaseous sulfur and particulates, like all other material not episodically injected into the stratosphere (as by volcanoes, etc.), must enter through the Hadley circulation, the pre-Agung to 1971 thinning of the Junge layer suggests a weakening of the Hadley circulation.

(3) Winstanley (1973) reported for the Sahel strip of Africa and India a continuing decline in summer monsoonal rainfall since the late 1920's apart from a temporary reprieve in the early 1950's. The recent drought was the result of the cumulative effects of a decade of below-average monsoon rainfall, with less and less rain each year through 1970. Since tropical convection cells penetrating the tropical tropopause are likely to decrease even more than summer ITCZ and monsoonal rainfall in general, Winstanley's data also indicates a progressive weakening (from about 1957 to 1970) of the Hadley circulation and thus of tropospheric-stratospheric exchange.

The above, of course, does not constitute proof. but does appear to indicate rather strongly that a progressive 10- to 13-year-long weakening of the Hadley cell and of tropospheric-stratospheric exchange is responsible for the progressive northern hemisphere increase in total $O_3$ observed up through 1970.

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## MEASUREMENT OF NO TO 45 KM

J. W. Drummond, J. M. Rosen, and D. J. Hofmann
Department of Physics and Astronomy
University of Wyoming
Laramie, Wyoming

On June 26, 1976, a chemiluminescent NO detector was flown to 45 km on a balloon at Sioux Falls, South Dakota. A pump was specially designed to provide a constant flow rate of about 3 liters sec$^{-1}$ to an altitude of 50 km. The NO detector had a sensitivity of 0.02 ppbv at 10% above the zero noise level. The flight data indicates a constant NO mixing ratio of 10.5 ppbv between 40 and 45 km. Figure 1 shows the vertical profile of the nitric oxide concentration for the June 27, 1976, ballon flight from Sioux Falls, South Dakota (lat 43.4°N). The instrument was launched at 1108 GMT and the data was taken on ascent. The local Sun times for the data at 12 and 45 km were approximately 0530 and 0730, respectively. The altitude of the tropopause was 10.2 km. The marked increase in NO at 18 km correlated with the altitude of the stratospheric wind reversal. Since the conference in September 1976, the on-board calibration gas has been reanalyzed by Matheson Gas Products, and the NO data have been decreased at all altitudes.
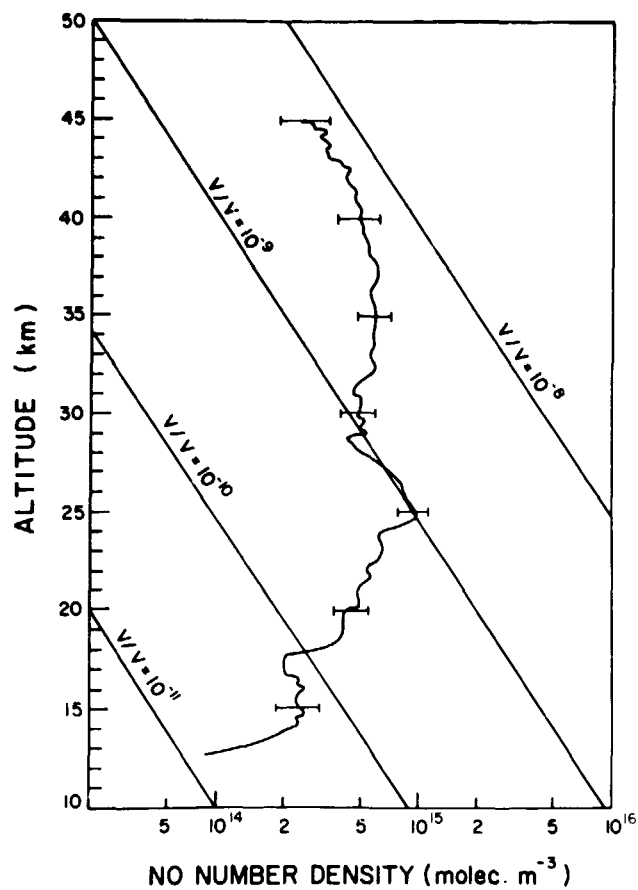
Figure 1. Vertical profile of the nitric oxide concentration for the June 27, 1976, balloon flight; lines of constant mixing ratio are superimposed.

# INVESTIGATION OF ATMOSPHERIC CHLORINE OXIDE
# THROUGH SOLAR ABSORPTION SPECTROSCOPY

R. W. Carlson
Department of Physics
University of Southern California
Los Angeles, California

The presence of atmospheric chlorine oxide has been investigated spectroscopically through absorption measurement in the vicinity of the ultraviolet ClO $A^2\pi_i$ - $X^2\pi_i$ bands using the McMath solar telescope of Kitt Peak National Observatory. Results obtained to date place an upper limit of $2 \times 10^{15}$ molecules $cm^{-2}$ for the vertical ClO column density.

The method for the atmospheric absorption measurements is to obtain solar spectra at two different solar elevations (i.e., two different airmasses) and investigate the logarithmic ratio of the spectra for features corresponding to ClO. Owing to strong $O_3$ absorption in this region, one can obtain useful signals only up to $\sim 2$ airmasses (or $\lesssim 60$ solar zenith angle). Comparison of such data with reference spectra obtained with the Sun overhead will show features corresponding to $\sim 1$ airmass absorption.

Three observing runs have been attempted thus far. The first two were directed toward the 3-0 band at 3035 Å, while the last run was devoted to the 4-0 band at 2993 Å. In the first (December 1975) attempt, the spectrum used for reference was obtained in July 1971, by Brault and Testerman (preliminary edition of the KPNO Solar Atlas). Subsequent measurements were made during the summer, allowing one to obtain low airmass reference spectra on the same day and identical instrumental parameters. Because of weather limitations, all of the high airmass data were taken in the morning.

The 3-0 band measurements show abrupt absorption increases within 0.1 - 0.2 Å of the ClO bandhead position, and shaded to the red as are the ClO bands. July 1976 3-0 band measurements also indicate that the strength of the feature varies with airmass and is therefore due to absorption by an atmospheric species. The absorption value is $\sim 2\%$ per unit airmass which, if interpreted as ClO, corresponds to $8 \times 10^{15}$ molecules $cm^{-2}$. However, the inability to observe rotational structure precludes positive identification with ClO, and one must consider the possibility of other molecular absorption features. There is suspicion that the observed structure is due to $O_3$ Huggins bands, although no ozone comparison spectra are available since high-resolution low-temperature $O_3$ spectra have not been investigated in this particular region.

The 4-0 band measurements (August 1976) do **not** show any readily apparent features at the bandhead, certainly not at the 4% per airmass which would be expected if the 3-0 structure was due to ClO, although one cannot experimentally rule out the possibility of extreme temporal variations (i.e., a factor of 5-10 over a month). If we discount such drastic temporal changes, then the upper limit to the chlorine oxide column abundance from the 4-0 band is $\sim 2 \times 10^{15}$ molecules $cm^{-2}$.

# A CRITICAL REVIEW OF ClO$_x$ AND BrO$_x$ RATE CONSTANT DATA OF ATMOSPHERIC IMPORTANCE

R. T. Watson
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

The reliability and consistency of all the rate constant data which has recently been reported from different laboratories, and is important in the understanding of the atmospheric chemistry of chlorine and bromine compounds, have been critically reviewed, with prime focus on the limitations placed upon the accuracy of the model calculations by the uncertainties in the kinetic data. Evaluated Arrhenius expressions are given in Tables 1 - 7 for all reactions of atmospheric importance, with realistic assessments of the uncertainties. In Table 6 the results of a series of reactions between the CH($^2\pi$) radical and some halogenated C$_1$ and C$_2$ compounds are given, and estimates are made for the tropospheric lifetimes of these compounds.

Table 1.  HCl formation

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Number of investigations used |
|---|---|---|---|
| (a)  Cl + $CH_4 \longrightarrow CH_3$ + HCl | $7.29 \times 10^{-12}$ exp $(-1260/T)$ | 200-300 | 4 |
| (b)  Cl + $H_2 \longrightarrow$ H + HCl | $2.7 \times 10^{-11}$ exp $(-2234/T)$ | 200-302 | 4 |
| (c)  Cl + $H_2O_2 \longrightarrow HO_2$ + HCl | $6 \times 10^{-13}$ | 295 | 2 |
| (d)  Cl + $HO_2 \longrightarrow O_2$ + HCl | $3 \times 10^{-11}$ | 295 | 1 |
| (e)  Cl + $HNO_3 \longrightarrow NO_3$ + HCl | $6.8 \times 10^{-15}$ | 295 | 1 |

Uncertainties between 200 and 260 K

(a) ± 20% ;     (b) ± 20% ;     (c) ± factor of 2

(d) ± factor of 3 ;     (e) ± factor of 3

Table 2. Magnitudes of various atomic chlorine sinks at 35 km

| Species | Concentration[a] molecule, $cm^{-3}$ | $k$, (237 K), $cm^3$ molecule$^{-1}$ s$^{-1}$ | $k$ (reagent), $s^{-1}$ | Comments |
|---|---|---|---|---|
| $CH_4$ | $9 \times 10^{10}$ | $3.58 \times 10^{-14}$ | $3.22 \times 10^{-3}$ | A major sink for atomic chlorine |
| $H_2$ | $7 \times 10^{10}$ | $2.18 \times 10^{-15}$ | $1.52 \times 10^{-4}$ | Minor sink |
| $H_2O_2$ | $(2 - 50) \times 10^8$ | $2.9 \times 10^{-13}$[a] | $(.58 - 14.5) \times 10^{-4}$ | Could be a significant sink ($\geq 10\%$) |
| $HO_2$ | $(3 - 14) \times 10^7$ | $3 \times 10^{-11}$ | $(0.9 - 4.2) \times 10^{-3}$ | Could be a major sink |
| $HNO_3$ | $(1.2 - 11) \times 10^8$ | $1.6 \times 10^{-15}$[a] | $(1.9 - 17.6) \times 10^{-7}$ | Unimportant |

[a]Modelled concentrations, Stolarski et al.

[b]Estimated from the 295 K data.

Table 3.  HCl degradation

| Reaction | Rate constant $(cm^3$ molecule$^{-1}$ s$^{-1})$ | Temperature range, K | Number of investigations used |
|---|---|---|---|
| (a)  OH + HCl | $2.96 \times 10^{-12}$ exp $(-425/T)$ | 220-460 | 3 |
| (b)  O + HCl | $1.14 \times 10^{-11}$ exp $(-3373/T)$ | 200-500 | 4 |

Uncertainties between 200 and 260 K

(a)  $\pm 15\%$ ;   (b)  $\pm$ factor of 2

Rates of HCl degradation at 35 km

| Reactant | Concentration, molecule, cm$^{-3}$ | k (237 K) | k (reagent), s$^{-1}$ | Comments |
|---|---|---|---|---|
| OH | $(4 - 20) \times 10^6$ | $4.93 \times 10^{-13}$ | $(2.0 - 9.9) \times 10^{-6}$ | Dominant sink for HCl |
| O | $(1.1 - 1.6) \times 10^8$ | $7.52 \times 10^{-18}$ | $(8.3 - 12.0) \times 10^{-10}$ | Unimportant |
| h$\gamma$ | - | - | $\sim 2.5 \times 10^{-8}$ | Unimportant |

Table 4. Cl – ClO equilibrium

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Number of investigations |
|---|---|---|---|
| (i) $Cl + O_3 \longrightarrow ClO + O_2$ | $2.7 \times 10^{-11}$ exp $(-257/T)$ | 205-298 | 4 |
| (ii) $O + ClO \longrightarrow Cl + O_2$ | $1.07 \times 10^{10}$ exp $(-224/T)$ | 220-425 | 2 |
| (iii) $NO + ClO \longrightarrow Cl + NO_2$ | $1.94 \times 10^{-11}$[a] | 298 | 2 |

[a]The temperature-dependences reported by Zahniser and Kaufman have not been used in these evaluations. However, for the O + ClO reaction the agreement at 237 K (midstratospheric temperature) is good ($\sim 12\%$).

Uncertainties between 200 and 260 K

(i) $\pm$ 15% ;  (ii) $\pm$ 50% ;  (iii) $\pm$ factor of 2-3

## Table 5. $ClONO_2$ chemistry

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Uncertainties, (200-260) K |
|---|---|---|---|
| $ClO + NO_2 \xrightarrow{M} ClONO_2$ | $5-11 \times 10^{-33}$ exp $(1033 \pm 42/T)$<br><br>$M = N_2$ $\quad$ ($\sim$1 - 6 torr) | 248-4?7 | At low altitudes the pure third-order expression may over-estimate k by a small amount $\leq 1.25$ (pressure falloff region). |
| $ClONO_2 + O \longrightarrow$ products | $4.5 \times 10^{-12}$ exp $(-840/T)$ | 213-295 | $\pm$ factor of 2 |
| $ClONO_2 + OH \longrightarrow$ products | $1.19 \times 10^{-12}$ exp $(-333/T)$ | 246-387 | $\pm$ 25% |
| $ClONO_2 + Cl \longrightarrow$ products | $1.5 \times 10^{-12}$ exp $(-640/T)$ | 245-298 | $\pm$ factor of 2 |
| $ClONO_2 + h\nu \longrightarrow$ products | $J = 7.1 \times 10^{-5}$ (14 km, 40° SZA)<br>$= 8.3 \times 10^{-5}$ (25 km, 40° SZA)<br>$= 17 \times 10^{-5}$ (35 km, 40° SZA) | | |

Table 5. ClONO$_2$ chemistry (Continuation 1)

Rates of ClONO$_2$ degradation at 25 km

| Reactant | Concentration, molecule cm$^{-3}$ | k(223k) | k(Reagent) | Comments |
|----------|-----------------------------------|---------|------------|----------|
| [OH] | $1.8 \times 10^6$ | $2.67 \times 10^{-13}$ | $4.8 \times 10^{-7}$ | Minor loss route |
| [O$^3$P] | $1.4 \times 10^7$ | $1.04 \times 10^{-13}$ | $1.5 \times 10^{-6}$ | Minor loss route |
| [Cl] | $1.2 \times 10^4$ | $8.50 \times 10^{-14}$ | $1.0 \times 10^{-9}$ | Unimportant |
| h$\nu$ | — | — | $8.3 \times 10^{-5}$ | Major loss route |

Table 6. OH reactions with halogenated alkanes

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Number of investigations | Troposphere lifetime, yr |
|---|---|---|---|---|
| OH + $CH_3Cl \longrightarrow CH_2Cl + H_2O$ | 2.18 x $10^{-12}$ exp (-1142/T) | 240-422 | 2 | 0.70 |
| OH + $CHFCl_2 \longrightarrow CFCl_2 + H_2O$ | 1.30 x $10^{-12}$ exp (-1127/T) | 245-422 | 3 | 1.11 |
| OH + $CHF_2Cl \longrightarrow CF_2Cl + H_2O$ | 1.23 x $10^{-12}$ exp (-1660/T) | 250-434 | 3 | 8.45 |
| OH + $CH_2FCl \longrightarrow CHFCl + H_2O$ | 2.84 x $10^{-12}$ exp (-1259/T) | 245-375 | 1 | .83 |
| OH + $CH_3CCl_3 \longrightarrow CH_2CCl + H_2O$ | 3.49 x $10^{-12}$ exp (-1562/T) | 260-405 | 2 | 2.07 |
| OH + $C_2Cl_4 \longrightarrow C_2Cl_4OH$ | 1.6 x $10^{-13}$ | 298 | 3 | .14 |
| OH + $CFCl_3 \longrightarrow$ Products | <1 x $10^{-15}$ | 297-480 | 2 | >4000 |
| OH + $CF_2Cl_2 \longrightarrow$ Products | <1 x $10^{-15}$ | 297-480 | 2 | >4000 |

$\tau 1/2 = 0.7/k[OH]$ ; average tropospheric temperature was taken to be 270 k. The average [OH] $\cong$ 1 x $10^6$ molecule $cm^{-3}$.

Table 7. Bromine chemistry

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Uncertainties, (200-260) K |
|---|---|---|---|
| Br + $O_3$ $\longrightarrow$ BrO + $O_2$ | $3.0 \times 10^{-11} \exp(-937/T)$ | 223-422 | $\pm$ 25% |
| O + BrO $\longrightarrow$ Br + $O_2$ | $3 \times 10^{-11}$ | 298 | $\pm$ Factor of 3 |
| NO + BrO $\longrightarrow$ Br + $NO_2$ | $2.1 \times 10^{-11}$ | 298 | Factor of 2 |
| ClO + BrO $\longrightarrow$ OClO + Br | $6 \times 10^{-12}$ | 298 | Factor of 2 |
| ClO + BrO $\longrightarrow$ Br + Cl + $O_2$ | $6.7 \times 10^{-12}$ | 298 | Factor of 2 |
| BrO + BrO $\longrightarrow$ Br + Br + $O_2$ | $2.85 \times 10^{-11} \exp(-450/T)$ | 293-573* | $\pm$ 50% |
| BrO + h$\nu$ $\longrightarrow$ Br + O | $J \sim 10^{-2}$ s$^{-1}$ | 298 | Factor of 10 |
| BrO + $O_3$ $\longrightarrow$ BrOO + $O_2$ | $<10^{-14}$ | 298 | ? |
| Br + $H_2O_2$ $\longrightarrow$ HBr + $HO_2$ | $2.6 \times 10^{-14}$ | 298 | $\pm$ Factor of 2 |
| Br + $HO_2$ $\longrightarrow$ HBr + $O_2$ | $3 \times 10^{-12}$ (estimate) | - | $\pm$ Factor of 5 |
| OH + HBr $\longrightarrow$ $H_2O$ + Br | $5.1 \times 10^{-12}$ | 298 | Factor of 2 |
| O + HBr $\longrightarrow$ OH + Br | $7.6 \times 10^{-12} \exp(-1571/T)$ | 267-600 | $\pm$ Factor of 2.5 |

Table 7. Bromine chemistry (Continuation 1)

| Reaction | Rate constant, $cm^3$ molecule$^{-1}$ s$^{-1}$ | Temperature range, K | Uncertainties, (200-260) K |
|---|---|---|---|
| HBr + h$\nu$ $\longrightarrow$ H + Br | J = 2.8 x 10$^{-9}$ (20 km) | | |
| | = 4.9 x 10$^{-7}$ (30 km) | | |
| | = 3.8 x 10$^{-6}$ (40 km) | - | Factor of 2 |
| | = 6.7 x 10$^{-6}$ (50 km) | | |
| OH + CH$_3$Br $\longrightarrow$ CH$_2$Br + H$_2$O | 7.93 x 10$^{-13}$ exp(-889/T) | 245-375 | ± 20% |

RATE CONSTANT FOR FORMATION OF CHLORINE
NITRATE BY THE REACTION ClO + NO$_2$ + M

M. T. Leu, C. L. Lin, and W. B. DeMore
Jet Propulsion Laboratory
Pasadena, California

A discharge flow/mass spectrometer apparatus has been used to measure rate constants for the reaction ClO + NO$_2$ + M. The results are given in Table 1 and compared with other current measurements of this reaction rate.

Table 1. Summary of results for ClO + $NO_2$ + M

| Reference | Rate constant, $cm^6$/sec | M | Pressure, torr | Temperature, K | Technique |
|---|---|---|---|---|---|
| This work | $(1.20 \pm 0.05) \times 10^{-31}$ | He | 1-7 | 299 | Discharge flow/MS |
| | $(2.66 \pm 0.35) \times 10^{-33} \exp [(1140 \pm 40)/T]$ | He | 1-9 | 248-417 | |
| | $(1.15 \pm 0.10) \times 10^{-31}$ | Ar | 1-4 | 298 | |
| | $(1.76 \pm 0.12) \times 10^{-31}$ | $N_2$ | 1-5 | 299 | |
| | $(3.69 \pm 0.24) \times 10^{-33} \exp [(1150 \pm 20)/T]$ | $N_2$ | 1-6 | 298-417 | |
| Birks et al.[1] | $0.82 \times 10^{-31}$ | He | 1-5 | 297 | Discharge flow/MS |
| | $(1.54 \pm 0.14) \times 10^{-31}$ | $N_2$ | - | 297 | |
| | $(4.0 \pm 0.8) \times 10^{-33} \exp [(1066 \pm 66)/T]$ | $N_2$ | - | 250-356 | |
| Zahniser & Kaufman[1] | $(0.83 \pm 0.03) \times 10^{-31}$ | He | 1-6 | 300 | Discharge flow/res. Fluor. |
| | $(3.54 \pm 0.10) \times 10^{-33} \exp [(950 \pm 10)/T]$ | He | 1-6 | 250-365 | (Detection of Cl from ClO by NO addition) |
| | $(1.52 \pm 0.08) \times 10^{-31}$ | $N_2$ | 2-4 | 300 | |

Table 1. Summary of results for ClO + $NO_2$ + M  (Continuation 1)

| Reference | Rate constant, $cm^6/sec$ | M | Pressure, torr | Temperature, K | Technique |
|---|---|---|---|---|---|
| Young[1] | $2.3 \times 10^{-31}$ | Ar | 5-20 | 300 | Discharge flow/res. Fluor. (Detection of Cl from ClO by NO addition) |

# THE TEMPERATURE DEPENDENCES OF THE ULTRAVIOLET CROSS-SECTIONS OF $CCl_2F_2$ AND $CCl_3F$, AND THEIR STRATOSPHERIC SIGNIFICANCE

C. C. Chou, W. S. Smith, H. Vera Ruiz, K. Moe,
G. Crescentini, M. J. Molina, and F. S. Rowland
Department of Chemistry
University of California
Irvine, California

Temperature effects on absorption cross-sections of $CCl_2F_2$ and $CCl_3F$ have been determined in the temperature range 300-210°K and wavelength region 220-190 nm. Stratospheric lifetimes for these molecules are calculated using the temperature-dependent cross-sections and one-dimensional transport models. The stratospheric lifetime for $CCl_2F_2$ is 9-18% longer, depending on the transport model, than previously calculated using room temperature cross-sections. The corresponding factor for $CCl_3F$ is only 3-6%. Our calculations also show that reduced cross-sections result in an increase in steady-state ClX concentration in the middle-upper stratosphere and therefore enhance the ozone removal by the $ClO_x$ catalyzed chain reactions at steady state.

# SEASONAL AND LATITUDINAL BEHAVIOR OF STRATOSPHERIC NO$_2$

J. F. Noxon
Aeronomy Laboratory
NOAA/ERL. Boulder, Colorado

Twilight sky spectra can be inverted to yield both the total stratospheric NO$_2$ abundance and its altitude; together with solar and lunar spectra this leads to values for both day and night stratospheric NO$_2$ as well as the tropospheric abundance. A year's ground and aircraft measurements show a summer maximum in NO$_2$, with little latitudinal change between 35° and 80°N, a seasonal variation of 2 below 50°N, and a variation of 6 north of 55°N. In winter the NO$_2$ abundance drops sharply between 50°N and 55°N but then remains constant to at least 70°N. Large changes can occur in a few days at one location in both abundance and altitude; these show a correlation with large-scale air motions in the stratosphere.

# RESULTS OF GLOBAL DETERMINATION OF OZONE
## DISTRIBUTION BY INFRARED LIMB SCANNING

J. C. Gille and P. L. Bailey
National Center for Atmospheric Research
Boulder, Colorado

Scanning the infrared limb of the earth to determine global ozone distribution has many advantages. The technique provides data on both the day and night sides, yields values below the ozone maximum, to 20 km, and has high vertical resolution, from weighting functions of order 3 km wide.

The limb radiance inversion radiometer on Nimbus 6 was designed to test this technique. Profiles of ozone have been derived over the range 20-55 km from the measured radiances (see Figure 1). Comparisons between inferred ozone profiles and rocket observations indicate good agreement. From these profiles, maps have been drawn on pressure surfaces up to 0.4 mb. They show a number of interesting features, including a variable wave number 2 pattern during southern hemisphere winter.
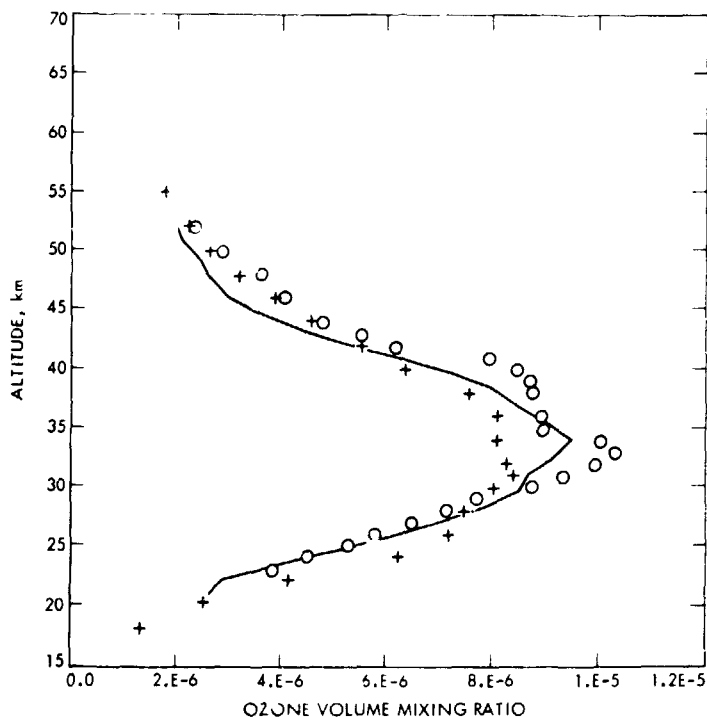


Figure 1.   Preliminary ozone mixing ratio profile determined from LRIR radiances is shown by the solid line. The profile was determined for the atmosphere over Wallops Island, Virginia, on July 29, 1975. Comparison with simultaneous rocket sonde profiles (circles and crosses) is shown. Retrieved profile has 14% rms difference from circles between 20-55 km.

# MEASUREMENTS OF THE NITROGEN CHEMISTRY OF THE OZONE LAYER FROM PROJECT STRATOPROBE

W. F. J. Evans, J. B. Kerr and B. A. Ridley
Atmospheric Environment Service
Downsview, Ontario, Canada

Measurements of NO, $NO_2$, $HNO_3$ and $O_3$ made on the same ballon flight from latitude 58.6°N, on July 22, 1974, are reviewed; these have been successfully simulated to within a factor of 2 with currently accepted nitrogen photochemistry. Further flights of the Stratoprobe payload were conducted during August 1975 from 51°N. In particular, a flight on August 17 yielded measurements of NO, $NO_2$ and $HNO_3$ altitude distribution consistent with the 1974 flight results (Figure 1). The ozone concentration profiles for the 1975 flights were similar to the 1974 ozone conditions (Figure 2); consequently, the measured odd nitrogen mixing ratio profile was found to be similar to the 1974 $NO_y$ measurement. The $NO_y$ profile (Figure 3) was approximately constant from 22 to 35 km at 10 ppbv. On four flights of Project Stratoprobe, no indication of any significant variability in the $NO_y$ mixing ratio has been found.
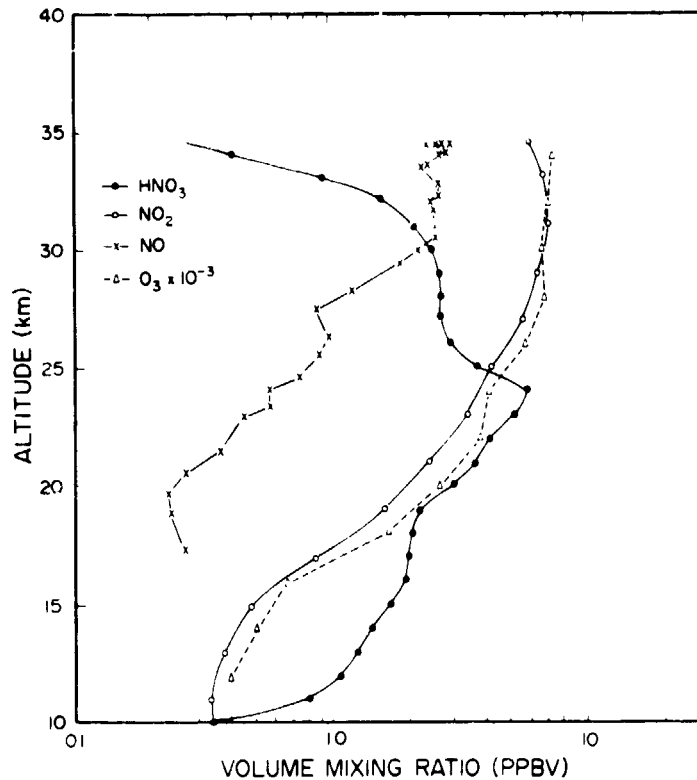
Figure 1. Measurements of key constituents in the nitrogen
chemistry of the ozone layer. These measurements
of ozone, nitric acid, nitrogen dioxide and nitrix
oxide were made on the same balloon flight on
July 22, 1974, from 58.5 N. The constituent
profiles have been successfully simulated using
currently accepted photochemistry schemes
(Evans, W.F.J., J.B. Kerr, D.I. Wardle,
J.C. McConnell, B.A. Ridley and H.I. Schiff,
"Intercomparison of NO, $NO_2$, and $HNO_3$ measure-
ments with photochemical theory," Atmosphere,
Vol. 14, No. 3, p. 189, 1976).
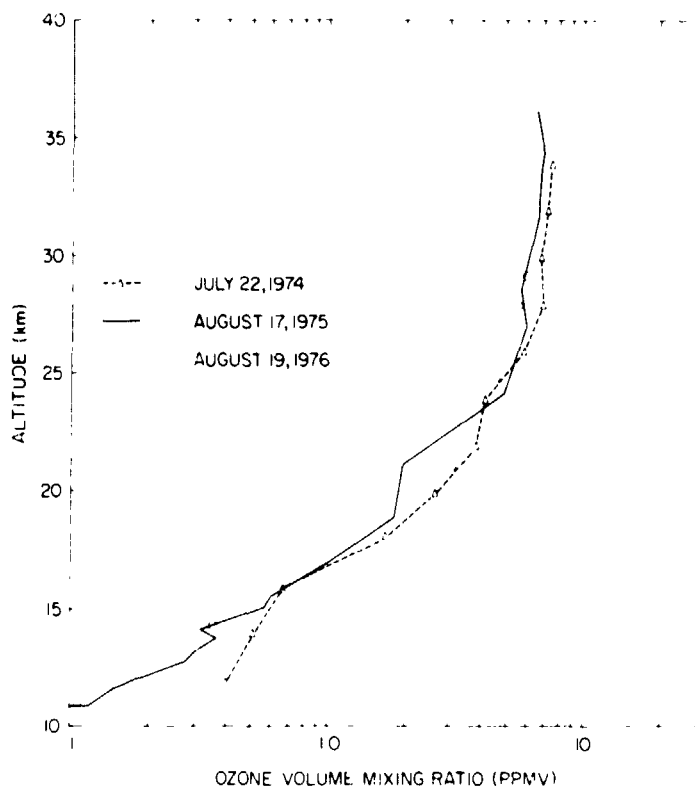
Figure 2. The ozone mixing ratio profiles for Project
Stratoprobe flights on three successive years.
These ozone mixing ratio profiles for late
summer in northern latitudes are surprisingly
similar considering they are from different
years. This demonstrates that latitudes of
50° to 60° in late summer represent an ideal
situation for the measurement of trace con-
stituents in the stratosphere since the ozone
layer is very stable and repeatable; meteoro-
logical effects are minimized since the flow
is stable and variations are small, providing
an excellent opportunity for the measurement
of typical constituent profiles. This balloon
launch location provides ideal conditions for
intercomparison experiments. Considering
these very similar ozone profiles, one would
expect very similar $NO_y$ profiles on the three
flights, as was actually observed.

35 ── ─ AUG 17, 1975, 51°
      • • • JULY 22, 1974, 58°
      ───── MODEL (PRINN ET AL)

ALTITUDE (km)

TROPOPAUSE

2    5    10    20

NO_y MIXING RATIO (ppbv)
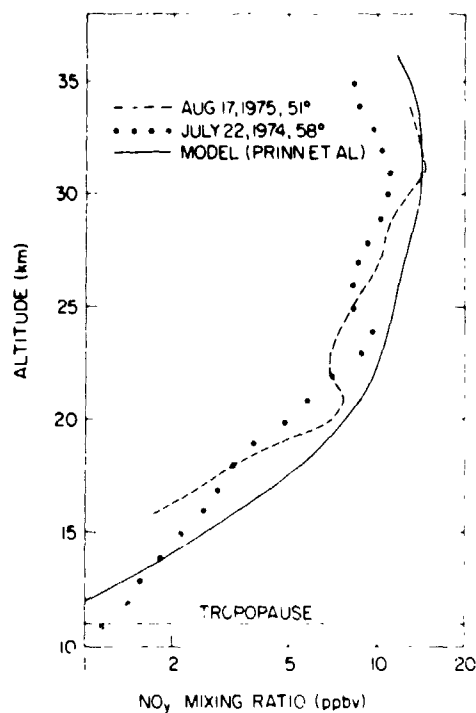
Figure 3.  The measured profiles of $NO_y$ from 51° N
           in 1975 are very similar to the $NO_y$
           profile measured at 58° N in 1974.
           These have been derived from the simi-
           lar profiles of NO, $NO_2$, and $HNO_3$ of
           Figure 1.  The measured profiles of
           the individual constituents in 1975
           and 1976 were extremely similar to the
           profiles for NO, $NO_2$ and $HNO_3$ of
           Figure 1.  The figure also shows that
           the measured $NO_y$ profiles are consistent
           with the Prinn et al. (1975) model for
           60° N, summer.

# SECTION II

## SOURCES FOR AND ATMOSPHERIC BUDGET OF $N_2O$ and $NO_x$

# ATMOSPHERIC $N_2O$:  SOURCES, SINKS AND PERTURBATIONS

M. McElroy
Harvard University
Cambridge, MA.

In his attempt to develop a food supply adequate to the needs of this planet's expanding population, mar has come to rely to an increasing extent on chemical fertilizers.  Industrial fixation of nitrogen for agricultural purposes has grown by rather more than a factor of 10 over the past 25 years.  It accounted for less than 3% of the total nitrogen fixed globally by natural processes in 1950, $3.5 \times 10^6$ tons as compared to $1.6 \times 10^8$ tons.  It grew at an average rate of 10.7% per year between 1950 and 1974, and there are no indications of an imminent decline in the growth pattern.  Estimates for N fertilizer production by the end of the century range from $1 \times 10^8$ to $2 \times 10^8$ tons.  If one adds to the world's inventory of fixed nitrogen quantities of the gas fixed by industrial processes in general, including transportation but excluding fertilizer - $1.5 \times 10^7$ tons in 1950, $4 \times 10^7$ tons in 1974, and perhaps $10^8$ tons in 2000 - it is hard to escape the conclusion that mar has already had a significant influence on the global cycle of nitrogen, and that his role must grow rapidly in the years ahead.  One would expect an increase in the rate at which fixed nitrogen should be removed by denitrification.  This paper is directed toward an attempt to estimate the associated rise in atmospheric $N_2O$ and its consequent effects on $O_3$.

If one accepts for the moment an asymptotic state in which fixation of nitrogen for fertilizer should stabilize at an annual level of $2 \times 10^8$ tons, with an additional $1 \times 10^8$ tons supplied by other anthropogenic agents, and if one assumes that the relative amounts of $N_2$ and $N_2$ evolved during denitrification should remain constant, one might anticipate an increase in the concentration of atmospheric $N_2O$ at some future date by about a factor of 3.  Our model, illustrated in Figure 1, incorporates of course a number of unproven assumptions.  It requires that fixation and denitrification should balance on a suitably long time scale.  It omits feedback mechanisms which might couple the atmosphere and biosphere, and which might conceivably alter the manner in which essential nutrients are redistributed under natural conditions.  It assumes that the loss process for $N_2O$ should respond in a linear fashion to a change in atmospheric concentration.  These limitations seem unimportant in the present context, however.  Fixation and denitrification must balance, at least on a geologic time scale:  the continued presence of $N_2$ in the atmosphere attests to this fact.  The major question concerns the time scale for anthropogenically driven denitrification. A global disruption to the cycle which regulates the natural dispersal of nutrients should entail an environmental perturbation much larger than any discussed here.  It is difficult to envisage a loss process for $N_2O$ which might respond in a highly nonlinear fashion to a change in atmospheric concentration.  Our model, with its assumptions and inherent limitations, projects a significant rise in the level of $N_2O$. The predicted drop in $O_3$ could be as large as 20% in the near future.
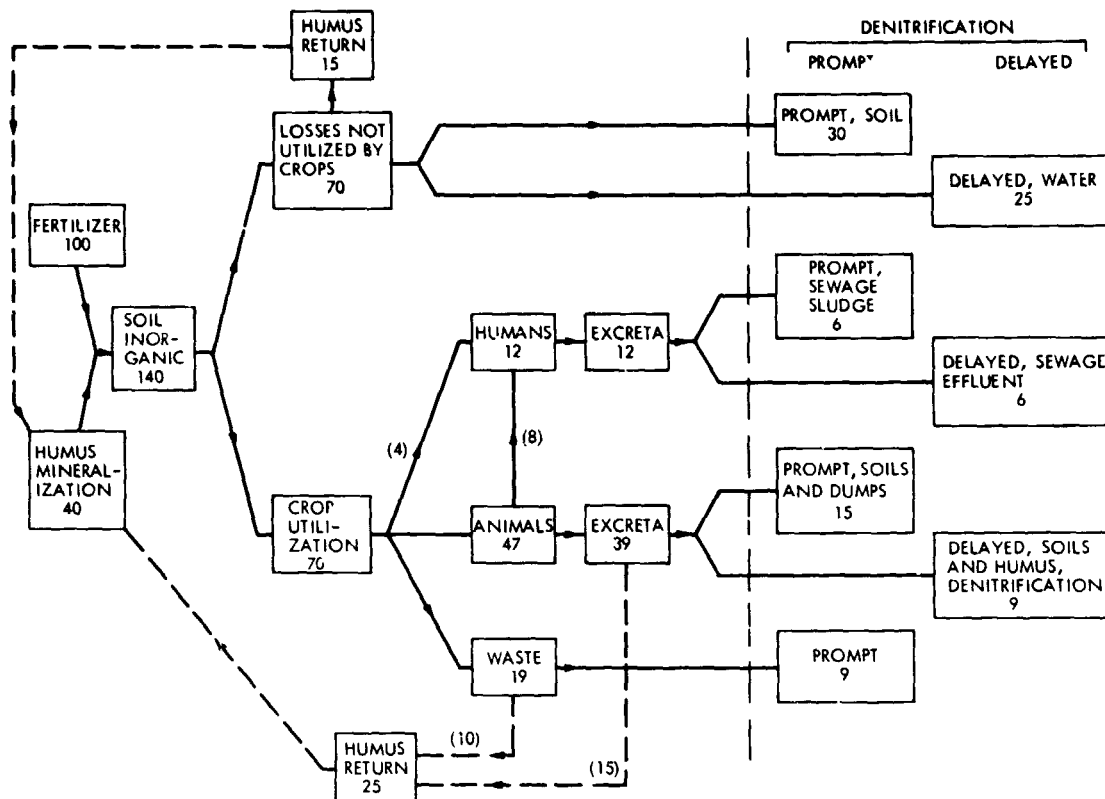
Figure 1. Transfer of nitrogen in the agricultural food chain
(arbitrary units), adapted from data given by the
National Academy of Sciences (1972). The relative
contributions of soil nitrogen and fertilizer are
intended to model average conditions in the United
States. The various time scales for denitrification
are discussed in the text.

Measurements of the spatial and temporal variability of $N_2O$
may be used to derive an empirical value for the lifetime of the gas
under normal atmospheric conditions. If we adopt Junge's (1974) value
for this parameter, about 10 years, and various estimates (Goody, 1954,
1969; Birkeland and Shaw, 1959; Rank, Slomba, Gardner and Wiggins,
1962; Craig and Gordon, 1963; Schultz, Junge, Beck and Albrecht,
1970; Rasmussen, 1975) for the equilibrium abundance, taken to correspond
to a mixing ratio of about $2.6 \times 10^{-7}$, we may conclude that the
rate for global production of $N_2O$ should correspond to about $1.2 \times 10^8$
tons (N) per year. If we combine this result with values quoted earlier
for fixation under natural conditions, about $1.6 \times 10^8$ tons per
year, we may estimate a globally averaged yield factor for $N_2O$ equal
to about 0.74.

It is hard to escape the conclusion based on this analysis that $N_2O$ must be a major product of denitrification. It remains to identify the nature of the source. One might be tempted to attribute production of about $8 \times 10^7$ tons per year to biological processes in the open ocean, with a further $4 \times 10^7$ tons per year attributed to denitrification on land. Such a choice would agree well with Hahn's (1974, 1975) conclusion, that the oceans are responsible for about $8.5 \times 10^7$ tons per year, and that soils contribute an additional $1.5 \times 10^7$ tons per year. One might assign in this model a source of about $2 \times 10^7$ tons year to fresh waters and estuaries, completing a global input of $1.2 \times 10^8$ tons per year. The distribution is in no sense unique, however, and a careful analysis, incorporating all reasonable constraints, appears to imply a much smaller role for the sea. The contribution from continental sources must be raised accordingly, although several of the models allow for a relatively large contribution from the oceans to the global budget of atmospheric $N_2O$.

# SOURCES AND SINKS FOR $N_2O$

C. C. Delwiche, Department of Land, Air and Water Resources
University of California, Davis, California

Although nitrous oxide ($N_2O$) has been recognized as a product of denitrification for almost a century, and the principal source of atmospheric $N_2O$ has been assumed to be biological, current estimates of the residence time of $N_2O$ in the atmosphere are not completely compatible with known terrestrial production process rates.

Assuming a residence time of 10 years or less and an atmospheric content of $6.3 \times 10^{13}$ moles (equivalent to a mixing ratio of $3.5 \times 10^{-7}$ on a volume basis), an annual production of $6.3 \times 10^{12}$ moles $N_2O$ would be required. The estimated rate of nitrogen fixation from all sources (including industrial processes and combustion reactions) is about $2 \times 10^{13}$ moles. If all of this nitrogen were subjected to denitrification, it would require that approximately 15% of this appear as $N_2O$. Field experience and laboratory observations suggest that the proportion of $N_2O$ produced in the denitrification process is 10% or less, assuming that quasi steady-state conditions prevail. Moreover, since a considerable fraction of this input of fixed nitrogen (about 33%) is of recent man-made origin, it is probable that much of this additional input finds its way to the sea, soil and ground waters and is not immediately subject to denitrification resulting in a new level of fixed nitrogen in the global system.

There is the additional problem that the assumed sink for $N_2O$ (stratospheric degradation) requires a comparatively rapid transfer across the tropopause and a stratospheric gradient steeper than that suggested by available data to explain a residence time of 10 years or less.

To obtain further information concerning processes of production and destruction of $N_2O$ we have carried out measurements of $N_2O$ in the soil profile under various conditions and have measured the $N_2O$ concentration immediately over the soil surface as a function of changes in barometric pressure. We have also reexamined the possibility of $N_2O$ production in corona and spark discharges to determine whether ionizing processes in the atmosphere could provide a significant additional source of $N_2O$.

These studies have revealed soil gas concentrations of $N_2O$ ranging from values near zero to $10^3$ times or more atmospheric concentrations. As a generalization, in soils of moderate metabolic activity in the absence of oxygen, $N_2O$ content can be very low. If nitrate ion is present and oxygen concentration low, $N_2O$ may be formed, sometimes in high concentration. In a few cases, low $N_2O$ values have been observed in the rhizosphere under conditions where oxygen would not be expected to be limiting. However, this may reflect the presence of microenvironments of depleted oxygen in a highly heterogenous system.

Measurements of $N_2O$ levels in the atmosphere immediately over the soil as a function of fluctuation in barometric pressure gave significant negative correlation with changes in barometric pressure only for situations where nitrogenous fertilizers had been applied and when only negative barometric changes were considered.

Observations of $N_2O$ production in corona and spark discharge in glass chamber yielded surprisingly high production rates, particularly in the case of a spark discharge where a yield of approximately $2 \times 10^{-7}$ mole $N_2O$ was obtained in 90 minutes with a 1-cm spark gap and a discharge rate of $5 \times 10^{-6}$ coulomb $sec^{-1}$. It is possible by making some reasonable assumptions to extrapolate these results to what would appear to be an unreasonably high production by a single lightning discharge. However, it is difficult to avoid the conclusion that ionizing processes in the atmosphere constitute yet another significant source of $N_2O$.

The following conclusions are indicated:

(1)   Soil gas concentrations of $N_2O$ vary over a wide range from values less than to much greater than atmospheric concentrations, and the soil therefore can serve both as a source and a sink for $N_2O$.

(2)   Under conditions of a dropping barometric pressure there is a significant negative correlation between atmospheric $N_2O$ content immediately over a nitrogen-fertilized soil and barometric pressure change.

(3)   When an unfertilized area was examined or when all barometric pressure changes were considered, correlations were still negative but not significant at the 5% level.

(4)   Corona and spark discharges in air in a closed container produced $N_2O$ in concentrations sufficient to indicate that ionizing processes in the atmosphere probably are a significant additional source of $N_2O$.

# THE SOURCES OF ATMOSPHERIC NITROUS OXIDE AT THE EARTH'S SURFACE

Jurgen Hahn
Max Planck Institut fur Chemie
Mainz, West Germany

Bacterial nitrification and denitrification may be considered to represent the most important processes for the generation of $N_2O$ in soil and water. Since the rates of denitrification and nitrification depend not only on the pH value and the oxygen concentration in the microbial habitat, but also on the temperature and on the supply of water, organic matter, and combined nitrogen, it is obvious that a great variety of ecological conditions prevail at the earth's surface with respect to $N_2O$ production. This is particularly true for soil where the oxygen concentration in the soil atmosphere and the pH value are determined by the soil type and structure, the moisture content, and the content of organic material.

In addition to the microbial processes mentioned, man-made sources of atmospheric $N_2O$ may be found in the catalytic oxidation of ammonia used for the production of nitric acid and in burning of fossil fuels. Although not located at the earth's surface, it should be mentioned that lightning might form another source of atmospheric $N_2O$.

Based on estimates of $N_2O$ fluxes due to the various sources and sinks, an attempt was made to construct a $N_2O$ balance of the troposphere. As shown in Table 1, the total flux of $N_2O$ into the troposphere was estimated to be 125 - 475 million metric tons (Mt) per year with 210 Mt $N_2O$ per year as the most likely value. These values were obtained from a tropospheric burden of $1700 \pm 200$ Mt $N_2O$ and a tropospheric turnover time of $8 \pm 4$ years. Independently, the $N_2O$ flux from different sources was estimated on the basis of individual data obtained from $N_2O$ measurements in air, soil air, and water. With the assumption that the air/sea boundary layer in the world ocean varies between 40 and $60\mu$ , measurements in North Atlantic sea water suggest a total marine net $N_2O$ production of 70 Mt $N_2O$ per year when extrapolated to a global scale (Table 1, row Ia). This value may be considered to be correct within one order of magnitude. Based on $N_2O$ measurements in the atmosphere of different soils, the entire soil source was estimated to be about 25 Mt $N_2O$ per year with a range of uncertainty of 10 - 100 Mt $N_2O$ per year (Table 1, row Ib). The net $N_2O$ production of fresh water (lakes and rivers) is essentially unknown. A first rough estimate would be 5 Mt $N_2O$ per year (Table 1, row Ie). Currently, industrial fertilizers seem to contribute to the tropospheric budget with 10 - 30 Mt $N_2O$ per year (Table 1, row Ic). It was assumed for this estimate that essentially no fertilizer is trapped in long-lived reservoirs such as the reservoir of soil nitrogen or the deep ocean, and that the yield factor for the net production of $N_2O$ in the processes of nitrification and denitrification with combined nitrogen from industrial fertilizers as a substrate is between 0.2 and 0.6.

Table 1.  N₂O balance of the troposphere

**Sources**

| | | mean value (10⁶ metric tons per year) | range | |
|---|---|---|---|---|
| Ia) | N₂O: | 70 | 25–250 | Marine sources |
| | N₂O-N: | 45 | 16–160 | |
| b) | N₂O: | 25 | 10–100 | Land sources (soil) |
| | N₂O-N: | 16 | 6–65 | |
| c) | N₂O: | 20 | 10–30 | Industrial N fertilizers |
| | N₂O-N: | 13 | 6–20 | |
| d) | N₂O: | 4 | 2–6 | Direct man-made sources |
| | N₂O-N: | 2.5 | 1–4 | |
| e) | N₂O: | 5 | 0–40 | Fresh water (lakes and rivers) |
| | N₂O-N: | 3 | 0–25 | |
| f) | N₂O: | ? | 15–90 | Lightning |
| | N₂O-N: | ? | 10–55 | |

**Sinks**

| | mean value (10⁶ metric tons per year) | range | |
|---|---|---|---|
| IIa) | 20 | 14–28 | Stratospheric processes (reaction with O(¹D) and photolysis) |
| | 13 | 9–18 | |
| b) | 3 | 1–5 | Tropospheric processes (photolysis and reaction with O(¹D), negative ions, OH and HO₂) |
| | 2 | 1–3 | |
| a+t) | 23 | 15–33 | Sum |
| | 15 | 10–20 | |
| c) | ? | (110–440) | Unknown sinks |
| | ? | (70–280) | |

Table 1. $N_2O$ balance of the troposphere  (Continuation 1)

| | Sources | | | Sinks | | |
|---|---|---|---|---|---|---|
| | mean value ($10^6$ metric tons per year) | range | | mean value ($10^6$ metric tons per year) | range | |
| a-f, $N_2O$: | >125 | 60-515 | All known sources | | | |
| $N_2O$-N: | > 80 | 40-330 | | | | |
| III) $N_2O$: | 210 | 125-475 | Total source (independent estimate) | III) 210 | 125-475 | Total sink (independent estimate) |
| $N_2O$-N: | 135 | 80-300 | | 135 | 80-300 | |

Direct man-made $N_2O$ sources (oxidation of ammonia or organic nitrogen compounds and burning of fossil fuels) seem to be of minor importance at present. These sources were recently estimated to produce about 4 Mt $N_2O$ per year globally (Table 1, row Id). On the basis of laboratory experiments, the $N_2O$ production due to lightning was estimated to be between 15 and 90 Mt $N_2O$ per year (Table 1, row If). However, it is still a matter of debate whether the results of laboratory experiments car. be applied to the real troposphere or not.

Adding up the fluxes from the various $N_2O$ sources, a total net $N_2O$ production of 60 - 515 Mt per year is obtained (Table 1, row Ia-f) which may be compared with the 125 - 475 Mt $N_2O$ per year estimated independently (Table 1, row III).

The sinks of atmospheric $N_2O$ are poorly known. As indicated in Table 1 (right-hand side), only about 25 Mt $N_2O$ per year of the 210 Mt of atmospheric $N_2O$ which should be annually destroyed under steady-state conditions are accounted for by known sinks. These sinks are chiefly photochemical destruction in the stratosphere and to a much smaller extent reaction of $N_2O$ with OH and $HO_2$ radicals, negative ions, and $O$ ($^1D$) in the troposphere, and photolysis of $N_2O$ in the troposphere. The major amount of atmospheric $N_2O$ is left for sinks still unknown. For more details, reference is made to a review paper on atmospheric $N_2O$ (Hahn, J., and C. Junge: Atmospheric $N_2O$ -- A critical review, to be published in Zt. fur Naturforschung, manuscript in preparation).

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# COMMENTS ON THE ATMOSPHERIC $N_2O$ BUDGET

S. C. Liu, T. M. Donahue, and R. J. Cicerone

The only known sink for atmospheric $N_2O$ is photolysis in the stratosphere (Bates and Hays, 1967; Johnston and Selwyn, 1975; Stedman et al., 1976), which destroys only about 10 Mt (N)/yr and gives $N_2O$ a lifetime of about 150 years. Certain gas-phase reactions are not completely ruled out. Biogenic sinks for $N_2O$ are observed in many experiments. $N_2O$ reduction into $N_2$ might be a major reaction of nitrogenase (Hardy and Knight, 1966), and many denitrifying bacteria can reduce $N_2O$ (Barbaree and Payne, 1967, Tiedje, private communication, 1976). However, no quantitative estimates of these sinks are available.

Without good estimates of either sources or sinks of $N_2O$, we cannot determine its atmospheric lifetime directly. However, Junge (1974), using an approximate mathematical analysis, related the lifetime of a trace gas to its standard spatial deviation. Some of his assumptions (e.g., relatively uniform sink and source function) might not apply to $N_2O$. Nevertheless, with a derived standard deviation of 8%, coupled with measurements by Hahn (1974), he deduced the lifetime of $N_2O$ to be 8 years with a factor of 2 uncertainty. Recent measurements of $N_2O$ in the atmosphere (R. F. Weiss, private communication, 1976; Craig et al., 1976; Yoshinari, 1976; Singh et al., 1976; Rasmussen et al., 1976) have shown different results. Each of these workers has multiple observations of $N_2O$ in marine and/or rural continental air that show little or no significant variability from day to day, that is, standard deviations of 2% or less except the latter reference, which showed 2.8%. The Scripps Institute data (the former two references above), perhaps the most convincing, were gathered between 70°N and 70°S in the mid-Pacific over several seasons and years. Little, if any, difference between 1964 and 1974 values were seen, except for a 1.5% increase with time, possibly due to combustion sources of $N_2O$ (Weiss and Craig, 1976). Careful separation preceded detection (in ratio to $CO_2$) by gas chromatographic, ultrasonic phase shift detection. Yoshinari employed an independent method, helium ionization GC detection. The Scripps group finds average $N_2O$ mole fractions of 0.296 ppm as did Singh, while Yoshinari found 0.328 ± 0.005) ppm, although Yoshinari's systematic accuracy is ±10%. Rasmussen et al. (1976) found a mean value of 0.330 ppm.

Earlier $N_2O$ measurements by Goody (1969), Craig and Gordon (1963), Hahn (1974), Schutz et al. (1970), Lahue et al. (1970) and others showed about 0.250 ppm, with significant variations that clearly implied a relatively short (10-year) $N_2O$ atmospheric lifetime if Junge's (1974) analysis holds. While much of the statistical variability of these data may be artifacts of early analytical methods and of sampling near sources (Hahn, 1975) there are seasonal trends (Goody 1969; Schutz et al., 1970) that one should not dismiss. By putting more weight on the recent measurements and taking into account the lack of positive identification of either a significant source or sink (greater than 50 Mt (N)/yr), we estimate the lifetime of $N_2O$ to be between 30 and 100 years. This implies, respectively, an annual $N_2O$ production of 50 and 16 Mt (N). If denitrification (270 Mt (N)/yr; see Figure 1)

is the source of $N_2O$, it also implies an $N_2O$ to $N_2$ ratio, respectively, of 1:4.4 and 1:16, assuming the ratio to be the same in the denitrification from the land and the ocean. A 1:16 ratio was considered likely by CAST (1976).

We believe only a small part (about 10%) of fixed soluble inorganic nitrogen in soils or seas is denitrified promptly. With the prices of nitrogen fertilizers tripling those before the 1973-74 oil embargo it has become profitable for farmers to return animal and human wastes to the land, instead of leaving them to be denitrified in barnyards and feed lots. Once the wastes are returned to the land the nitrogen in the wastes would approximately follow the nitrogen cycle shown in Figure 1. Because the large humus content in the soils and oceans needs a long time to change due to the projected nitrogen fertilizer usage, appreciable ozone reduction (say 10%) will be delayed. It should be kept in mind that the projected 6% per year increase in the rate of industrial fertilizer usage is based on the implicit assumption that the efficiency of fertilizer for crop production will remain at the present levels. Our calculations show that future growth in the usage of industrial nitrogen fertilizers could cause only 1 to 2% global ozone reduction by the year 2025. However, centuries from now the ozone layer could be reduced by as much as 10% if denitrification in soils is the major source of atmospheric $N_2O$.
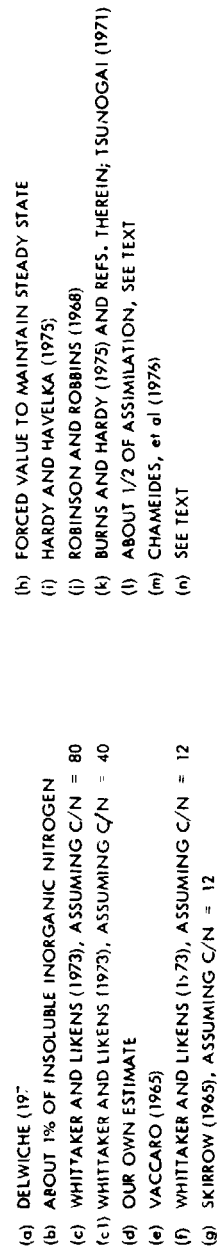
Figure 1. Nitrogen cycle of the land and the ocean; units are in million tons (N) for reservoir contents or million tons (N) per year for transfer rates.

(a) DELWICHE (197

(b) ABOUT 1% OF INSOLUBLE INORGANIC NITROGEN

(c) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 80

(c.1) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 40

(d) OUR OWN ESTIMATE

(e) VACCARO (1965)

(f) WHITTAKER AND LIKENS (1973), ASSUMING C/N = 12

(g) SKIRROW (1965), ASSUMING C/N = 12

(h) FORCED VALUE TO MAINTAIN STEADY STATE

(i) HARDY AND HAVELKA (1975);

(j) ROBINSON AND ROBBINS (1968)

(k) BURNS AND HARDY (1975) AND REFS. THEREIN; TSUNOGAI (1971)

(l) ABOUT 1/2 OF ASSIMILATION, SEE TEXT

(m) CHAMEIDES, et al (1976)

(n) SEE TEXT

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# GAS CHROMATOGRAPHIC MEASUREMENTS OF ATMOSPHERIC $N_2O$

R. J. Cicerone
Space Physics Research Laboratory
University of Michigan

A group of us at The University of Michigan have assembled two chromatographic systems to measure atmospheric $N_2O$ concentrations. Our goals in this research are to improve the analytic methods where necessary and possible, to deduce seasonal and secular trends in tropospheric $N_2O$ concentrations, if any, to identify sources of atmospheric $N_2O$, and to quantitatively estimate the size of various sources and sinks so that the workings of the $N_2O$ cycle and its residence time in the atmosphere can be determined.

Our two laboratory systems employ $^{63}Ni$ electron capture detectors operated at 350 C. One system uses a Porasil B-packed stainless steel column while the other employs a Porapak Q-packed cutter column in series with a mole sieve 5A-packed analytical column. Absolute calibration of the chromatographs has been accomplished through use of two independent flow dilution methods: feedback-flow dilution (FBF) and permeation tube flow dilution (PTFD). In both systems we begin with pure $N_2O$ and prepare diluted flows over the desired concentration range. Absolute concentrations generated by FBF and PTFD have agreed to $\pm 3\%$. More details of the instrumentation will be furnished in two papers now being prepared: one on the calibration methods and another, more lengthy report, on our measurement results and precision.

Through early September 1976 we have obtained $N_2O$ measurements of two general types: exploratory and quantitative high precision ones. In the former category are primarily our attempts to identify $N_2O$ sources. We have gathered air samples from open fields, both agricultural and unfarmed grasslands, from near compost piles, manure piles, cattle feedlots, near water bodies that collect surface water from fertilized areas and from several urban sites. We have also develope a gas collector for soil studies wherein we measure the amount of $N_2$ evolved from various soil environments vs time. Representative fluxes e found from fertilized grass in August were $6 \times 10^8$ $cm^{-3}sec^{-1}$. We also measured detectably elevated $N_2O$ concentrations near manure and compost piles and found that breaking the crust on compost piles released relatively large amounts of $N_2O$; i.e., outward $N_2O$ fluxes before breakage were five times smaller. No detectable $N_2O$ elevations have yet been seen near feedlots or fertilized fields. Air samples in these studies were gathered in polyethylene syringes and in stainless-steel flasks.

In another semi-exploratory investigation we have measured the $N_2O$ concentration in automobiles being tested with different catalytic converter exhaust systems. Depending on the vehicle and mode of operation we found from 0.3 to 10 ppm $N_2O$. Extrapolations to global emissions and results for uncatalyzed vehicles will be reported in a later paper. A related measurement made on a city street during rush hour traffic after one week of stagnant air conditions showed up to 6 ppm $N_2O$.

The August and early September mean concentration of $N_2O$ at sites just north and east of Ann Arbor, Michigan was $328\pm13$ ppb by volume. The $\pm4\%$ statistical error indicated here includes both real variance and instrumental imprecision.  Earlier summer and fall data will be reported elsewhere.

# NITROUS OXIDE: ATMOSPHERIC CONCENTRATIONS 1964-76, INDUSTRIAL SOURCES, AND AIR-SEA EXCHANGE

R. F. Weiss, W. Dowd, and H. Craig
Scripps Institution of Oceanography, La Jolla

New high-precision measurements show that the $N_2O$ mixing ratio in Pacific marine air is constant to <0.5% over the latitude range 50°N to 60°S, and suggest a long tropospheric residence time for $N_2O$. Samples from legs 9 and 10 of Pacific Geosecs Expedition (May 1974) and Carrousel Expedition form comparable north-south sections along ~120°W. This comparison shows an increase in tropospheric $N_2O$ over the decade of about 1.8%, which may be due to anthropogenic sources. Our measurements of fuel oil and coal combustion products show that up to 40% of the observed increase may be explained by this effect. During Pleiades Expedition (May 1976) in the eastern Pacific, the first experiments to measure directly the partial pressure of $N_2O$ in surface ocean waters were carried out, together with simultaneous gas-exchange studies based on dissolved radon measurements.

# MEASURING NITROUS OXIDE FLUXES RESULTING
# FROM DENITRIFICATION IN SOIL

D. E. Ralston
Department of Land, Air and Water Resources
University of California
Davis, California

Nitrogen fertilizers or wastes applied to soil may be denitrified if reducing conditions exist within the soil profile. The reduction of nitrate and nitrite results in volatile gases, usually nitrous oxide and molecular nitrogen. These gases diffuse from the soil profile at rates dependent upon the rate of denitrification and the rate of diffusive gas transport. A field plot on Yolo loam soil at Davis, California, was used to evaluate denitrification from nitrate fertilizer applied at a rate of 300 kg of N/ha. The nitrogen fertilizer was enriched with the stable isotope, nitrogen-15, in order to trace the fertilizer nitrogen in the gaseous denitrification products, the crop, the leachate water, and the soil. The concentration and isotopic ratio of $NO_3$, $N_2$, and $N_2O$ were measured as a function of soil depth and time (Figures 1-4). The gaseous concentration gradients and measured soil gaseous diffusion coefficients were used to calculate fluxes of $^{15}N_2$ and $^{15}N_2O$ from the soil. The production of $N_2$ and $N_2O$ began immediately after application of the fertilizer. For soil conditions at which near maximum denitrification would be expected, approximately 40% of the applied nitrogen was denitrified. The total $N_2$ flux was generally more than an order of magnitude greater than the $N_2O$ flux.
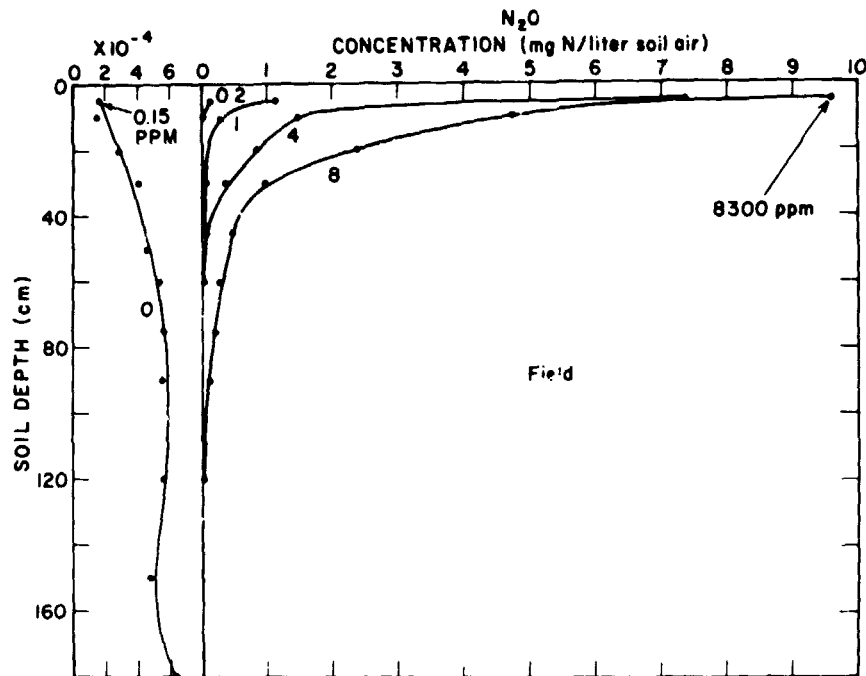
Figure 1.  Nitrous oxide concentration profiles in a
           4.4 m² field plot cropped with grass at
           five different times (days) after applica-
           tion of 300 kg N/ha of nitrate fertilizer.
           Each data point is the average from two gas
           samplers.  Concentrations decreased after
           day 8.  The abscissa is divided into two
           scales with the left scale going from 0 to
           8 · 10⁻⁴ mg N liter⁻¹ soil air.
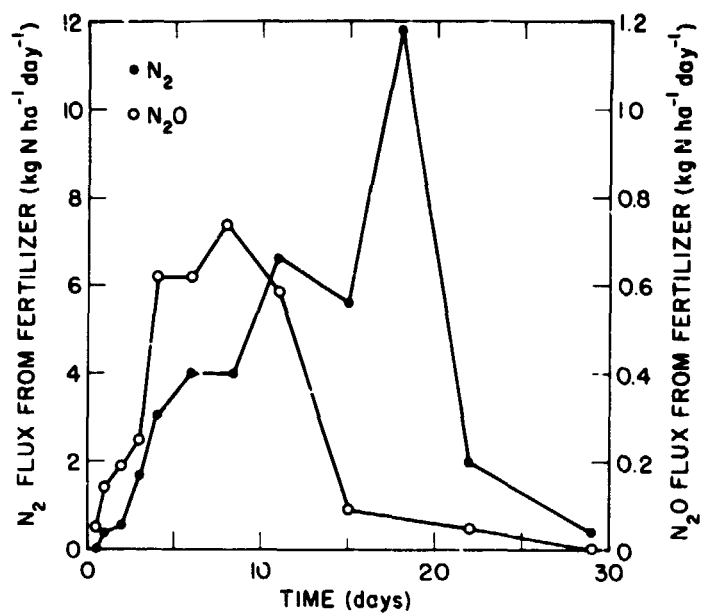
Figure 2.   Nitrous oxide and nitrogen gas
diffusing from the surface of a
field plot cropped with grass as
a function of time after applying
nitrate fertilizer.  Note that the
scale for $N_2O$ is 10 times smaller
than that for $N_2$.  Each data point
is the average gas diffusion (flux)
determined from two gas samplers.
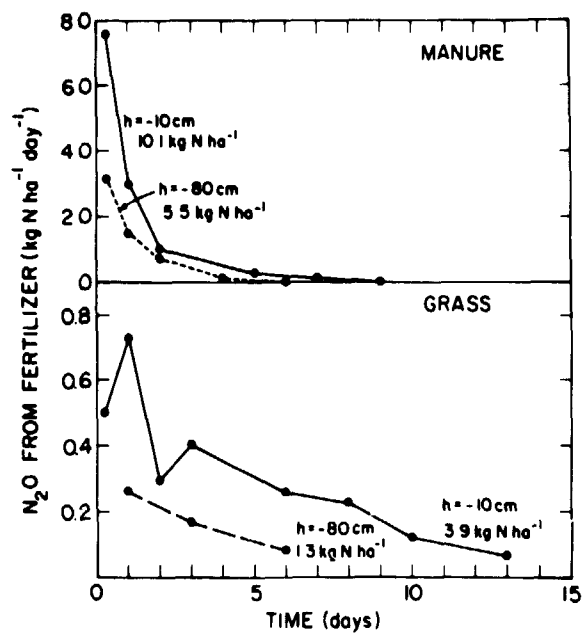
Figure 3. Nitrous oxide flux of field plots for which manure had been mixed with the top 10 cm of soil and for plots cropped with grass as a function of time after applying nitrate fertilizer. The flux was calculated from the amount of $N_2O$ accumulating beneath a chamber placed over the soil surface for 1 or 2 hours of each sampling day. The plots were maintained at two values of soil-water pressure head (h = -10 cm and n = -80 cm). The numbers below each soil-water pressure head treatment are the total amounts of N denitrified as determined by calculating the area beneath each flux curve.
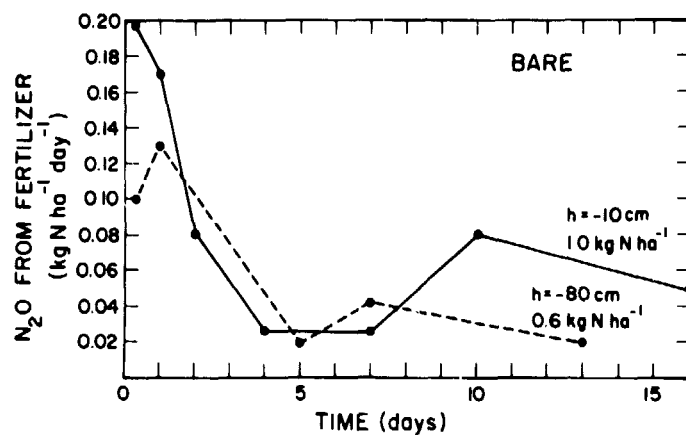
Figure 4.   Nitrous oxide flux from uncropped field plots as a
            function of time after applying nitrate fertilizer.
            The soil-water conditions and the methods used for
            determining the flux were the same as those of
            Figure 3.

## NITROUS OXIDE IN THE SEA

Tadashi Yoshinari
Department of Microbiology,
Macdonald Campus of McGill University,
Ste. Anne de Bellevue, Canada

From studies on the distribution of $N_2O$ in the North Atlantic, it was deduced that the production of $N_2O$ could be significant in terms of the oceanic nitrogen budget. $N_2O$ in the water will eventually escape from the sea-surface to the atmosphere.

The $N_2O$ and $O_2$ profiles in the slope water off Nova Scotia (a), Gulf Stream (b), and Sargasso Sea (c) measured in different seasons are shown in Figure 1. There was a negative correlation between the $N_2O$ and $O_2$ concentrations in the water columns, and the $N_2O$ concentration reached its maximum at the oxygen minimum layer. From the concentration gradient of $N_2O$ at station (b) and (c), the rate of $N_2O$ escape from the entire ocean surface was estimated to be $10^{12}$ g $N_2O$/year, if we assume the coefficient of eddy diffusivity to be 1 $cm^2$/sec. This is, however, a conservative estimate for the following reasons:

(1)   The $N_2O$ production seems to correlate with the biological activity in the water, and the present estimate is based upon the data in the western North Atlantic where biological activities are not high.

(2)   The coefficient of eddy diffusivity could be higher than 1 $cm^2$/sec within the depth range studied. Consequently, the present estimate could approach $10^{13}$ g $N_2O$/year.

(3)   Based upon the data in Fig. 1, it was calculated that the zone of $N_2O$ supersaturation extended closer to the surface (20% supersaturation at a depth of 25 meters) in station (a) than in stations (b) and (c). This suggests that the rate of $N_2O$ escape across the sea-surface may be significantly higher in coastal waters than in open waters.

Figure 1. Vertical $N_2O$ and $O_2$ profiles at three different stations in the western North Atlantic: (a) slope water off Nova Scotia (42 18' N, 61 24' W), (b) Gulf Stream (39 07' N, 62 21' W), (c) Sargasso Sea (35 52' N, 63 44' W).

## N$_2$O PANEL DISCUSSION

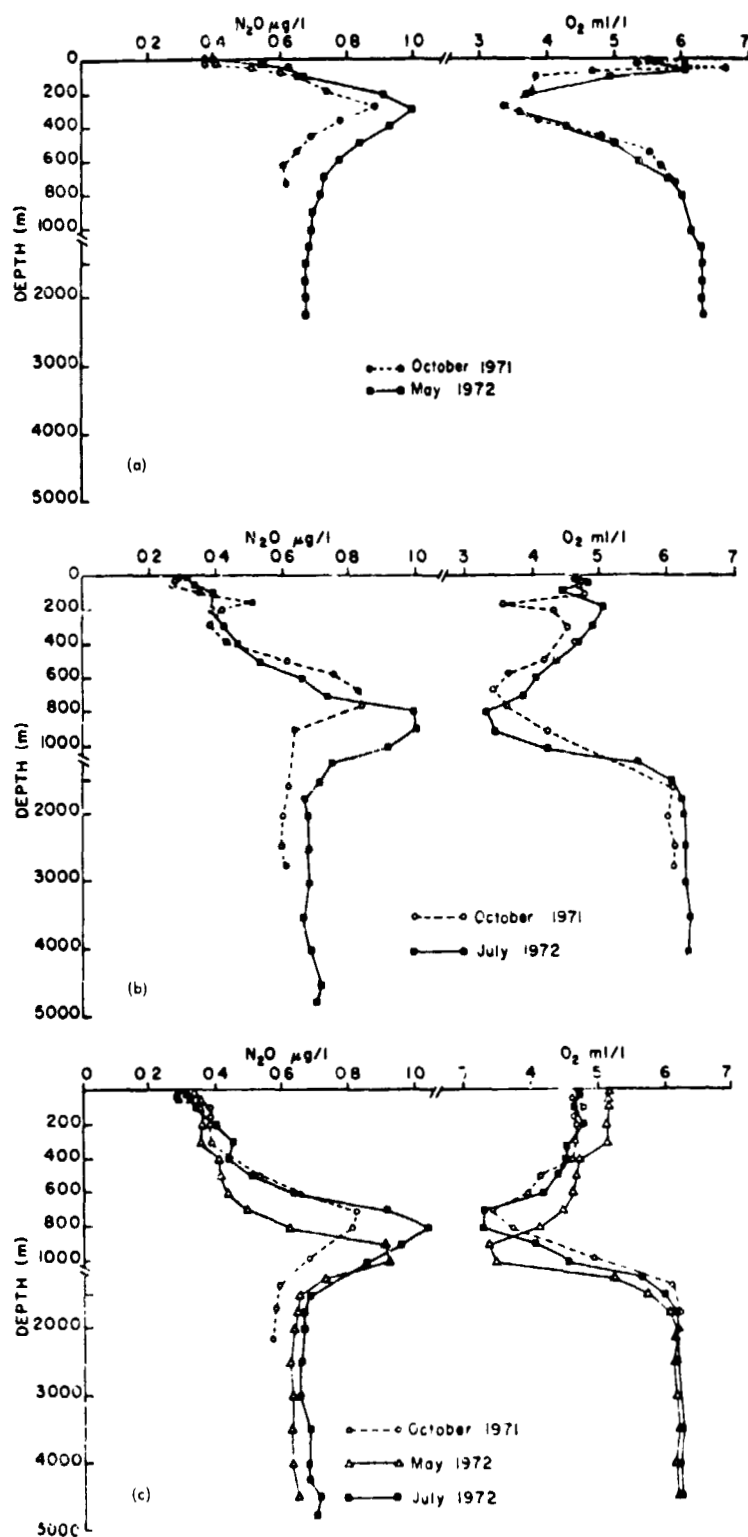### H. Schiff, Chairman

#### H. Schiff:

What I tried to do was simply jot down some of the questions and points that people have been raising today. We have, of course, the old perennial one of the sources and sinks: the natural versus the man-made ones. The natural ones we have more or less identified. It is difficult to give exact figures for the sources, but they are in the region of 175 megatons per year from the land plus the 10 megatons by lightning. Fertilizer has an effect more easy to quantify, and it has been going up by both Mike's figures and Paul's. T'. figures give 3-1/2 tons in 1950, 40 megatons in 1974, and 1000 megatons predicted by the year 2000. McElroy and company were predicting fairly prominent effects near the year 2000, whereas I think Crutzen and Donahue were talking about a much longer period. I don't think tnere was a basis argument that there would be changes in ozone, but the time scale with which these effects would occur, as I understood it, was the major disagreement. Then we ran into all these uncertainties of which I've got a few listed here. The question of fluxes from the land, about which we heard something today. I wish we could get together and identify the differences. For the ocean it depends on whether one uses the Hahn figures for the degree of productivity of the ocean or the Yoshinari ones. The question of tropospheric lifetime: stratospheric photolysis is anywhere from 100 to 200 years. We have the 8 to 20 year figure of the German group. On the other hand, we've heard from the Schmeltekopf group that the variability is not nearly as large. I realize that we are going to get into trouble if we go back to consider lifetimes, but I think the panel should discuss that. Then there are questions of biology, of which I have just listed a few here. For example, the number of times the nitrate is recycled before denitrification. Mike uses 5 by land and 30 by water, and Paul went to immediate denitrification. What do we know about that situation. How much of the N$_2$O is released by fixation? Some of the measurements we heard before bear on that. We certainly should talk about the fixation release, and the denitrification release, and the dependence of those things on some of the parameters that we have heard today. The question of the immediate release of the fertilizer in the form of ammonia, and subsequent action of oxidation of ammonia, is something else that I want some clarification on. I think Mike has already talked about what happened in two cycles.

With that, Hal, why don't you come over and pick it up and then we will get into the free-for-all.

H. Johnston:

Everybody has agreed that this is a very complicated subject. It has all the complexities of the ozone depletion problem plus the oceano-graphic and biological effects. Sometimes when you get something very, very complicated, at least to get started it might not be a bad idea to see if you can oversimplify it. That's what I want to present again. I indicated this once at the AGU meeting last spring. I indicated that you can write a very simple account of this, where you make about the same assumptions people make in the more complicated calculations, and you end up not too far from the same values. Now the oversimplification I want to use assumes a steady-state calculation. That is, you have a steady .itrification fixation rate, and a step function to a new steady value. And after a long time you ask what would be the decrease of ozone and what other independent variables does it depend on? Now you don't use these simple steady-state linear equations for the final solution to the problem, but I think they are not bad ideas at the beginning to try to identify the important independent variables and to try to get a perspective on the independent variables. There is one simple, super-dandy equation that explains a lot.

The global     ction in fraction of ozone depends on the following quantities: the ꞏ   ꞏ function increase in the nitrogen fixation $n_f$, the nitrous oxide global inventory, and the product of four dimension-less quantities, alpha, beta, gamma, and tau:

$$\frac{-\Delta O_3}{O_3} = \left(\frac{\Delta n_f}{N_2O}\right) \alpha\beta\gamma\tau \tag{1}$$

This is the percentage reduction in ozone in the steady-state as a result of a step-function increase in fixation rate. If we have 100 million tons per year increase in the nitrogen fixation rate, what would the effect be, steady-state?

The following figures illustrate what alpha, beta, and gamma are. Tau is the atmospheric lifetime of nitrous oxide, and the values for this lifetime range from 4 years up to 100 years plus. So that tau could be determined by independent considerations. Figure 1 defines the dimensionless quantity alpha. It is the fraction of denitrification that goes into nitrous oxide. I have heard soil scientists talk, and they would say typically within 5 to 10% of this, but this is one of the unknowns. This is the thing capable of being independently determined from experiments, as has been illustrated by one of the r cent talks. Figure 2 illustrates the factor beta, which is the frac-tion of fixed nitrogen that is denitrified promptly: that is to say within a few decades. You will notꞏe that I have deliberately left the time scale unspecified here. If you fix a sample of nitrate, you may have prompt denitrification of a small fraction of it. This was illus-trated by a recent talk. If the nitrate is incorporated into annual plants it will certainly be a longer time than if it goes into larger plants and animals. So you have these various long time scales. If it
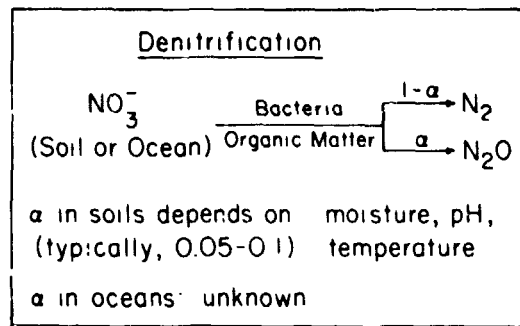
Figure 1. Definition of the quantity a in Eq. (1).
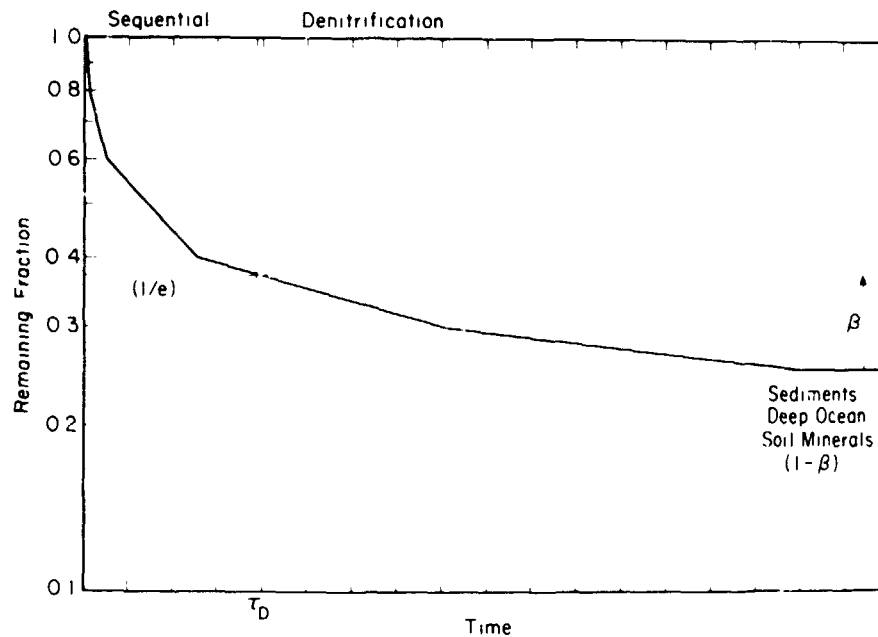


Figure 2. Definition of the quantity β in Eq. (1).

ever went down to deep sediments or soil minerals, then for the kind
of time scales we are talking about, decades or centuries, it would
be unavailable. So the fraction of fixed nitrogen that is denitrified
promptly within a few decades is the other factor we have in this
equation.

Figure 3 illustrates the third factor gamma, which is the sensi-
tivity of stratospheric ozone to an increase in stratospheric oxides
and nitrogen. Using it this way we are just talking about the linear
effect; we are talking about small effects. The dashed line is the
climatic impact assessment program line. That is 1/5. The triangle

$$-\frac{\Delta O_3}{O_3} = \frac{1}{5}\frac{\Delta NO_x}{NO_x}$$
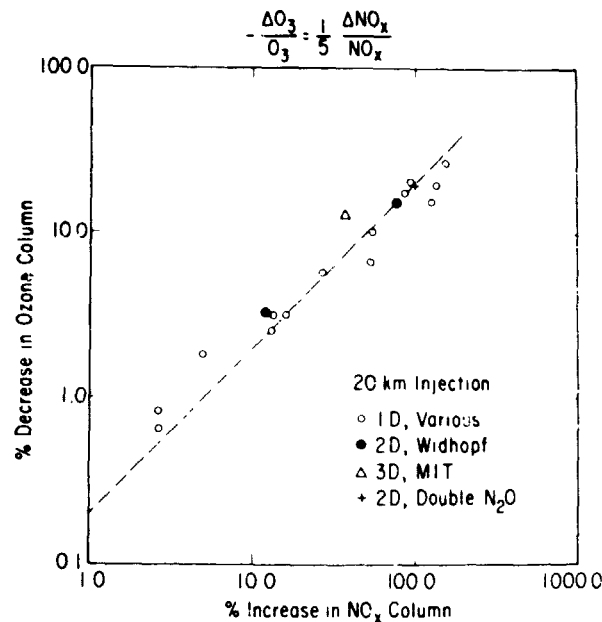


Figure 3. Definition of the quantity $\gamma$ in Eq. (1).

is the one 3D model of the subject; that is the MIT 3-dimensional model.
I give a factor of about 1/3. I haven't seen much discussion of that;
it has the effect of sweeping added materials out of the stratosphere
a little bit faster than some of the 1D models. On the other hand
it gives a larger sensitivity of stratospheric ozone than the 1D models.
You can have that factor anywhere from 1/3 to 1/10 or 1/15th if you
want; what are small factors like that in this kind of a discussion?

So now, if we pull this together and use beta equal to 1, that
will give an upper bound; that is to say, all fixed nitrogen is denitrified
within a few decades. It would say, "we can then take alpha and tau
as our variables, and what is the effect of 100 million tons per year?"
This kind of spreads the thing out. The results are given in Figure
4, where we regard tau as an independent variable that will be determined
by all the sources and sinks -- the lightning, oceans, and what not --
and tau is uncoupled now from the other things. About the only idea
that comes out of this is that if you applied a 100 million tons per
year to land, the fraction denitrified is expected to be 5 or 10%.
And then you fall into two camps. If the effect occurs rapidly, because
there are sources and sinks like this from lightning or the oceans,
then the effect will not be very big, about a 1% effect for a 100 million
tons, more or less. On the other hand, if the lifetime is long, then
a small effect will occur soon, and if the effect is large it will
be late. So if you have a large effect because of long lifetime, a
10% or so effect will not show up for about 100 or 200 years as a mean
time.

$$-\frac{1}{\beta}\frac{\Delta O_3}{O_3}\ \%$$

| $\tau$ \ $\alpha$ | 0.025 | $\alpha$ Land | | $\alpha$ (Including Ocean) | |
|---|---|---|---|---|---|
| | | 0.05 | 0.1 | 0.2 | 0.4 |
| 5 | | 0.4 | 0.3 | | |
| 10 | | 0.8 | 1.5 | | |
| 20 | | 1.5 | 3 | | |
| 40 | | | | | |
| 80 | | | | | |
| 160 | | 12 | - | | |
| yr | | | | | |

$\Delta N_F$ = 100 MT/yr, added to land.

Figure 4. Percent depletion in ozone vs $\alpha$ and $\tau$.

This is a very simplified point of view. The experts may cringe at seeing their high form of science expressed in such simple terms, but it is useful for the non-experts if you don't take it any farther than you should. It's just a linear equation. Its a steady-state equation to give you an idea of what's going on, and what are the independent variables, and what are the variables that can be evaluated independently of the others. I think it has some merit in pulling this very complicated thing together. Still, the factors alpha and beta depend on the location of the application of the fixation of nitrogen and that, of course, makes it a very complicated problem.

H. Schiff:

It suddenly dawns on me that we haven't given a chance to the representatives of the Donahue camp to say anything on this subject so let's give them a chance.

S. Liu:

I have two points to make. A professor at Michigan State told me he studied denitrification all his life and now he suddenly found his proposal of how to get rid of waste by denitrification to be irrelevant. The second point I want to make is to emphasize what Professor Johnston just said. The lifetime of $N_2O$ really decides the ratio of $N_2O$ to $N_2$ in the denitrification. If the $N_2O$ lifetime is 10 years, then you cannot escape the conclusion that the $N_2O$ to $N_2$ ratio produced in denitrification should be around 70%, and most of the measurements so far indicate something like 1 to 10%. Therefore, it makes sense to reexamine the lifetime of $N_2O$.

The 10-year lifetime for $N_2O$ really comes from the highest estimate of around 60 million tons of production from the ocean, plus a small fraction from the rest. The second evidence is Junge's paper. He pointed out in his paper that the standard deviation in the German group measured is around 8%. Using his formula, he arrives at a lifetime for $N_2O$ of about 2 years or less. If you examine how he got his formula, there is one crucial assumption: he assumed that all the production is randomly distributed around the globe, which we know today is not true. It is really very different from a random distribution. Therefore, this lifetime does not apply to $N_2O$. The third thing we found was that if we collected $N_2O$ samples from the feedlot or the grass, there is almost an effect of 100 less than the 10 year lifetime produced by the German group.

### H. Schiff:

I am not quite sure how to play this. Maybe what we ought to do is give the panel a chance to engage in combat. That is what I was going to say, and maybe Mike wants to comment on these three points. After that we will invite questions from the floor, but gentlemen I ask you to obey the Marquis of Queensbury rules during this fight.

### J. Hahn:

Let's say at first that I agree with you. [Laughter] The tropospheric lifetime is really a key quantity in the whole thing, and you have been talking about this equation, this relation which was derived by Junge from plotting evaluations of different trace gases, not only $N_2O$ but CO, $CH_4$ and others. He used the global mean of the standard variation, and of course, in agreement with you, you cannot take this from one location. But, using a global mean of the standard variation, and modified with a tropispheric residence time, then you get a number of 4.14, which is an empirical number. From his plot one can see that this number is correct within a certainty factor of 3. In other words, if we had a number for the known mean of the standard deviation, we would be able to calculate what the tropospheric residence time would be.

Now the only problem is the shift from the residence time to the standard deviation. It is necessary to take all these standard deviations from long enough sets of data, and that is important. If we take five bases of measurements, they don't tell us anything. We require long enough sets of measurements, and where do we find them. I agree we do not have enough to come to a very conclusive statement. But if we take what we have, even with a very low variation, then we don't come any higher than to a residence time of 30 years. This is uppermost residence time I would negotiate with. On the other hand, our data from the continent, which I admit are locally influenced, give a residence time of 1.8 years. So the lifetime should be somewhere between these two extremes.

**H. Schiff:**

Do you accept that as an extreme, Mike?

**R. Weiss:**

Well I would like to say that the standard deviation of all of the measurements that we made during one year, taken over a range of latitude from 16° north to 70° south, or something in that ballpark, showed that the variations were essentially equal to the standard deviations of our calibration standard measurement. In other words, the real variations must be much less than 1/2%, and if you plug that variation into the Junge equation, which I think of as an empirical equation and it seems to be reasonable for some of the other gases, one gets for residence time a value much longer than 28 years.

**J. Hahn:**

Yes, perhaps 30 years. A lower limit of 28 years.

**H. Schiff:**

So Hahn is already outside your range. That data was remarkably constant.

**R. Weiss:**

Except for the hemispheric difference we saw in '64, we have no indication of any variation at all within our experimental accuracy of 1/2%, and that also applies for seasonal variations as much as we've measured them.

**H. Schiff:**

Mike do you want to say something?

**M. McElroy:**

Well I guess four points have been brought up. An issue of Scientific American that just appeared on my desk does a reasonable job of surveying the economics of fertilizer. The cost to construct the plant required to produce 200 megatons of fertilizer a year is $13 billion. That is not an exorbitant amount of money, given the importance of food production. The price of fertilizer is up, so is the price of food. The price of home heating oil is up, and we still pay the bill. On the question of alpha in Harold's model, I think that is a very reasonable way to do things, to simplify things. I think that we all do that privately, in our trying to understand what our

results mean. But it seems to me that there is an assumption on the part of several members of this panel that the soil is the only place nitrification can take place, or the ocean. I don't think that is true. Thinking about the way nitrogen moves through the system, and considering Hahn's data, we should look very carefully at shallow rivers and estuaries. If there is, indeed, a very high yield of $N_2O$, perhaps it is not in the soil but it is really there. I think we need more data along those same lines.

On the question of the ocean contribution, it seems to me that the only thing that can make the lifetime exceedingly long in the context of Hal's discussion, is if the ocean controls the $N_2O$ budget. So that one has to tap a very, very large reservoir, and I find myself puzzled by the different sets of data which the oceanographers all seem to propose with equal confidence. On the one hand there is 135 megatons a year from Germany. There is 1 megaton a year from Japan, and there is less than 45, under any circumstances, from Southern California. That's two orders of magnitude, and everybody is very confident in their data. Finally, not to be overlooked, I think is the rise in $N_2O$ which Weiss talked about, and that rise is about twice as large as you can attribute to coal combustion alone and is actually a little larger than what we get with the coal and fertilizer combined if you add them both together.

R. Weiss:

If the tau is long. If the tau is short, then we are looking at a quarter of the source from the coal and maybe half of the source from fertilizer if you take $N_2$ over $N_2O$ of 90%.

H. Schiff:

O.K. are there any other points that the panel wants to make?

R. Cicerone:

I would like to go into the logic once again: about why the residence time is so important. Namely, what Dr. Ralston reported doing. Ralston's paper, to me, was one of the most important things I have seen in 2 years of thinking about this. It is the first time I have ever seen a nitrogen budget study done with an identification of the gaseous products involved. In the April AGU meeting we talked about this. Dr. Delwiche, I think, confirmed it, that there have been such experiments. Don Ralston reported somewhere that we not only have the budget study but percentage yields of $N_2O$ and $N_2$. Now, just for the record, we called and he found $N_2O$ divided by $N_2$ yields of less than 1/10th. Now let's relate this to the residence time arguments. Let me just put a parenthetical remark in here -- none of this is certain; it is an enormous problem, and we would all do well to pay a fair amount of attention to it.

Let me just try to put some logic together.  Now, if the biological denitrification is the principal source of tropospheric $N_2O$, then all we have to do is know the fraction of $N_2O$ released in the total denitrification, because we can assume that the total denitrification rate is about equal to the fixation rate of nitrogen, which is a couple hundred megatons per year.  If the $N_2O/N_2$ yield is of the order of say 6 or 7%,  then the flux of $N_2O$ out of biological denitrification is on the order of 15 megatons per year.  That would argue for the long atmospheric residence time.  Think about a 100-year residence time to feed the atmospheric $N_2O$ content with a total source of 15 megatons a year.

What are the other arguments for long atmospheric residence time of $N_2O$.  I think there are four.  Number one is the standard deviation of the air samples of the Weiss and Craig data from Scripps; also the standard deviation of Hung Wa Sing's data at SRI, and Rasmussen's atmospheric data.  All are small standard deviations and if you go through the Junge argument you get the long lifetime; also the fact that Weiss and Craig do not see latitude gradients of any significance at all, except near the south pole.

The second argument for long atmospheric residence time is the smaller sources of nitrous oxide being deduced from the ocean now by Yoshinari and by Rasmussen.  Hahn's extensive work, I think, has led to a smaller estimate than he originally had.  Also Rasmussen's recent data, which he just reported to me today, yielded smaller sources of $N_2O$ from the ocean than we thought before.

The third category of evidence with long atmospheric residence time is the fact that, despite tremendous work amongst the aeronomy community over the years, beginning with Bates and Hayes, we really have only identified photolysis by sunlight in the UV.  So we are left with only one sink that we can identify.  Tremendous efforts have taken place in the NOAA Aeronomy Laboratory in Boulder.  Now we have Ralston's data, which tells us that under heavily fertilized conditions, but under controlled experiments, we have a low yield of $N_2O$ to $N_2$, once again making a self-consistency here with a long atmospheric lifetime. Obviously this is not conclusive but is a good start.  I am pleased to see Ralston's type data here.  I imagine Delwiche had something to do with encouraging him to do it.  It is just tremendous data.

### H. Schiff:

Mike I am sure you would like to comment.

### M. McElroy:

I agree that it is tremendous data and I actually enjoyed reading the paper that is in the literature on which his talk was based.  The paper is exceedingly important.  In some sense the surprise to me was that he actually saw as much $N_2O$ as he did.  Also, an important point that he made in his talk, which should not be allowed to slip away, is

that the $N_2O$ appeared more rapidly than the $N_2$ did. He offered two potential explanations for that, one was that the $N_2O$ was withdrawn into the groundwater, perhaps after it was made. The second was that $N_2O$ is a precursor in denitrification. Let us say that if you take the second point of view, the amount of $N_2O$ that comes out, or the yield, is rather critically a function of the amount of pore space available: essentially, the lifetime of the $N_2O$ once formed before it is released to the air versus the time constant for it to be reduced further to $N_2$. That leads me to think qualitatively in terms of a relatively high probability that denitrification would terminate at $N_2O$ in shallow waters, such as the Rhine, and that it might not have a chance to go all the way to $N_2$, leading therefore to a larger yield of $N_2O$.

The question of the lifetime. Let's state it the way it really is. Experimental data say that there is little variability in the Pacific. The Pacific is a very large ocean. The experimental data, of Goody, for example (very clean, looking at the sun, constant light source for 3 years) says that there is considerable variation in Boston. You cannot throw that away. The uncertainty in his data is 4%. The range goes from 2.2 to 3.3. It cannot be thrown away. It is difficult to find another sink for $N_2O$ to account for the short lifetime. That doesn't mean it doesn't exist. But to get a short lifetime for $N_2O$ by photolysis, all you require, if you do the photolysis in the visual, is a cross section of order $10^{-24}$ $cm^2$. An optically forbidden dissociation in the visual could easily go undetected in the lab, and give you a relatively short lifetime. The other possibility is that a long time ago Hertzberg made measurements of the population rate of overtone bands of $N_2O$ lying above the first dissociation limit of the molecule. I don't know what happens to those vibrational states once they are formed, but I can tell you that in the atmosphere they are formed with a J value which is of the order of $10^{-7}$. What happens to those very high lying vibrational states in the atmosphere I don't know.

## H. Schiff:

Hal, do you want to come in?

## H. Johnston:

Well it is just that I hadn't told him that we already made measurements of this in the visible. There is no $N_2O$ absorption.

## M. McElroy:

What is the limit?

## H. Johnston:

Rayleigh scattering.

**R. Weiss:**

I would like to present a fifth argument to add to Ralph Cicerone's list for long lifetime. And I think that one can be gotten by working the problem backwards, taking what people have proposed for anthropogenic sources for $N_2O$ and comparing that to our observed increase. If you limit yourself to combustion and fertilizer production, and you take the numbers that Rasmussen's group and we have measured for combustion, and you take something like maybe even 10% denitrification to $N_2O$ in the fertilizer production rate, and you plug that into the increase that we observed, you come out with a long residence time: something on the order of 100 years. I don't think there is a way to get around that one either.

**H. Schiff:**

I think we ought to give the audience a chance. So let's have this the last one.

**J. Hahn:**

I want to emphasize one thing Mike McElroy wrote up. This speaks for short lifetime. There was not only this increase measured by Goody et al. He measured at the same time the same increase in a given place 4000 km away. So it was really at least a hemispheric phenomenon, which speaks for a short lifetime.

**M. McElroy:**

It is fair to point out, and I hope people don't lose sight of this, I showed a graph on the fertilizer calculations that we did with a 100-year lifetime. The importance of the effect is not done away with by having a long atmospheric lifetime. The fertilizer problem is one to be studied seriously whether the lifetime is 10 years or 100 years.

**H. Schiff:**

O.K., lets throw this open for general discussion. Let's start over there.

**Voice in audience:**

I got the impression, I guess from Harold Johnston's remarks, that the ultimate effect is far worse if the lifetime is larger. Is that accurate?

**H. Johnston:**

I guess they didn't get the point here. The lifetime from the denitrification source, and admitting the possibility of lightning as a major source or something else we don't know about as a major source, then the longer the lifetime the greater the effect. All things being equal, the alphas and betas being equal, the longer the lifetime the greater the ozone reduction. Yes.

**Voice from audience:**

What are the estimates of nitrogen fixation, which is what you are using to couple the lifetime?

**H. Schiff:**

You mean the ratio of $N_2$ to $N_2O$.

**Voice from audience:**

The global fixation rate that you would be using to fix the denitrification rate.

**M. McElroy:**

I gave a number that's relevant. The question is how large could it be, and the answer is that it cannot be larger than 300, otherwise there is no point. 300 megatons a year.

**Voice in audience:**

I have a question about whether or not the time experiments described by Dr. Ralston shed light on the yield. I'd like to refer to a remark that Jurgen Hahn made during his talk. It is very clear that the yield of $N_2O$ depends on the pore space available, and he had a very, very wet soil. I think Mike was about to reach that point and went on to something else. I am amazed that he saw any $N_2O$ at all, because he was worrying me quite a bit. I think that it is difficult to accept the idea that the yield should be 70%. It is easier to think that maybe lightning or fires or something else are important sources of $N_2O$. It is logical to deduce that, depending on how many you need to balance the system. I don't think that the Ralston data was intended to, nor does it, tell you very much about the yield under average conditions.

**H. Schiff:**

Question?

**Voice in audience:**

I saw in Dr. Hahn's paper a comment that his sources are over-
balancing the sinks by a figure of 90 megatons per year. It is the
only discussion of the mismatch between source and sink that I have
really heard, specifically.

**M. McElroy:**

That is the whole lifetime question. That is what this dis-
cussion is about.

**Voice in audience:**

Are there any comments whether this is an unknown source, or
whether lightning could account for it?

**H. Schiff:**

We have to put that in the context of the range that we're talking
about. You can't take a central value alone and look at the match, but
surely you must say what your degrees of uncertainty are. Are we in any
position with data today to make that kind of a balance? We certainly
aren't with the CFMs. I am surprised if we are with the nitrogen.

**H. Johnston:**

It can be said if the lifetime is short there exists an unknown
sink: a big one.

**H. Schiff:**

What I am saying is that there is an uncertainty in that, and so
can we ever unscramble and say that we have enough data to pin anything
down well enough to make a balance at this date.

**R. Cicerone:**

May I ask Dr. Kraus a question? We tried to determine if
lightning could be a global sink for $N_2O$, and examined different theo-
retical arguments. It looks absolutely impossible. I want to say
something about Connie Delwiche's and other people's, statements about
$N_2O$ being produced in strokes. Don Stedman has made 10 or 12 measure-
ments using spark chambers looking for $N_2O$, in addition to fixed nitro-
gen. He can't find any $N_2O$ being produced in spark chambers. We are
trying to get access to the 1-meter spark chamber in Minneapolis, and
we have been granted that now. We will try again under different spark

conditions, but I just can't accept the large numbers for the $N_2O$ source that your data was giving at this point.


### C. C. Delwiche:

I think that maybe you misinterpreted my argument. My argument was that it becomes absurd to try to extrapolate this sort of a thing to atmospheric production of $N_2O$. There are several problems. I am strongly convinced that the residence time must be longer than the figures we now have. If you try to account for it solely on an input from nitrogen fixation and denitrification, it doesn't work. The numbers on the fraction of fertilizer nitrogen which is denitrified are unrealistically high, and unless there is some gigantic source, such as the sea, and the evidence is that it is quite the opposite, then we just don't have enough nitrogen being fixed to then denitrify even at a high rate to account for it. My numbers say a residence time of 200 years if you optimistically take a additional source, forest fires possibly, although I am a little bit uneasy about the thermodynamics of that. Lightning, possibly, but certainly not the order of magnitude that would be required to balance the books. All of it argues for a longer residence time. Now with regard to the spark chamber -- it works. Come and see me sometime and I will demonstrate it for you [Laughter].


### S. Liu:

One thing I want to comment on is this -- if you discharge continuously you swamp the whole system with $NO_x$, which has been known to make $N_2O$. In the atmosphere, you just don't have that kind of situation.


### C. C. Delwiche:

Well, of course it may be that the $NO_x$ concentration in the chamber would add to it, but we think we pretty well eliminated that by using successive sizes of chamber from 250 ml to 5 liters and the effect is the opposite: the smaller the flask the less the production. So that argument apparently is not valid, but it is something to watch. We had expected the opposite.


### Voice in audience:

I found two approaches proposed today to improve or reduce the uncertainty of the nitrous oxide budget. The one was to study the ratio of the $N_2O$ production to atmospheric $CO_2$, which apparently is moderately understood a lot better, and the other one, which is with respect to ocean concentration, is to measure the dissolved oxygen concentration. I would appreciate two comments as to why this coupling should reduce the uncertainty in North America to one against the other, or are they complementary.

R. Weiss:

I am not sure I understand the question.

Voice in audience:

There were two effects to reduce the uncertainty of the $N_2O$. One said that you have some kind of known ratio of the $N_2O$ concentration to the $CO_2$ concentration, and that the latter one is known to much better uncertainty.

R. Weiss:

Well let me say that the modeling in the deep ocean is infinitely easier than the modeling in the surface water of the ocean, because the things that happen there are retained and the vertical profiles can be modeled according to the same sort of diffusion and convection modeling that I have gathered that people do in the atmosphere. That is the basis of Dr. Yoshinari's estimate of the flux of $N_2O$ from the intermediate waters into the surface waters: it is modeling one parameter against another. We can do that between carbon, oxygen, and the neutrients, $N_2O$, and practically anything you want, and you find that the ocean is remarkably homogeneous. The production rates are things that we have studied the world over, like the nutrient-$CO_2$-oxygen system, and it is relatively uniform no matter what ocean you are in and can be easily understood.

Carrying this to an estimate of the flux between the atmosphere and oceans involves the uncertainly of what goes on in the surface waters: whether $N_2O$ is produced or consumed in the surface waters. Dr. Yoshinari also showed that $N_2O$ can be consumed in these reactions, so that he can get more $N_2O$ if he inhibits that consumption with acetylene. I wasn't really trying to say that one can in some scientific way conclude that there is a certain flux of $N_2O$ based on the $CO_2$ flux. But rather that if one can obtain an empirical relationship between the $CO_2$ and the $N_2O$, which are both clearly related to biological processes, that one can then use the much more extensive $CO_2$ measurements to make some global estimates.

Voice in audience:

I thought when he talked about $CO_2$ that he meant atmospheric $CO_2$.

R. Weiss:

The plot I showed was for partial pressure $CO_2$ in the surface waters. The atmospheric concentration mirrors that very slightly due to mixing time.

**Voice in audience:**

I think this goes back to our conversation quite some time ago, when we were first talking about your data. I think I want to raise a question concerning your 1964 data and 1974 data. As you explained to me then, and it might be worthwhile to explain to others, that the samples taken in 1964 were not measured until 1975. You have something that you have to be concerned about, and that is whether or not you might have lost 1 or 2% during the 11 years of storage.

**R. Weiss:**

That is right.

**Voice in audience:**

Have you solved that to your own satisfaction?

**R. Weiss:**

Not yet, no. There are two ways to approach the problem. One is to look for reasonable explanations for why the $N_2O$ might be consumed. For those chemists in the audience who might be able to help me with this, I'll explain how the samples were stored. The $CO_2$-$N_2O$ fraction was extracted from the samples shortly after they were collected, and that fraction was sealed in a glass break-seal tube and put on a shelf in a box in the dark. If the residence time of $N_2O$ in the atmosphere is long, surely it is long in those flasks [Laughter]. We made for our calibration an $N_2O$-$CO_2$ mixture which is essentially the same as the stored sample, and that mixture is now 2 or 3 years old. We have been making mixtures during those 2 or 3 years, and we see no evidence of the degradation of the first mixture we made over those 2 or 3 years. We'll keep the mixture and then some years in the future we will be able to say with even greater certainty.

**Voice in audience:**

The question that you can't really ever answer is, what happened between the time Bill Dodd collected the sample until he transferred it to the sealed flask?

**R. Weiss:**

Well, the same thing should be happening to the samples which we collected in 1970, which also came back on the ship and were extracted later. Those samples were collected over a year, so that the time between the extraction and the collection varied from a few months to a year, and we see no effect there either.

<u>Voice in audience</u>:

I thought you told me, however, that you grease the stop cocks.

<u>R. Weiss</u>:

Yes, he used different types of flasks, and it's always infinitely complicated to explain all the details, but the 1974 measurements include measurements made with the type of flask that was used in 1964 as well as with the new type of flasks. There was no difference.

<u>C. C. Delwiche</u>:

I wanted to make one quick comment with regard to the $CO_2/N_2O$ ratios in case someone might have gotten the wrong impression. There are certain limitations when attempting to determine something from this ratio in a highly anaerobic system. It is the ratio of the carbon to nitrogen source, and as I pointed out earlier, electron acceptors are at a premium so under highly reducing conditions the $CO_2$ itself becomes an electron acceptor, and at the time you get a reduction of $N_2O$ you would also get a reduction of $CO_2$.

<u>R. Weiss</u>:

That's right.

<u>Voice in audience</u>:

I am a bit confused. I first understood that the major problem was the lifetime. Is the lifetime short, or is it long, and does it make a difference? Then I heard that no matter what the lifetime is, the effect is real. What I would like to point out is that a consensus is needed, and we need to discuss measurements in the future which can clarify the issue.

<u>H. Schiff</u>:

I think I might be able to induce Mike to answer that.

<u>M. McElroy</u>:

I think it is a misunderstanding. There are two lifetimes that people are talking about here. One is the lifetime of $N_2O$ in the atmosphere; is it 100 years or a lot less? The other question is, what is the lifetime of fixed nitrogen in soils? And if the lifetime of fixed nitrogen in soils is 500 or 1000 years, then the fertilizer problem occurs very late -- not in my lifetime.

The point I am making is that built into our calculation is a soil effective delay of 50 years, so that the atmospheric lifetime of 100 years really doesn't make that much difference.

**H. Schiff**:

Does that answer your question?

**Voice in audience**:

Yes, but what measurements do we need in the future, and what things can be done?

**R. Weiss**:

I think it depends on what the missing links are, and what you do. If you measure the atmospheric increase as a function of time you don't really need to know what the lifetime is. On the other hand, if you are interested in resolving the problem by measuring each of sources and sinks, then you must know the lifetimes in order to do the problem.

**Voice in audience**:

These problems are serious problems, no matter what happens. But I would like to report that I still see two rays of optimism here. One is that so far, there has been no attempt to make the fertilizer manu- facturers a villain. In other words, we have put the blame on mankind in general, and his total number, which is quite different from what has happened with auto emissions, SST's, and with Freons. I think that is a step forward. The second point is that it is my understanding -- I am not an expert in this field and I'd like some comments, particularly from Dr. Delwiche here -- that in approximately 50 years our supplies of phosphorus are going to be exhausted. After that we can only support a population of 3 billion anyway, no matter how much nitrogen we use. That would seem to put another limit on the problem.

**H. Schiff**:

Do you want to comment on that?

**C. C. Delwiche**:

I don't particularly want to, but I guess I have to [Laughter]. The point is that the phosphorus problem is overstated as are many of these things. The quality of phosphate reserves in the first place is a continuum from high quality to poor quality. Secondly, the manage- ment of phosphate right now is of such a nature that a very small amount of it gets into the plant at a particular time.

Now that doesn't mean it is lost, but this is the problem of phosphorus fixation. There are other problems of getting phosphorus out of the soil. But there is a lot of phosphorus there. I don't buy the 50-year figure, but if we want to get wild, then long before that problem arises, our methods of plant production will be much more sophisticated, provided some of the long-hairs or long-beards will permit it. By that I mean the old timers who are thinking about the old agriculture. If they will permit us to go to some rational means of plant production, rather than the old-fashioned thing of looking upon soil as a fertile thing. These comments will probably get me into a lot of trouble, but nevertheless I think that is the point.

H. Schiff:

Well, you have been a very tolerant audience. I think it might just be worth-while resurrecting an old story at the end to sum this up: There are three men on a train in Texas who look out the window and see a black sheep in the field. One is a theoretical modeler who says "Well, from this, gentlemen, we can immediately conclude that all sheep in Texas are black." The second modeler said, "Well, I think we can do better than that because we can estimate the size of this field, and we know this area of Texas, and therefore we can determine how many black sheep there are in Texas." To which the laboratory scientist sitting next to them said, "Gentlemen, you are not at all justified in any of these calculations. All you are really justified in saying is that in Texas there is a sheep, one side of which is black." [Laughter]

SECTION III

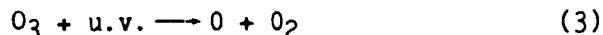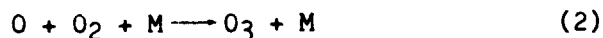SOURCES FOR AND ATMOSPHERIC BUDGET OF THE HALOGENS

# STRATOSPHERIC CHEMISTRY OF THE CHLOROFLUOROMETHANES

F. Sherwood Rowland,
Department of Chemistry
University of California,
Irvine, California

My purpose here is to summarize briefly the important chemical reactions involving the chlorofluoromethanes and stratospheric ozone. This has, of course, been done in great detail in the recent National Academy of Sciences report released only three days ago.[1] Much of my discussion will therefore be devoted to the additional scientific material added since the closing date for the NAS report.

The four Chapman reactions (Eqs. 1-4) were quite satisfactory

$$O_2 + u.v. \longrightarrow O + O \qquad (1)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (2)$$

$$O_3 + u.v. \longrightarrow O + O_2 \qquad (3)$$

$$O + O_3 \longrightarrow O_2 + O_2 \qquad (4)$$

as an explanation for the existence of stratospheric ozone in 1930 and for many years afterward, but became progressively less satisfactory with the increasing scientific knowledge of the 1950's and 1960's. The natural ozone levels were again reasonably well-explained with the addition in 1969-1970 of the $NO_x$ catalytic chain involving reactions 5 and 6, and with the CIAP investigations of 1972-1974[2]. The odd-electron, free radical character of the

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (5)$$

$$NO_2 + O \longrightarrow NO + O_2 \qquad (6)$$
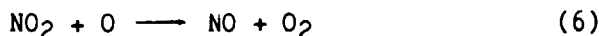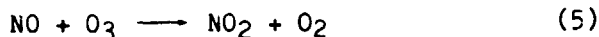
$NO_x$ species illustrates the possibility for intervention by man in the ozone cycle through the direct introduction into the stratosphere of free radicals (e.g., $NO_x$ from supersonic transports) or molecules which can react to release free radicals in the stratosphere. Our focus here is on the $ClO_x$-chain (Eqs. 7,8)

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (7)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (8)$$
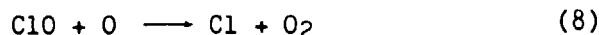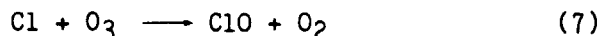
described first by Cicerone and Stolarski,[3] and upon the photodecomposition of the chlorofluorocarbons to release atomic chlorine, as outlined by Rowland and Molina.[4,5]

The most important chlorofluorocarbon compounds involved in the stratospheric chlorine problem are $CCl_2F_2$ (Fluorocarbon-12), $CCl_3F$ (FC-11), $CClF_2CClF_2$ (FC-114) and $CCl_2FCClF_2$ (FC-113), etc. These

molecules are transparent to visible and near-ultraviolet radiation, but can be dissociated in the mid-stratosphere at wavelengths between 1900-2200Å. The photoabsorption cross sections of these molecules are shown in Figure 1, together with estimates of the intensity of ultraviolet radiation with overhead sun at altitudes of 30, 25, and 20 km. The observed decrease with increasing altitude of the mixing ratio, or mole fraction, of FC-11 and of FC-12 is in good agreement with the predictions (Figure 2), demonstrating that the photodecomposition of these fluorocarbon compounds does occur in the stratosphere as hypothesized.

These experimental data on FC-11 were obtained from stratospheric air samples returned to the laboratory for analysis by gas chromatography. The photodecomposition of $CCl_2F_2$ releases one Cl atom immediately, and the second very soon thereafter. With $CCl_3F$, two and usually three Cl atoms are released in the stratosphere after photolysis and the subsequent chemical reactions.

After release from the chlorofluorocarbon compounds, the distribution of Cl among the various possible stratospheric chlorine compounds is determined by a large set of chemical reactions, of which the most important are summarized in the following diagram. The reaction rate

$$HCl \xrightarrow[\text{CH}_4,\text{HO}_2]{\text{OH}} Cl \xrightarrow[\text{O, NO}]{\text{O}_3} ClO \xrightarrow[h\nu]{\text{NO}_2} ClONO_2$$
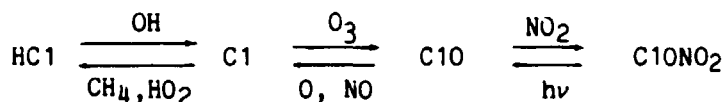
constants at stratospheric temperatures and the actual stratospheric concentrations are reasonably well known for all of these reactions, but some improvement in estimates of both rate constants and concentration is still to be expected. For example, there is still some discrepancy between the measurements of the low temperature rate for $Cl + CH_4$ from various research groups. Our own recent measurement for this rate[6] agrees better with the lower value of DeMore-Leu and Clyne-Walker than it does with the currently preferred value obtained by several groups using chlorine atomic resonance for detection of the disappearance of chlorine. The disagreement here (a factor of about 1.3) is neither serious nor trivial. In the stratosphere, the concentration of $HO_2$ is still known only through indirect methods.

Stratospheric measurements _in situ_ have been carried out through infrared observation of the setting sun. As illustrated in Figure 3, the tangential paths sample the lowest altitude most heavily, but are somewhat sensitive throughout the entire stratosphere above the tangential altitude. The spectra of Figure 4 show the presence of $H_2O$ chiefly in the troposphere, $HNO_3$ chiefly in the stratosphere, and $CO_2$, $CCl_3F$ and $CCl_2F_2$ in both. Through evaluation of similar spectra, the
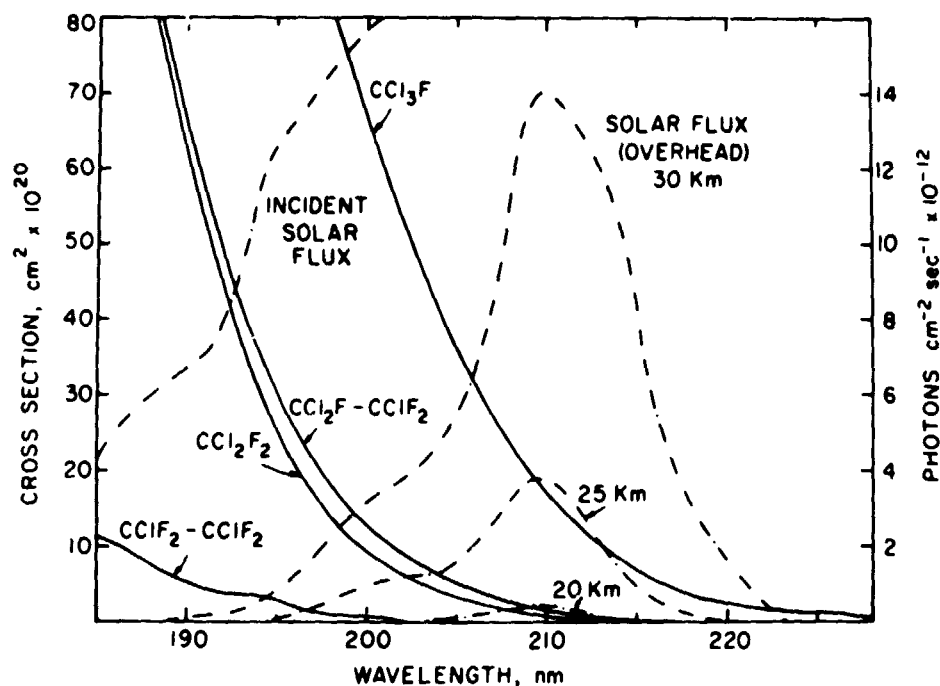
Figure 1. Photoabsorption cross sections for fluorocarbons 11, 12, 113 and 114. Solar fluxes for overhead sun at 20, 25 and 20 km shown as dotted lines.
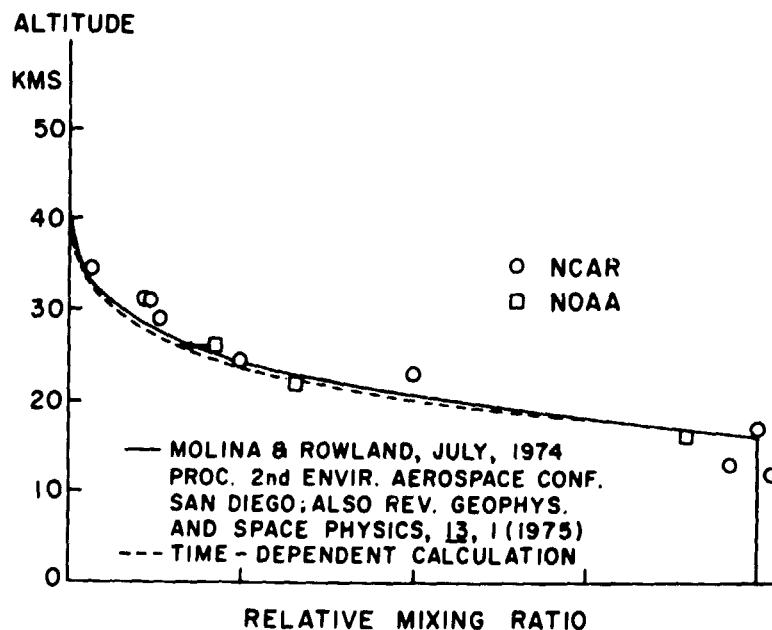


Figure 2. Comparison of observed mixing ratios of $CCl_3F$ versus altitude with predicted values.
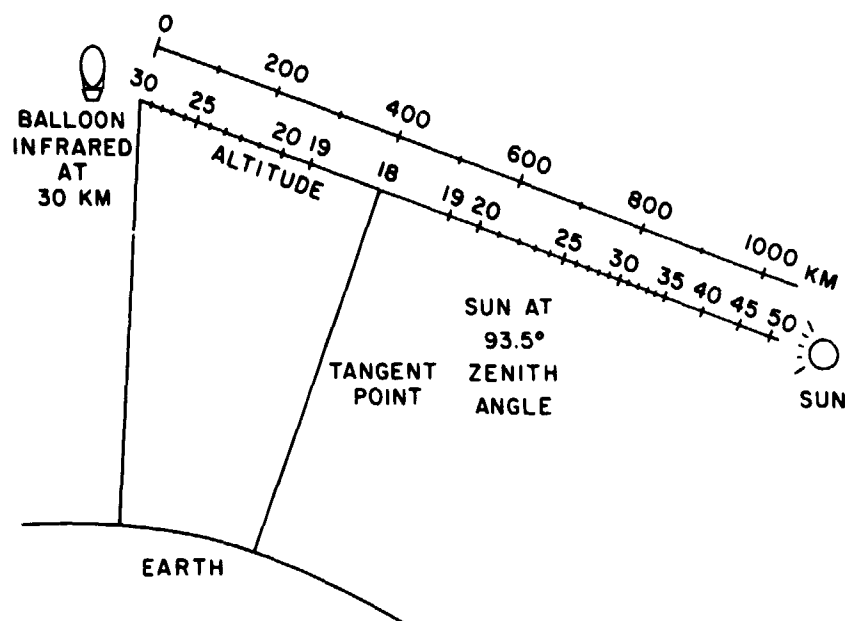
Figure 3. Altitude profile for 93.5° zenith angle from 30 km (tangential at 18 km).

concentration of HCl in the stratosphere has been shown to agree reasonably well with the model predictions. The filter measurements by Lazrus et al. shown in Figure 5 are in general agreement with the infrared observations of HCl, although the falloff in observed HCl above 30 km in the filter measurements still needs a confirmed quantitative explanation.

In January 1976, we suggested that chlorine nitrate ($ClONO_2$) might be detectable in the stratosphere, and this suggestion has now been intensively investigated. Many of the uncertainties have now been cleared up connected with chlorine nitrate, and it is known to absorb throughout the near-ultraviolet and into the visible to 4600A. The appreciable absorption in these regions of the spectrum has made it necessary to calculate ozone removal with a diurnal model since the previous models using a 24-hour, half-intensity, constant sun have substantially overestimated the fraction of Cl bound in $ClONO_2$, and therefore the $ClONO_2$/HCl ratio. The calculated amount of $ClONO_2$ in these models is also sensitive to multiple scattering of radiation with wavelength longer than 3000Å, which tends to reduce further the estimated $ClONO_2$/HCl ratio. In the National Academy of Sciences report, the inclusion of chlorine nitrate in the calculation reduced the estimated ozone depletion by a factor of 1.85. With less chlorine nitrate predicted in present calculations, this reduction factor for the inclusion of chlorine nitrate is considerably smaller than 1.85, perhaps 1.3-1.4.
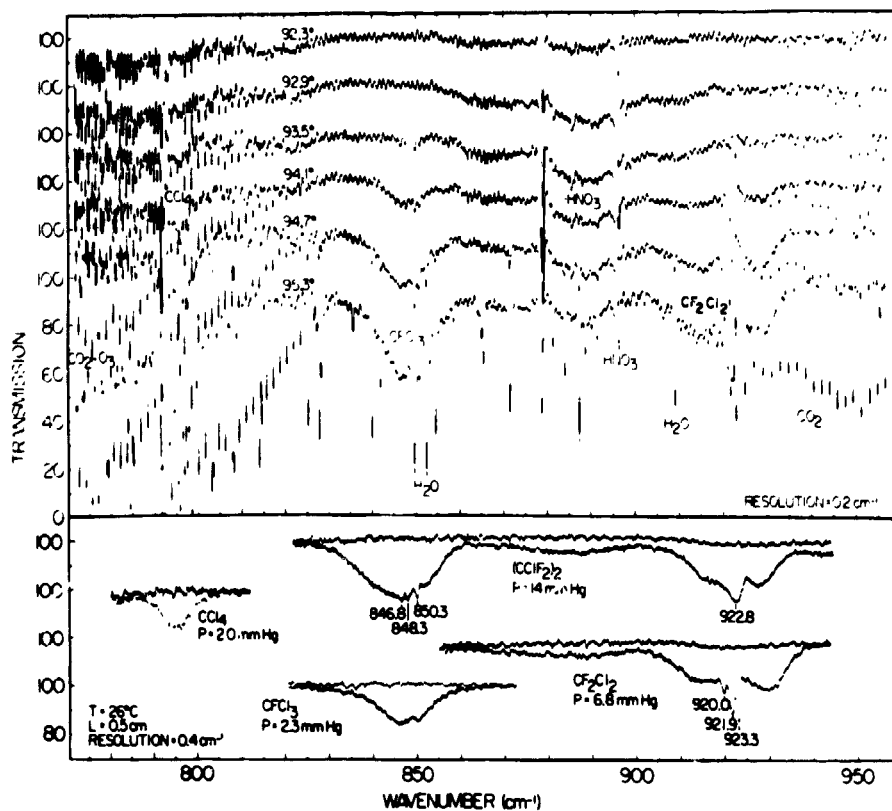
Figure 4. Statospheric infrared spectra taken by D. Murcray, University of Denver, 1975. Zenith angles as labeled (92.3° to 95.3°).



Figure 5. Hydrogen chloride vs altitude from filter collection measurements of A. Lazrus et al., National Center for Atmospheric Research.

There is new photochemical information about one other compound, ClONO, chlorine nitrite, which has recently been suggested as a possible stratospheric sink for chlorine. Drs. Luisa Molina and Mario Molina have synthesized chlorine nitrite, and have measured its near-ultraviolet and visible absorption spectrum. Chlorine nitrite is a much stronger absorber than molecular chlorine, which has a lifetime of about 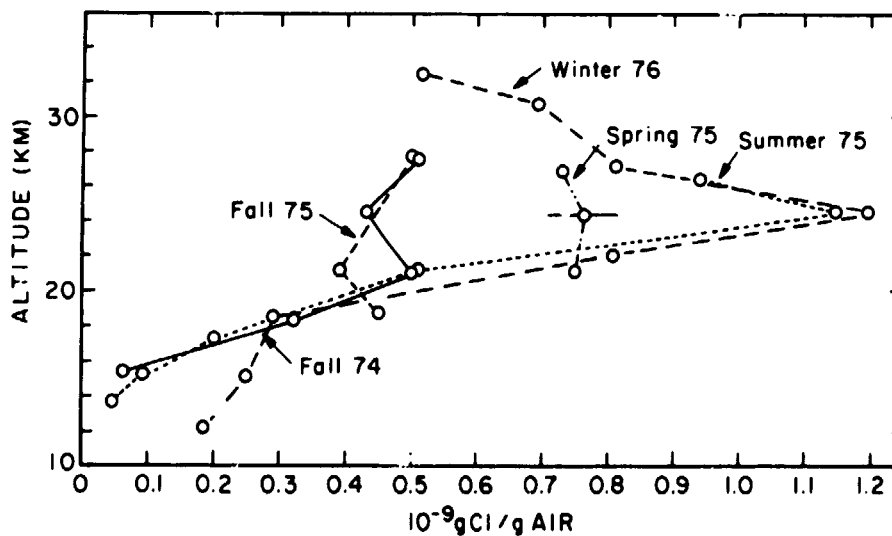10 minutes in bright sunlight. With a lifetime of 3 minutes or less, chlorine nitrite has absolutely no significance as a stratospheric sink for chlorine.

The estimates of long-term ozone depletion by the chlorofluorocarbon compounds are dependent upon the essential absence of tropospheric removal processes, i.e., the absence of tropospheric sinks. No important tropospheric removal processes have been identified, and an overall test for undiscovered tropospheric sinks can be made by a comparison of the amount of FC-11 actually present in the atmosphere with the amount already released. We made such a comparison in October 1975 for $CCl_3F$,[7] and concluded that there was more FC-11 in the atmosphere than had been reported to be released. Subsequently, the Manufacturing Chemists Association has made an upward revision of the amount of FC-11 released. With these revised release data, we have again made a comparison of atmospheric concentration versus estimated total release. Our estimate of release as of September 1975 is 2680 kilotons of $CCl_3F$, and differs only slightly from the M.C.A. estimates, primarily in a lesser contribution from eastern Europe in our calculation. When corrected for loss by photolysis in the stratosphere, the expected current atmospheric burden is about 2400-2500 kilotons.

Rasmussen has given the measured concentration in the northern hemisphere (i.e., Pullman, Washington) in September 1975 as 123 parts per trillion. Our own absolute calibration for $CCl_3F$ lowers this to about 110 PPT at that date, within the limits of accuracy given by Rasmussen for his measurement. With 110 PPT in the northern hemisphere troposphere, we estimate the total atmospheric burden as of that date a 2360 kilotons of $CCl_3F$, in excellent agreement with the expected burden.[3] There is thus almost no room for loss to all tropospheric sinks put together. Probably the most important factor in this estimate of total atmospheric burden is our calculation of the amount present in the southern hemisphere, for which we have used the factor of 0.8 times that in the northern hemisphere.

There is a substantial amount of information available on the mixing rates between the northern and southern hemispheres through Keeling's 20-year study of $CO_2$ concentrations at Mauna Loa, Hawaii, and in Antarctica. His estimate of such mixing times is not less than 6 months, and not more than 2 years. We have calculated the expected South/North ratio from the M.C.A. release pattern, using mixing times of 1 and 2 years as shown in Figure 6. The expected S/N ratio in September 1975 with a two-year mixing time is 0.8; with one-year, 0.9. Our use of 0.8 may have slightly underestimated the concentration of FC-11 in the southern hemisphere, providing even less room for tropospheric sinks.

HEMISPHERIC MIXING OF $CCl_3F$
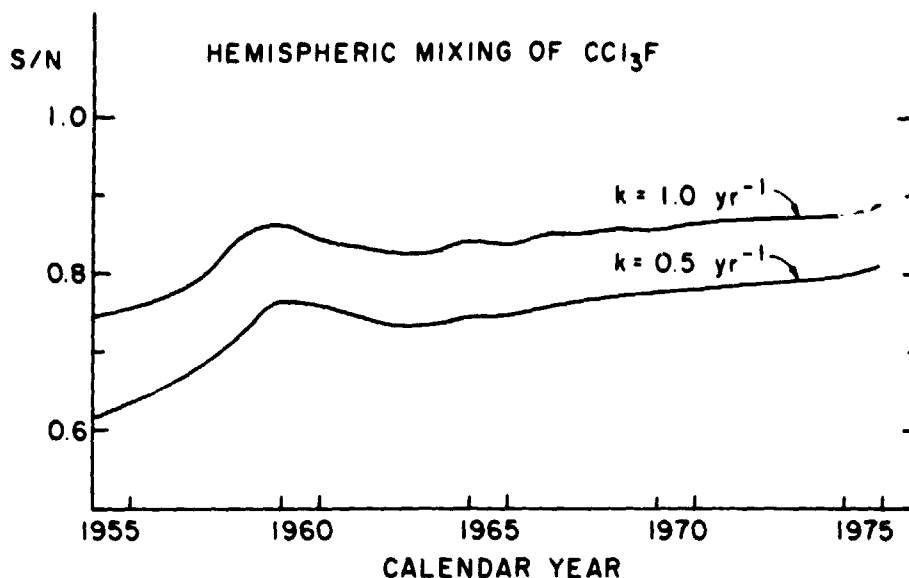


Figure 6.  Predicted ratios of $CCl_3F$ in southern and northern
hemispheres, using 1-year and 2-year average mixing
times.

Finally, Figure 7 shows a calculation by Cicerone, Liu and Donahue
which indicates a substantial depletion of ozone by chlorine in the
vicinity of 40 km, practically independent of whether chlorine nitrate
is included in the calculation or not.  The loss of ozone between 35-
50 km occurs in all of the models; the effect of chlorine nitrate is
to prevent destruction of ozone (by tying up ClO and $NO_2$) in the 20-
30 km region; in either case, there is a substantial change in the
ozone profile.  In these calculations, the profile of HCl versus altitude
shows structure somewhat similar to that indicated by the Lazrus data
of Figure 5.  In these model calculations, the alterations in the HCl
profile occur because a much larger fraction of the Cl is present as
ClO than in earlier calculations, and thus is spending a larger fraction
of its time in the ozone-removing cycles.
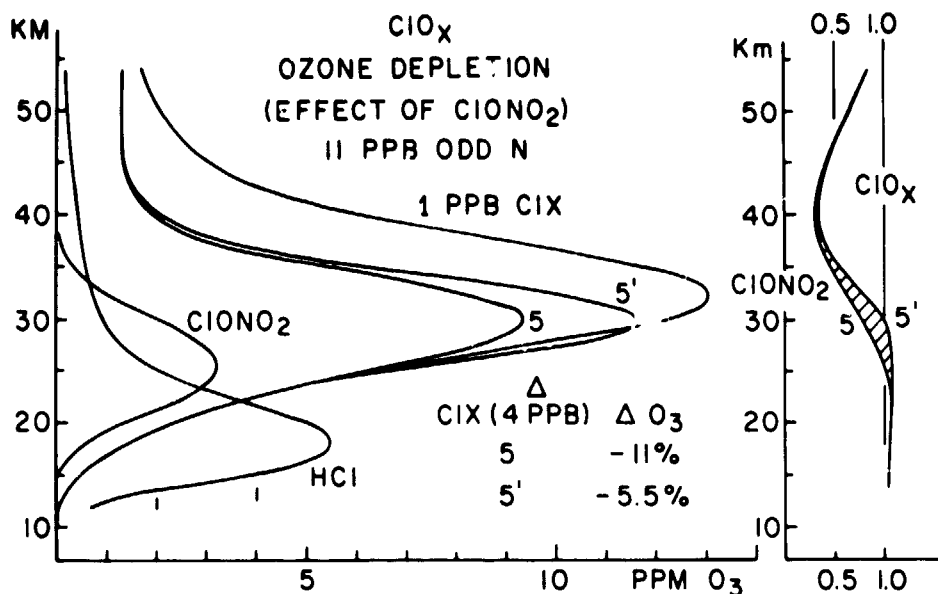
Figure 7. Model calculation of ozone depletion vs altitude
(Cicerone, Liu and Donahue, University of
Michigan, 1976). Center: ozone profiles with
1 PPB C1X, and 5 PPB C1X. C1ONO$_2$ was included
in the calculation labeled 5', and omitted in
the one labeled 5. Right: ratios of ozone
concentrations for 5 PPB divided by 1 PPB. The
inclusion of C1ONO$_2$ has the effect shown by the
cross-hatched area. Left: concentrations of
HC1 and C1ONO$_2$ for Profile 5'. Note that the
C1ONO$_2$/HC1 ratio has been exaggerated beyond
that expected in the stratosphere.

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4. Molina, M. J., and F. S. Rowland, Nature, 249, 810, 1974.

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7. Rowland, F. S., and M. J. Molina, Memorandum to N.A.S. Panel on Atmospheric Chemistry, Oct. 23, 1975.

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## STATUS OF WSU'S INTERHEMISPHERIC HALOCARBON
## AND NITROUS OXIDE MEASUREMENTS

R. A. Rasmussen
Atmospheric Resources
College of Engineering
Washington State University
Pullman, Washington

Figure 1 illustrates the halocarbon measurements which have been made from the mid-troposphere through the lower stratosphere by Washington State University over the past 18 months in three different field studies. The geography studied ranges from detailed vertical profiles over the Pacific Northwest and Alaska to determining zonal concentration gradients from 80 N to 60 S during WSU-MCA's Cross-Equatorial/Trans-Pacific Flights in June 1976. These latter flights were designed to quantitate, in a very short period of time, the geographical variation of the fluorocarbons and related chlorocarbons concentration distributions on an interhemispheric scale. In all of these studies a Learjet equipped with an air pressurization system was used to fill internally passivated stainless steel canisters and provide an air flow to instruments for recording onboard real-time observations of $CFCl_3$, $CCl_4$ and ozone. More detailed halocarbon and $N_2O$ data were obtained by analysis of the canister samples for $CFCl_3$, (F-11), $CF_2Cl_2$ (F-12), $CCl_4$ and $CH_3Cl$ and are given in Table 1. The F-11 results are emphasized for the purpose of this abstract. More complete interpretation of the data will be given in the formal presentation of this paper.

The data sets demonstrate two unexpected phenomena:

(1)   A greater scatter in the fluorocarbon and $N_2O$ concentrations in the lower stratosphere relative to the more uniform concentration distributions observed in the mid to upper troposphere. The variability in the lower stratospheric concentrations indicates a more complex behavior than is assumed by most models of the stratosphere. The data show that both the concentrations and the vertical gradients in the lower stratosphere change over the period of a week. Thus the lower stratosphere is not in equilibrium with regard to fluorocarbon and $N_2O$ concentrations. A coherent airmass transport mechanism through the tropopause into the stratosphere is proposed to explain the temporal and spatial variations observed.

(2)   The fluorocarbon-12 and 11 concentration distributions obtained on the Cross-Equatorial/Trans-Pacific Flight from 80 N to 60 S latitude in June 1976 indicate a much smaller interhemispheric difference of 10-12% than expec.ed. In addition, no steep gradient for F-12 and F-11 was observed from 70 N to the equator; neither was there a marked fall-off through the intertropical convergence zone (ITCZ). Rather the data show a rather homogeneous concentration

distribution for the northern hemisphere and a gradual decrease in the fluorocarbons from the ITCZ through the southernmost latitude (60 S) studied. These data would indicate that the world's atmosphere is mixing more quickly and more efficiently than previously thought. It also suggests that pollutants are spread more easily than presently modeled across the world. No interhemispheric differences have been observed for the concentration distributions of $N_2O$ (33C ± 3 ppb).

Table 1.  Cross-Equatorial/Trans-Pacific Flight interhemispheric differences as of June 1976

|  | $F_{12}$ | $F_{11}$ | $CC1_4$ | $CH_3C1$ |
|---|---|---|---|---|
| Pullman background | 235 | 143 | 135 | 109 |
| New Zealand | 210 | 127 | 98 | 76 |
|  | 11% | 11% | 27% | 30% |
| 59°S  20,000' | 208 | 130 | 119 | 67 |
|  | 11% | 9% | 12% | 39% |
| 59°S  41,000' | 183 | 114 | 87 | 56 |
|  | 22% | 20% | 36% | 49% |

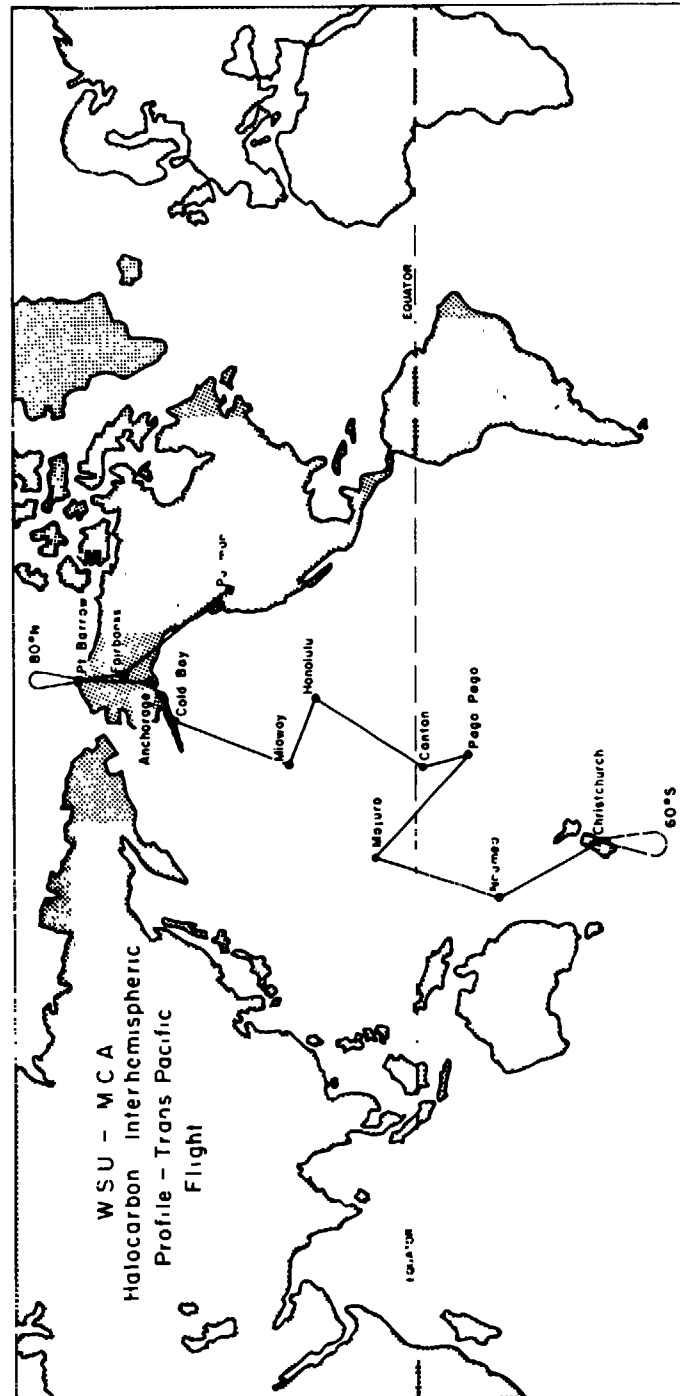Concentrations, parts per trillion

Figure 1. Halocarbon interhemispheric profile, trans-Pacific flight.

## THE PRESENT STATUS OF FLUOROCARBON-OZONE THEORY

J. Peter Jesson
E. I. Du Pont de Nemours & Co.
Wilmington, Delaware

The sequence of release of the fluorocarbons into the atmosphere, through the various stages, to eventual removal of the chlorine from the atmosphere was followed step by step.

Accurate production and release figures have been obtained through a survey of the manufactures conducted by independent accountants. The totals to the end of 1975 were given. The production figure for the communist countries were derived from estimates submitted to the accountants by three of the sponsoring companies. Release to the atmosphere is close to 85% of the amount produced at any given time and was obtained by breaking down sales in terms of end use (refrigeration, aerosol, closed cell foam, etc.) and combining this with a release pattern for each application. For instance it takes roughly 20 years for all the FC-11 in closed cell foam to be released, whereas aerosol propellants are released quickly.

The next step was to compare the amount of fluorocarbon released with that present in the troposphere at any given time. There have been extensive measurements of FC-11 over a period of five years. Most of these have been at mid-latitudes in the Northern Hemisphere. Whatever the latitude, any given set of measurements has to be converted to a global average before they can be compared with calculation. There is a higher concentration in the Northern Hemisphere, where the fluorocarbons are produced, than in the Southern Hemisphere. Experimental latitude data were obtained by Lovelock on a voyage of the Shackleton from the north to the south and back in 1971-1972. A least squares fit to the data was used to generate empirical latitude conversion factors.

The final step to determine the tropospheric lifetime is to compare the latitude-corrected experimental data with expected concentrations calculated on the basis of known fluorocarbon release and assumed tropospheric lifetime and eddy diffusion profile. The data of Lovelock taken in both the Northern and Southern Hemispheres over a period of five years were also considered, including an experimental least squares fit to over 200 data points at Adrigole. The fact that the Northern and Southern data after correction are close together is an indication of the internal consistency of the procedure.

The lifetime, assuming the Hunten eddy diffusion profile, is between 15 and 20 years. Similar lifetimes are calculated from the data of other workers (SRI, WSU). A lifetime of 20 years would lead to reductions in ozone depletion estimates by more than a factor of 3.

We believe that diffusion is, in fact, quite a bit faster than suggested by the Hunten profile. A best fit to observed stratospheric fluorocarbon data was obtained with the Crutzen II diffusion profile. Faster diffusion leads to longer calculated tropospheric lifetimes,

using the procedures just discussed. With the Crutzen II scheme, a lifetime of about 50 years is calculated.

The next step in the sequence of events is photolysis of the fluorocarbons to give chlorine atoms. A one-dimensional model of diffusion and photochemistry has been developed using the Wuebbles-Chang reaction set supplemented by about 15 reactions involving chlorine. The radiation is globally averaged and the photodissociation rates are recalculated as the ozone profile changes. The model includes N atom reactions, and the total odd nitrogen is in good agreement with recent quasi-simultaneous measurements of Evans (9,7,6,3 ppb vs 9,12,8,5 35 to 20 km).

In the odd hydrogen chemistry the slow rate of $2 \times 10^{-11}$ $cm^3$ $mol^{-1}$ $sec^{-1}$ for $OH + HO_2$ was chosen. This leads to higher OH concentrations in the stratosphere (nearer to measurements) than the older fast rate models ($2 \times 10^{-10}$).

In calculating present-day odd chlorine mixing ratios, the known flux boundary conditions for FC-11, FC-12 and for methyl chloroform and fixed mixing ratio lower boundary conditions of 100 ppt and 750 ppt, respectively, for $CCl_4$ and $CH_3Cl$ were used. About 1 ppt HCl is calculated (not including $ClONO_2$) and there is no significant decrease in HCl mixing ratio with altitude.

Observed HCl data vary from about 0.5 to 1.3 ppt maximum mixing ratios. The important experimental feature is a drop in mixing ratio above 24 km in the winter 1976 data. The drop is to less than half the peak value; it is difficult to see how this could be explained by transport.

Calculations including chlorine nitrate again show no dip. It would appear that $ClONO_2$ cannot explain the HCl data. The predicted present-day mixing ratios of $ClONO_2$ from the model are $5 \times 10^{-11}$ at 18 and $5 \times 10^{-10}$ at 25 km, so that the presence of $ClONO_2$ cannot be excluded by available atmospheric infrared measurements.

We have repeated the measurements of Rowland and Molina on revised $ClONO_2$ absorption cross sections. Our data are in excellent agreement. Further work on the temperature-dependence of the cross section and the nature of the photolysis products is required. Chlorine nitrite (ClONO) and nitryl chloride ($ClNO_2$) are additional possibilities as stratospheric intermediates. Data for steady-state ozone depletion at 1974 production levels were given. For a modified Hunten profile without chlorine nitrate, and assuming an infinite tropospheric lifetime, 7.2% effect at steady-state is calculated, which is not too dissimilar from the results from other models. Including chlorine nitrate reduced this by a factor of 1.6.

For the modified Hunten profile, the best fit to the tropospheric lifetime is around 20 years. Not including chlorine nitrate, a 20-year lifetime reduces calculated ozone depletion by about a factor of 3. Including $ClONO_2$ we get an overall best estimate of 1.5% depletion at steadystate, achieved by the year 2250, again using the modified Hunten scheme.

If we choose to select a profile such as Crutzen II which fits the observed fluorocarbon concentrations in the stratosphere, the corresponding calculations lead to a 50-year lifetime and an overall best depletion estimate of 5.4% without $ClONO_2$ or 2.0% with $ClONO_2$.

To consider the risk of a few more years of production while finding out what is actually happening in the stratosphere, time-dependent calculations were carried out for various scenarios. These give a present-day effect of 0.4% including chlorine nitrate. The maximum effect would occur around 1990 at about 1%. The incremental effect for an additional two years of production is 0.1%. There is therefore insignificant risk for a two-year program.

# DELIBERATIONS AND FINDINGS OF THE ATMOSPHERIC CHEMISTRY
## PANEL OF THE NATIONAL RESEARCH COUNCIL

Frederick Kaufman
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania

[Prof. Kaufman presented a summary of the findings of the Atmospheric Chemistry Panel of the National Research Council on environmental effects of halocarbons.  The report, entitled "Halocarbons: Effects on Stratospheric Ozone," was released earlier during the week of the conference and is available from the National Academy of Sciences, Washington, D.C., U.S.A.]

# THE EFFECT OF HCl FROM SOLID-FUELED ROCKET ENGINES
# ON STRATOSPHERIC OZONE:  A TWO DIMENSIONAL MODEL STUDY

W. J. Borucki
R. C. Whitten
V. R. Watson
NASA-Ames Research Center
Moffett Field, California

C. A. Riegel
L. A. Capone
San Jose State University
San Jose, California

The Ames two-dimensional model of stratospheric trace constituents has been employed to evaluate the effect of the chlorine emissions from solid-fueled rocket engines on the ozone layer. We find a strong seasonal effect with a maximum reduction centered at the launch latitude (30 N) in summer. The "corridor effect" is weaker in spring and fall and appears to vanish in winter. We also find that if shuttle operations should cease, the time required for the ozone decrease to be reduced to one-half its steady-state value is about 2 1/2 years, and that interhemisphere transport is rather rapid. We also find that, after 10 years of flight operations (Figures 1 - 2), the globally averaged ozone loss is consistent with results from a one-dimensional model.
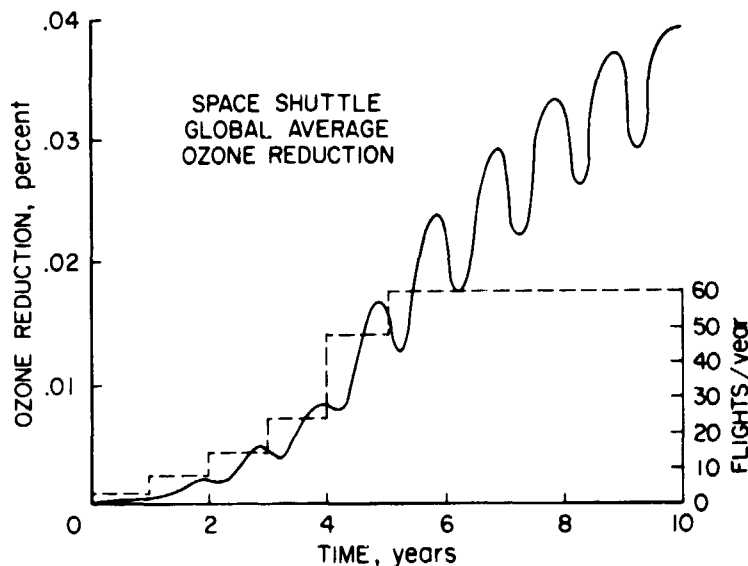


Figure 1.  Time-dependence of the globally averaged ozone reduction
using the Ames Research Center two-dimensional model.
Also shown is a possible space shuttle launch schedule.
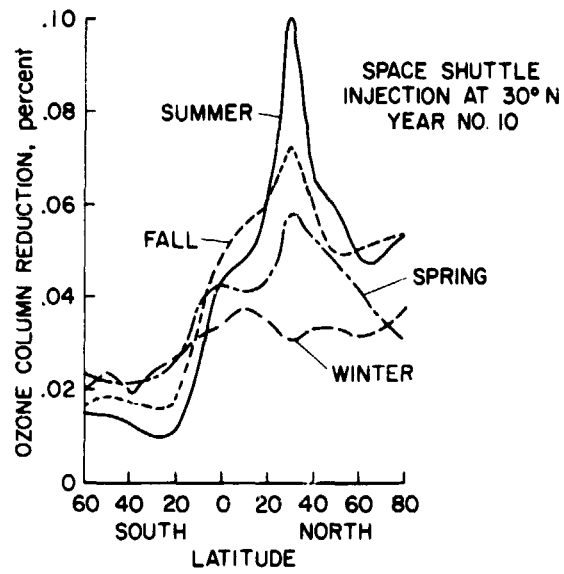
Figure 2.  Computed ozone column reduction as a function
of latitude and season after 10 years of space
shuttle operations, using Ames Research Center
two-dimensional model.

# EFFECTS OF DIURNAL VARIATIONS AND SCATTERING ON OZONE IN THE
# STRATOSPHERE FOR PRESENT-DAY AND PREDICTED FUTURE CHLORINE CONCENTRATIONS

Robert Kurzeja
Advanced Study Program
National Center for Atmospheric Research
Boulder, Colorado

The effect on ozone of diurnal variations in the concentrations of chlorine, nitrogen, hydrogen and oxygen compounds was studied with a diurnal integration of the photochemical equations at 30 latitude. The vertical distribution of the sum of the nitrogen oxides was specified and ozone was assumed to be in photochemical equilibrium. Calculations were performed for three different distributions of $Cl_x$ ($Cl_x$ = Cl + ClO + HCl + ClO $NO_2$), one representative of present-day conditions, a second consistent with predicted $Cl_x$ concentrations for the year 1996, and an intermediate case.

The results were compared with approximate calculations employing average daytime dissociation rates and 24-hour-averaged dissociation rates. It was found that the methods employing daytime averaged dissociation coefficients yielded more accurate ozone concentrations at all altitudes, and, more importantly, were more reliable indicators of changes in total ozone column amount resulting from fluorocarbon pollution.

Several useful approximations are developed to improve the accuracy of photochemical models designed to s udy the effects of chlorine compounds on ozone.

The effects of scattering were included in the model with the parameterization of Lacis and Hansen. It was found that upward reflection of sunlight from clouds was quite important for chemical species dissociated at wavelengths greater than 290 nm. Chemicals found to be significantly affected were NO, $NO_2$, $N_2O_5$, $ClONO_2$, HCl and $O(^3P)$. A simple technique for including the effects of scattering and reflection in photochemical calculations is presented.

# THE RATE CONSTANT FOR Cl + CH$_4$ FROM 200-500K

J. H. Lee, J. V. Michael, W. A. Payne, L. J. Stief and D. A. Whytock
Laboratory for Extraterrestrial Physics
NASA/Goddard Space Flight Center
Greenbelt, Maryland

The rate constant for the reaction, $Cl + CH_4 \longrightarrow HCl + CH_3$, important for stratospheric modeling, has been measured by the flash photolysis-resonance flourescence technique over the temperature range 200-500 K. When the results at 14 different temperatures are plotted in Arrhenius form, a definite curvature is noted as shown in Figure 1. Thus, between 318-500 K the rate constants give $k = (2.14 \pm 0.30) \times 10^{-11} \exp(-1608 \pm 50/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. However, in the range of stratospheric temperatures, 200-276 K, $k = (5.51 \pm 0.62) \times 10^{-12} \exp(-1192 \pm 25/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The least squares fit to the data over the entire temperature range gives

$$k = \left(5.44 \begin{array}{c} +16.34 \\ -4.08 \end{array}\right) \times 10^{-19} \; T^{2.50 \pm 0.21} \exp(\frac{-608 \pm 62}{T})$$

cm$^3$ molecule$^{-1}$ s$^{-1}$.
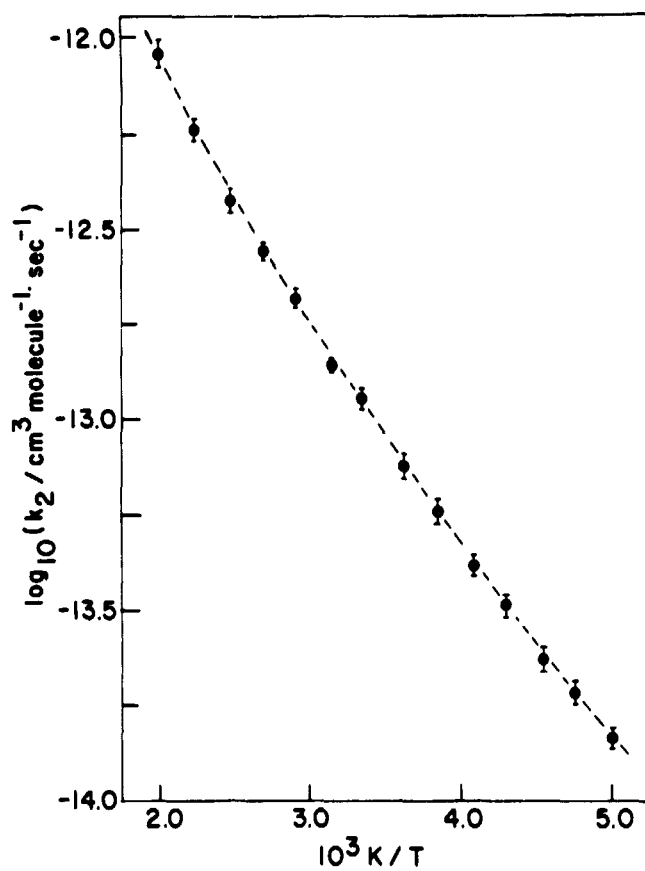
Figure 1. Experimental data for the rate constant of the
reaction of Cl + CH$_4$ $\longrightarrow$ HCl + CH$_3$ as a function
of temperature T(K).

# MICROWAVE AIRCRAFT MEASUREMENTS OF STRATOSPHERIC MOLECULES

J. W. Waters, R. K. Kakar, H. K. Roscoe, and P. N. Swanson
Jet Propulsion Laboratory
Pasadena, California

J. J. Gustincic
Consulting Engineer
Marina del Rey, California

A. R. Kerr
Goddard Institute for Space Studies
New York, New York

R. J. Mattauch
University of Virginia
Charlottesville, Virginia

A program to measure stratospheric molecules by passive microwave techniques from aircraft has been initiated at the Jet Propulsion Laboratory. Two series of flights performed to date using the NASA CV-990 and C-141 aircraft have resulted in the first detection of upper stratospheric emission from spectral lines of $O_3$ at 1.789 and 1.626 mm and $H_2O$ at 1.635 mm wavelengths (Figure 1). Figure 2 illustrates measurements at 1.792 mm wavelength, which have placed a tentative upper limit on stratospheric ClO approximately 3-5 times greater than predicted by present atmospheric models. (Figure 3).
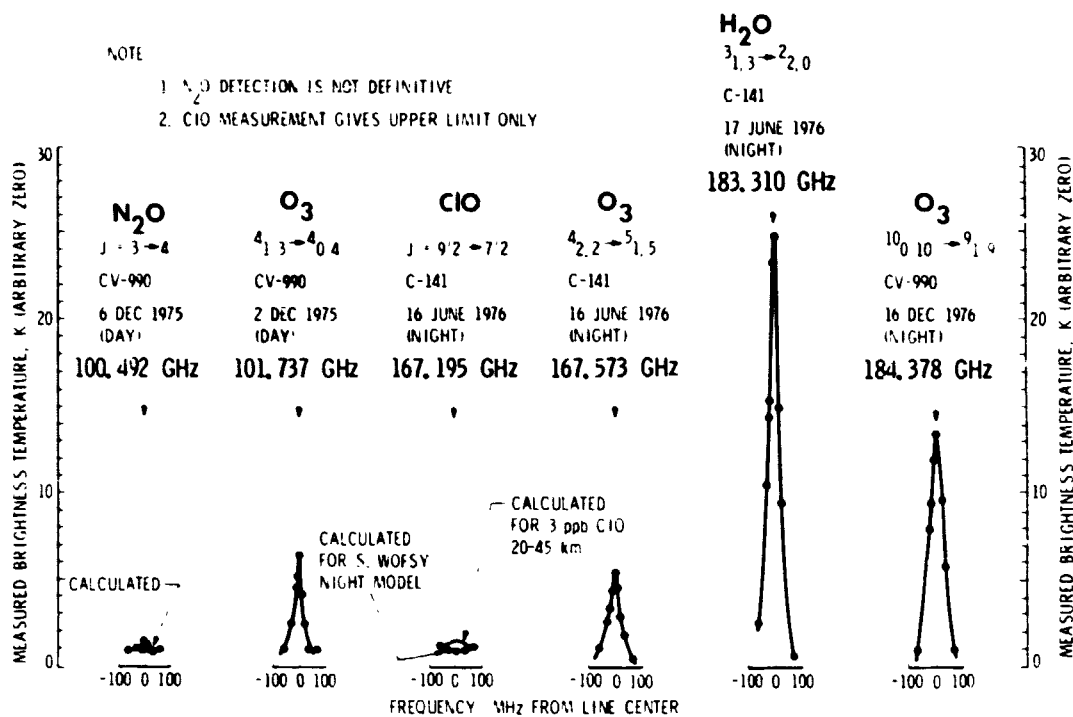
Figure 1.   Aircraft measurements of atmospheric emission
            with microwave limb sounder.
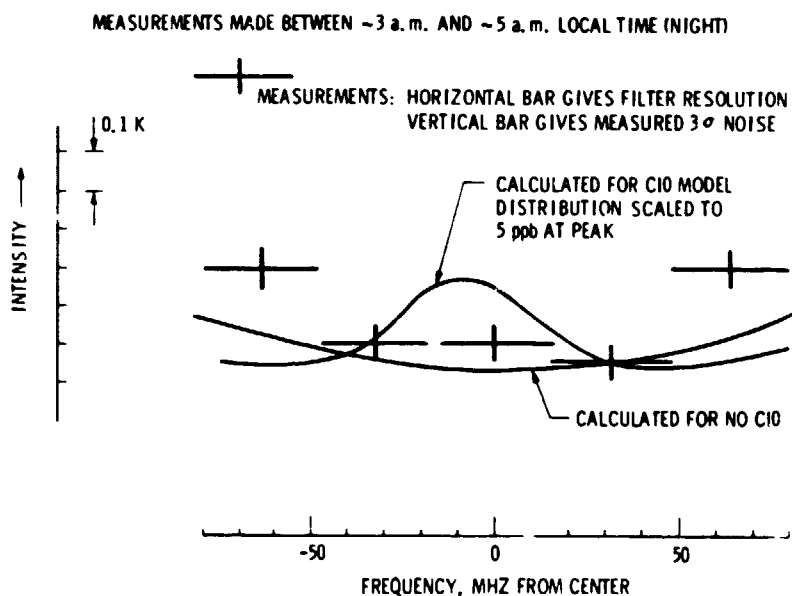


Figure 2.   ClO results from June 16, 1976, C-141 MLS flight.
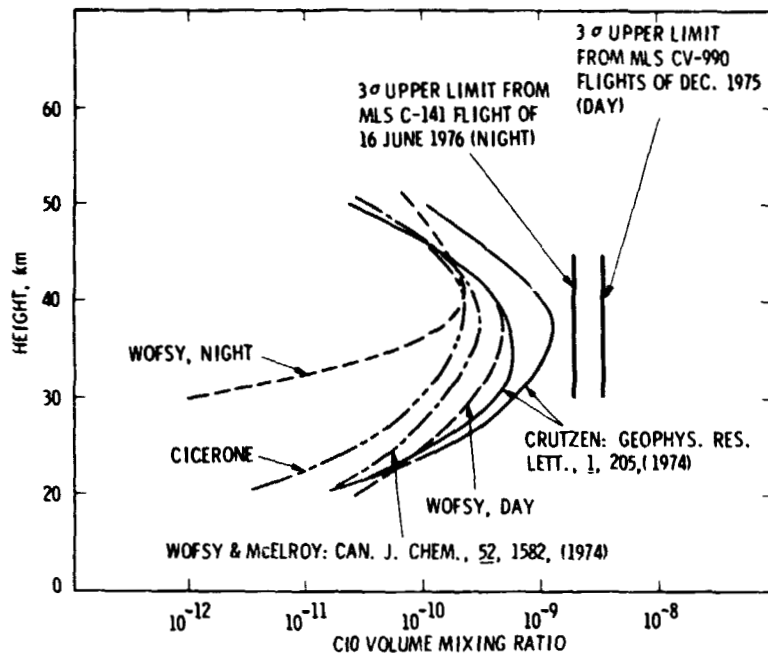
Figure 3.  Comparison of experimental upper limits with
current model predictions.

# A SIMULTANEOUS MEASUREMENT OF Cl AND ClO IN THE EARTH'S STRATOSPHERE

J. G. Anderson
University of Michigan

One of the most important requirements for assessment of the reduction of ozone by halocarbons in earth's stratosphere (Figures 1 and 2) is measurement of the amount of Cl and ClO present in the stratosphere. An experiment to simultaneously determine the in situ concentration of both Cl and ClO in the earth's stratosphere using atomic resonance fluorescence has been developed and was launched on a balloon on July 28, 1976, from Palestine, Texas, 32°N latitude. The balloon lofted the instrument package to an altitude of 43 km, from which it was dropped on a self-stabilized parachute for the measurement phase of the flight. The ClO concentration (Figure 3) was found to increase from $3 \times 10^7$ $cm^{-3}$ at 41 km to $4.5 \times 10^8$ $cm^{-3}$ at 36 km, decreasing below 29 km to $1 \times 10^8$ $cm^{-3}$ at 26 km. Atomic chlorine was found to decrease from $2 \times 10^6$ $cm^{-3}$ at 42 km to $4 \times 10^5$ $cm^{-3}$ at 35 km. The Cl/ClO relative measurement agrees well with recent model calculations (Figure 4).



SYSTEM OVERVIEW
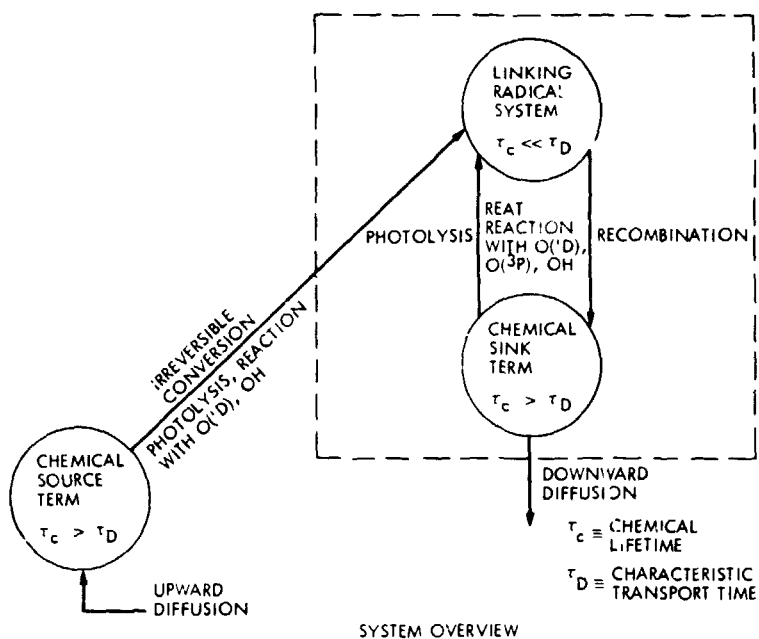
Figure 1. Overall stratospheric chemical system flow diagram.
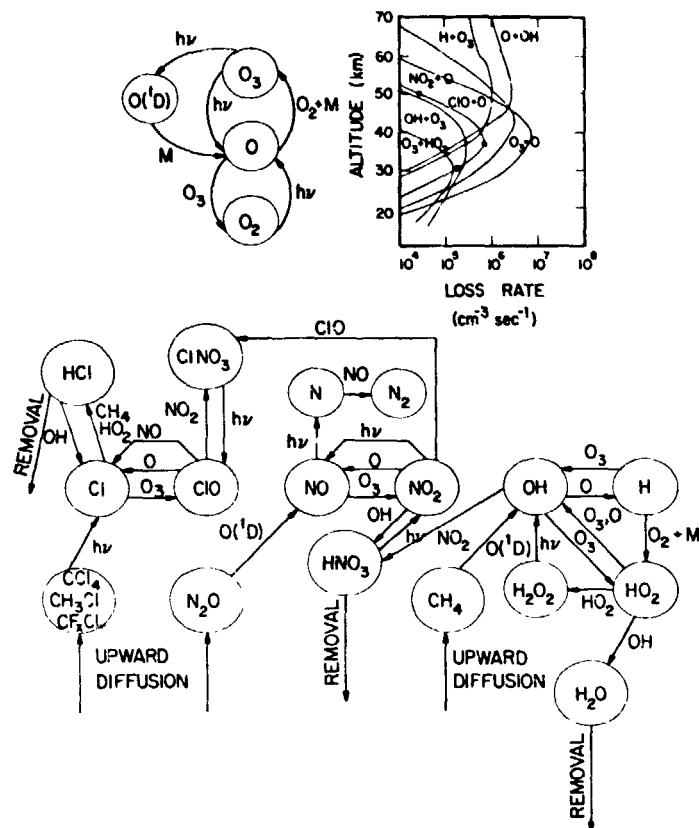
Figure 2.   Details of the stratospheric nitrogen, oxygen,
and chlorine chemical systems and typical
model results.
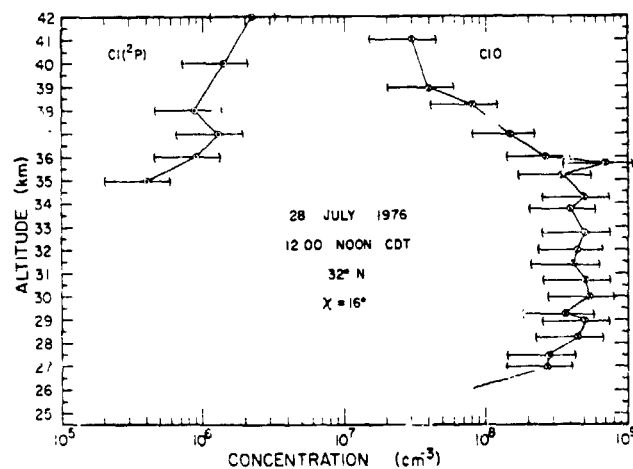


Figure 3.   Balloon flight measurement results.
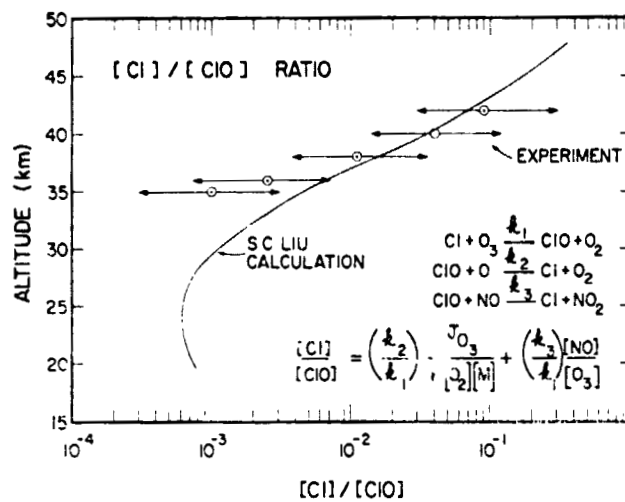
Figure 4. Comparison of experimental vs model results for the Cl/ClO ratio in the stratosphere.

HALOGENS PANEL DISCUSSION

F. Kaufman, Chairman

### F. Kaufman:

Ladies and gentlemen, panel members, I am your ruthless chairman. I will just say that since many chlorine compounds are lacrimaters, we could go from Harold Schiff's transparency to a similar one which I didn't bother to make up -- about crying. I think the ground rules are that anyone who has spoken, unless he has something very urgent and breathtaking to discuss, should not have any time. I would urge all other panel members not to make any presentations unless they have something particularly important to tell us. I think perhaps we ought to start with Dr. Lovelock because he said that he had some additional material and would like a little extra time.

### J. Lovelock:

I first encountered the fluorocarbons in 1969 and soon grew to recognize them as useful tracers of opportunity: substances which you could use to label air masses. In those days such research was very unfashionable, and if you did it, it was a sort of scientific wildcatting and you got no support. But it was to my fancy, and I did do it and set sail on the Shackleton and produced the results that Peter Jesson showed you this morning. A sideline of this was that it also provided Sherry Rowland and Mario Molina with the experimental basis from which they were able to build up with consummate skill the case against the fluorocarbons.

I think the matter that I was going to talk about, mainly the north-south ratios and the distribution in the atmosphere, has already been covered extremely well by Rasmussen and Peter Jesson. Indeed, I think you could say that we had one Viking show last night and we had another even more splendid Viking show this morning. Talking of Viking, an interesting point that comes out of Peter Jesson's talk is that there does seem to be some sort of case for the presence of a tropospheric sink of 2 or 3% perhaps, and what on earth could it be. The list that the panel gave didn't include anything that could possibly fit, and I guess everybody has been wondering, just as we have, what it might be. It may well be, I suppose, as everybody has known, that a sum of a lot of small ones is going to add up to this. But one still requires among them one or two that will produce the necessary 2 or 3%, and the sea looks like one possibility. But there is another one which makes the Viking account yesterday rather timely, I think.

One surprise that came from the chemistry that was found on Mars was the participation of the soil dust in the atmospheric chemistry of that planet. We are getting some signs that the wind-blown aerosol from the Sahara may be participating in the atmospheric chemistry of the halocarbons on earth. I think this might well be one of the more promising lines to look at in our search for sinks.

There is just one other general comment I would like to make and that concerns the consequences of the UV. It has been said that there is a linear relationship between ozone depletion and the incidence of skin cancer. It is argued that any depletion, no matter how small, will inevitably add to the sum total of human misery or death. Well, it may be true that pale-skins who move to sunny places, or who sun bathe or otherwise expose themselves, are in danger of a minor and almost never fatal form of skin cancer. But I don't think there is any evidence worthy of scientific consideration to support the hypothesis that small changes in the ambient UV flux of our normal habitat is harmful. Indeed there is good evidence that unlike other carcenogenic radiation, such as X-rays, there is an optimum level of UV. And UV is a normal component of a natural environment. We are adapted to it and to its variations. To illustrate my point I've got a plot here (Figure 1) which shows latitude going from 60 deg north or south of the equator and a number of atmospheric properties. The solid line is a flux of UVB, that is between 290 and 310 nanometers at the surface. The stars on the diagram are the incidence of malignant melanoma in various sites of the world, and you can immediately see the association which led many to think that UVB and melanoma are just simply linearily related to one another. But you will see also on that diagram a number of other atmospheric properties. For example, temperature also varies, believe it or not, as one moves north of the equator. It is a fact that mutagenesis in cells increases in rate with temperature, and one's skin tends to be warmer in the tropics.
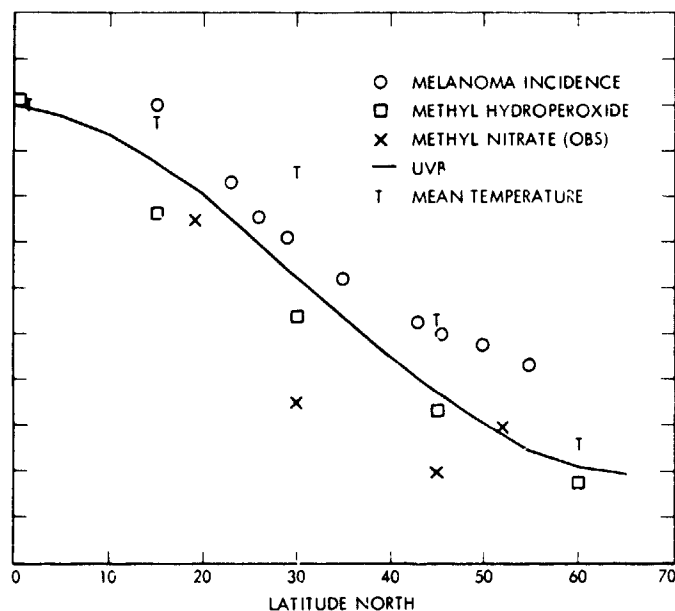


Figure 1. Normalized correlation with latitude.

All sorts of other things change with temperature. But perhaps more interesting are the computations Steve Wofsy gave me which give the amount of methylhydroperoxide that might be expected to be present in the atmosphere. These are squares on this diagram. They follow also very closely the same type of relationship. Now methylhydroperoxide is listed as a mutagen. Whether it's in sufficient quantities to be a causal agent is something we just don't know. Finally, since we have only calculations, we don't really know that they are there. There are the crosses that are measured concentrations of methylnitrate, which I found on a cruise of the Meteor, 1973. Methyl nitrite is a potential mutagen, and the sort of compound against which we're correlating the incidence of melanoma.

I think you can see it is not as simple a matter as correlating cancer with properties such as UVB, and I would finish by saying it took very many years of patient research to establish a causal relationship between cigarette smoking and lung cancer, and no comparable study whatever exists to relate any form of skin cancer with UVB. We are, I think, so to speak, straining at sunburn while smoking a Camel.

## F. Kaufman:

There is a considerable body of new evidence on malignant melanoma that shows correlation. Now this is not a proof, but both the incidence of UV on the body (you may have seen the X-rated picture in the NAS committee report) and the latitude dependence are correlated, and of course you show other dependences. I don't think methyl nitrate has increased in recent years. The Scandinavians are very rich now and go traveling, and they now have 10 times the malignant skin cancer because many of them are going for tropical vacations. In Connecticut, statistical studies have shown women to have had a tenfold increase in malignant melanoma from before the second world war to after. I am not saying that this establishes causal relationships, but I would just say before I totally knock it down, let's be careful. This is a philosophical statement. The fact that you find other possible causal relations does not get you off the hook. It may be right. How much Russian roulette would you like to play. Can we rule it out? Of course we can't rule it out. Is it a plausible correlation? It seems to be.

I think there were four points that Fitzpatrick made both in the NAS report and in the press briefing which indicated a correlation, and that there do seem to be other effects involved as well. Malignant melanoma is now a rapidly increasing illness of the affluent, not of the people who work in the sun. Whereas, the ordinary, older carcinoma was the illness of farmers and people who had their face and hands in the sun all the time and over long periods of time. I don't think we have settled this. I am not even sure there is any great point in continuing this. All I say is that there surely is a danger flag, a red flag up, which indicates not to overdo it but not to underdo it, and I would not want to be again in the middle.

J. Lovelock:

I agree with all you say about the danger that has been raised, but throughout this affair the thing that struck me is a tendency to select evidence for one side of the argument only. No consideration of these other potential sources was presumably considered in the deliberation. I understand they took the Register General statistics of Great Britain, where the incidence of melanoma is rising faster than that of any other cancer, even lung cancer. But the incidence of other forms of skin cancer, which are certainly more related to UVB, is declining. This is a very puzzling statistic.

F. Kaufman:

I don't think it is very puzzling. I think that is exactly what you would expect.

Unidentified panel member:

I just wanted to make a very brief comment on what Dr. Lovelock said. I think it was a very valid point to raise about other correlations and the sort of newness of the melanoma question, but I'm interested in terms of the methane degradation products that he shows on his graph. I would like to mention that it is quite clear that these products will respond to a change in stratospheric ozone, probably almost as rapidly as UVB does, because they are related to the production of $O('D)$ and $OH$ concentrations and that sort of thing. The only reason I raise this point is that if one establishes that some of these other compounds in the atmosphere play a role in skin cancer or in other health or environmental problems, they form a very complicated problem which is not constant now and will not be constant for all times. They are affected by air pollution and stratospheric ozone levels.

F. Kaufman:

They are highly pollution-dependent. They find tremendous incidence in Los Angeles and none in beautiful Utah. I think we are getting into areas that we cannot contribute. We ought to get back to ClO. Sherry?

F. S. Rowland:

I just returned from a photobiology meeting in Rome at which I listened to the reports of the medical people from Denmark, Norway and Germany. Each of these people concluded that the primary cause of melanoma was ultraviolet radiation, and among the things from which they drew their conclusions was a sex differential in the fact that melanomas appear on the legs of the women and on the backs and shoulders of the men, and they do not appear on those parts of the skin which are completely covered at all times. It is the same kind of thing that Fitzpatrick has been showing. The effects in Norway, where a study was conducted over a 20-year period, show that certain types of melanoma, melanoma of the foot which you will hear about, have not increased and probably have some other origin. But the melanoma on the exposed parts

has been rising steadily; the incidence there has gone up by a factor of about 4, and they are expecting another factor of 5 in Scandinavia. This is a quotation from Prof. Magnus, who presented his report in Rome. I am not an M.D. I am just reporting what they said.

F. Kaufman:

Before we leave this subject area perhaps the audience would like to burst forth.

R. Scorer (in audience):

Just to sort of illuminate this, I think it is important to emphasize what Dr. Fitzpatrick said. Was there any expected increase in melanoma due to changes in ozone, or is it small compared to the increase that has already taken place in the last 20 or 30 years due to causes that have been identified and which individuals can cope with if they want to. Now to highlight that list a bit further, I should say that rickets, which is due to lack of UV, has increased in Britain in the last 20 years. This is mainly because black people have migrated to Britain. This increase is entirely in the black population. What they need is a bit more UV.

F. Kaufman:

I think we should rule out anything that has to do with a voluntary versus involuntary breakdown. We all know that anyone who puts sun screen lotion on himself would not get any melanomas, just as anyone who doesn't smoke will not get lung cancer, at least incrementally due to smoking. But what is imposed on us by other forces is another matter.

H. Schiff (in audience):

I'd like to get clarification on dust as a sink. You talked about the possibility of removal by dust. Can you clarify how that reduces the steady-state concentration, unless you have evidence that the halocarbons are permanently taken out by dust.

J. Lovelock:

I would be glad to, but the pieces of evidence are about sixfold and it would take a long time. Can we discuss it privately afterwards? It is a fairly complex story. I am not trying to dodge, but it mostly relates to carbon tetrachloride, which does show quite good signs of such a thing.

F. Kaufman:

But do you have any evidence of heterogeneous chemistry that breaks down, and in what way is Sahara sand different from other.

**J. Lovelock:**

It strongly absorbs carbon tetrachloride, and it is very difficult to get it back off as gas.

**Voice in audience:**

Just last evening I was talking to a gentleman who was from the National Institute of Health, who told me of the increase in cancer in the high altitudes of Mexico. Recall that Mexico City is over 7000 ft. The increase certainly has not been due to ozone because, as we know, there is no ozone depletion and we know ozone has been increasing over the last decade. Also, I don't believe those people have changed their lifestyle, and this brings up the thought that this would suggest that there might be some other cause.

**M. Molina (in audience):**

There is absolutely no information at that point. There are many changes in Mexico City, including better medical care for those... (confusion).

**F. Kaufman:**

Order in the court --

**F. Kaufman:**

Let's go to ClO. Is there a distinguished panel member who would like to start out with anything related to ClO before we give Jim his additional minute and a half.

**S. Wofsy:**

I would like to emphasize the question of one-dimensional models in budget studies, especially as far as chlorine is concerned, and go back to Jim's results and maybe I'll anticipate some of the things he might want to emphasize. We have to be quite careful I think about using a one-dimensional budget study. By budget studies I mean how much total chlorine is there in the atmosphere. The danger of using Jim's ClO measurement and inferring from that one measurement how much chlorine that implies has been emphasized by many people here today. The atmosphere is extremely variable and the causes of that variability are not included in a one-dimensionable model; they represent some sort of a global average. Budget studies really need measurements at many different places and many different times so that we can get a good global average. There is one important thing that has been referred to as a weak test of models, and that is a ratio: a chemical ratio of Cl atoms to ClO. Now a one-dimensional model calculates this, as far as we know, in a proper way. These things are supposed to be related according to reaction rate, with reaction times that are very short compared to transport times. So that regardless of whether or not the transport properties are done correctly or incorrectly, the model should predict in a local situation the proper Cl to ClO ratio if it has the

right ozone value and if we know the O to $O_3$ ratio. Now the O to $O_3$ ratio is probably the least disputed of the unmeasured calculated quantities in a model. It is one of the easier things to calculate.

I think this is a valid test that can be performed in a one-dimensional model, and the one-dimensional model should calculate this properly. Everything that should affect the ratio should be in the one-dimensional model, assuming that you have done your photolysis of ozone correctly and all your multiple scattering and all those things. So I think it is important to emphasize the ratio in that measurement, more than the single measurement of the magnitude. As we get more and more measurements at different latitudes at different seasons I think we can really begin to answer budget questions.

The other ratio question I would like to point out is ClO to HCl. Anderson's ClO compared to all the HCl measurements we've seen falls outside the limits you would expect from a model. We've shown in a poster session here a model where we propagated errors through a model and show one-sigma uncertainty limits, and that ratio falls outside of those limits, but that may be due to the fact that Jim is measuring at one place at one time while the HCl measurements were made at another place and at another time with another instrument. It is very important to measure that ratio at the same time and place so that we can make the comparison, and then maybe we can try to answer the question of how much total chlorine there is.

### F. Kaufman:

You always say it validates a model. It validates a local photochemistry. It is just simple chemistry. The O to $O_3$ ratio, which no one will seriously argue with, is uncertain to within a certain range, and there are three rate constants to it: 2-1/2 rate constants because $Cl + O_3$ and $ClO + O$ are the major ones, and $ClO + NO$ comes in in a minor way. That has really nothing to do with models.

### S. Wofsy:

It is telling you that there is apparently no other significant way of getting from ClO to Cl without going through the catalytic cycle. It's a very oasic building block of a model, and it is just photochemistry, and that is all we have so far that we can absolutely test in the atmosphere.

### F. Kaufman:

Nevertheless, we will have to get back to the budget question, I think. We haven't stated yet how much there is, right? We want to hear.

### J. Anderson:

First of all I should say that I am not a theoretician in these matters and I wish to avoid getting emotionally involved in the calculations [laughter] because it tends to disturb my ability to make experiments.

But let me just point out one thing. The ratio of atomic chlorine
to HCl is the ratio of the rate constant of the return step between
OH and HCl, times the OH concentration, divided by the rate constant
for reaction between Cl and $HO_2$, plus the rate constant of Cl plus
methane. Now there is very important data taken by Burnette ··· ·
Noxon on the total column of OH and its variability. The experiment
used a high-resolution Fal·e-Perot experiment sitting on the ground
measuring a total column of OH above the ground, and virtually all that
total column resides in the stratosphere. The lower limit from their
measurements was roughly equivalent to the total column that we mea-
sured in the January OH flight, and they see fluctuations of I believe
a factor of 4 above these values. John is that correct?

**J. Noxon:**

What you said is true.

**J. Anderson:**

That is all that matters. So that means that the ratio of reac-
tive chlorine to stable chlorine is proportional to tne OH concentration
and that says that before you make inferences relating a Cl or ClO
measurement to HCl you have got to be very careful about this ratio. Of
course, if OH goes up, $HO_2$ will respond. Their ratio is independent
of hydrogen chemistry, but the reason we are interested in this ratio is
that it is primarily dominated by the ratio of the rate constants  and
the ratio of the OH concentration to $CH_4$. So I would warn against
relating in a direct sense total chlorine in the stratosphere to ClO.
Now, if you take a typical OH concentration and use a ClO concentration
that we have measured during the July 28 flight, you require 4 or so ppb
of total chlorine. That number is somewhat indigestible, I would say
by a factor of 2 or so, to the chlorine budget.

**Unidentified voice in panel:**

I have one question I wanted to ask Jim, and I guess it is a
little bit of a crime in view of the extreme beauty of the experiments
he has described to ask for more, but I think at one time he was think-
ing about the possibility of having a flash system in his probe so that
he could flash HCl and look at the resonance fluorescense of the chlo-
rine and in that way get simultaneous measurements of HCl.

**J. Anderson:**

We are planning on looking at HCl by a different technique. There
is an addition of chlorine to convert HCl to Cl atoms, and by pulsing
chlorine on and off you simply observe HCl in the presence of chlorine
and nothing in the absence. I must say you can check this out in the
laboratory and verify it, of course. I prefer that technique to photolysis
because the velocities required to preclude wall removal, i.e., the
time required, dictate a total photolysis flux that is difficult to
achieve, and it is very hard to demonstrate converting all the HCl
over to Cl atoms. That is why we're leery about that method.

**S. Wofsy:**

I just wanted to make the remark that what you get for Cl from Jim's measurement depends on how you do the calculation, and it seemed to me that some calculations I did with 2-1/2 ppb Cl went nicely through the lower end of his measurement range.  So it depends a lot on the OH concentration and other things which are easily adjusted at this time.

**Voice in audience:**

During the presentation this morning Peter Jesson called attention to the HCl bend-back in the vertical profile.  And the Academy report really didn't pay much attention to that.  I was wondering if I could get a reaction from people as to how important that is and what it might mean.

**F. Kaufman:**

Al Lazarus is responsible for the measurements.

**A. Lazarus:**

I would first like to say that we did it at 36.7 km at the begir·ning of September: very close to the time that Jim started to do it.  On the neutral side of our filters, above the aerosol layer it does collect chlorine.  We measured the efficiency for ClO only with bad conditions, not at ambient conditions, which we plan to do very shortly.  But there are two points.  One is that the mixing ratio of chlorine on the neutral side of our filters was 1.8, which I think is pretty close in terms of number concentrations to Jim's result.  The second thing is that the HCl concentration that we measured was quite high relative to other measurements we've made.  The total chlorine on the impregnated side of the filter came out to 3.4 ppb by mass, which is quite high, and for which the ratio of ClO t  HCl is not what the model predicts.  I would just make a very tentative statement at this time concerning the decrease of HCl above 27 km.  We've had a series of flights at 32 km and they consistently have shown less HCl than at 27 km.  We've only had two flights at 37 km, and I don't want to say a lot about it, but at that altitude HCl tends to go back up again in concentration.  So from very preliminary data, it looks more like a dip but not a continual decrease.

**A. Lazarus** (in response to a question from Julius Chang concerning the reality of dips and wiggles in data for concentrations versus altitude):

We have completed a hemisphere of cross-section of 75 north to 10 deg south up to 32 km for HCl concentrations.  There is considerable latitude variability.  We have seen the concentration at 32 km less than at 27 in all of these latitudes, but the absolute values of these concentrations vary very much.

**F. Kaufman:**

Will our infrared friends have anything to contribute to this.

**M. Ackerman:**

There are quite a few measurements of HCl and Cl compounds using the infrared lamp method, and I think my colleagues Odell Raper, who represents the JPL measurements here, and Dr. Murcray, who is also in the audience, will agree with me that it should be remembered that when people put arrow bars on numbers in a paper that they usually mean some-thing. All our data are presented in the form of an envelope of number densities of mixing ratios. This is due to the fact that, by defini-tion, the limb-scanning technique is a rather imprecise technique: especially when you have to use low resolution and when you have few measurements during a scanning period. You need many, many points during the limb-scanning and you need high spectral resolution to have accurate data to achieve an accurate inversion. People who are using these methods should remember that when we give an envelope it means that the number densities could be at any altitude at any place in that envelope, and you can imagine any kind of wiggles you wish - if you really wish to have wiggles inside that envelope.

**Unidentified voice in parel:**

I would just like to make a comment on what Julius had to say. First of all, I think I did carefully qualify the question of the turn-back of the HCl and the question of transport and the question of the accuracy of the measurements and the question of atmospheric varia-bility. The point with regard to the log plots is fine but I think in none of the calculations that we did with the currently assumed kinetic parameters did the HCl turn back on itself. Finally, I would say that that one profile is the only profile that I have seen that goes to that altitude and shows that magnitude of dropout. I am not aware of any wiggles of that kind of magnitude.

**F. Kaufman:**

I think Ralph has one slide to show of a model calculation.

**R. Cicerone:**

There is a lot of information here (Figure 1) so I will be as brief as I can. The solid squares labeled LCD are middle calculations; that is, when we take middle-level kinetic rate parameters for the entire stratospheric system, coupled with an inventory of odd chlorine sources, including the fluorocarbons 11 and 12, carbon tetrachloride and methyl-chloride, so that at high levels we have a total background of odd chlorine and 1.8 ppb; this is just the HCl mole fraction or mixing ratio I am showing here. On top of this we have in the troposphere Barney Farmer's range of inferred HCl values, with my calculation on what we would expect. So these squares are middle-level HCl calculations and are clearly showing a decrease on Julius' desired linear scale. I stopped at 40 km because we were interested in something else when I
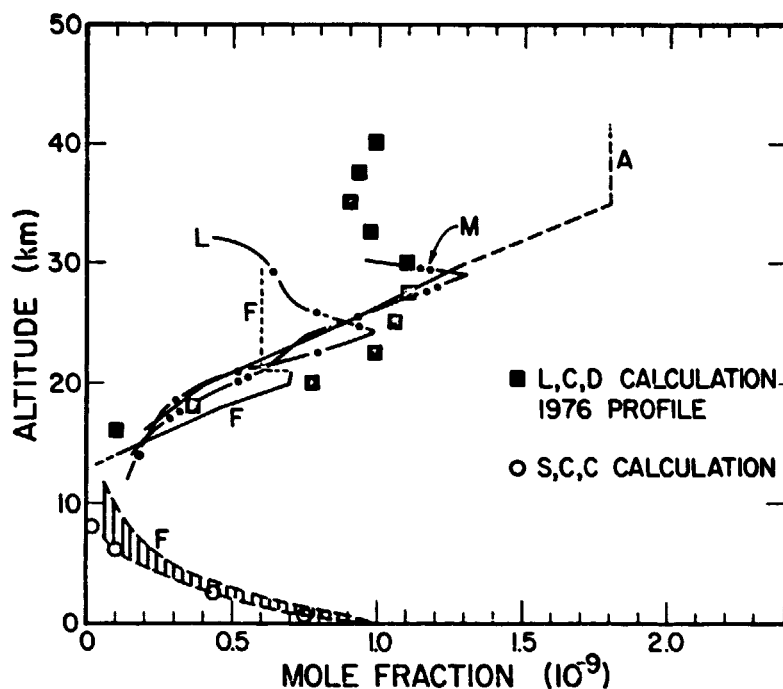
Figure 1.  Hydrochloric acid mole fraction (mixing ratio) vs
altitude.  Filled squares and open circles are
calculations.  Experimental measurements are A:
Ackerman, F:  Farmer, L:  Lazarus, M:  McElroy.

prepared the graph last week, but it continues up to almost 1.8 ppb
above 50 km.  Also, we have Ackerman's measurements, and I must apologize
for the way I extrapolated them because I have a disagreement with
Ackerman's numbers between 30 and 35 km.  These are Murcray's data from
Geophysical Research Letters.  These are Farmer's data from Geophysical
Research Letters, and these are from Lazarus' published data in JGR and
the "dear colleague" letter he circulated recently.  I don't see a
factor 3 disagreement based on source strengths on this linear scale at
the lower altitudes at all.  I do see a clear bendback without biasing
any rate constants.  It may not be right; it may be a function of the
coefficient we used.  We used Don Hunten's old coefficient multiplied
by 2.  But this is a middle-level model and I don't know why but it is
there.

F. Kaufman:

      Well shall we have a brief comment by Sherry.

F. S. Rowland:

      This is just in connection with the suggestion of the Sahara sands;
that because of the effect on carbon tetrachloride, there might be a
sink for fluorocarbon 11 and 12.  Carbon tetrachloride has a boiling
point that is much higher than that of fluorocarbon 11, which boils at
24°F, and fluorocarbon 12, which boils at -40°F.  So that the adsorbing
effects which might very well contribute to the variation of carbon

tetrachloride would be expected to be progr 'ively less if you are
dealing with fluorocarbon 11 and with fluorocarbon 12. And finally,
when we are looking for tropospheric sinks, I think we need to keep in
mind that half of all the carbon dioxide that has been put into the
atmosphere from fossil combustion is still there, despite the fact that
all the biological systems in the world use it to live on and it is
very soluble in the ocean. It still takes 20 years for these tropo-
spheric sinks to get rid of the carbon dioxide.

### F. Kaufman:

Our chairman would like to tell us a brief story, three quarters
of an hour or so.

### J. Friend:

Two comments I would like to make with regard to tropospheric
sinks. One concerns very much what Sherry just mentioned, and one
concerns the discussion that went on this morning about the profiles of
chlorofluoromethanes. If there is an active tropospheric sink of some
compound, let's say you are looking for one for fluorocarbon 11, then
you would expect that the active sink would maintain some sort of a
gradient of latitudinal profile, and we are going to examine the known
one that Lovelock has found to see what estimate for a tropospheric
lifetime we can come up with. Now if you are releasing something which
has no active sink, for instance Krypton 85 or something like carbon
dioxide which has a sink that is complicated by exchange with the sur-
face oceans, then I don't think it is valid to make the direct com-
parison. The point is that it is not valid to make the direct compari-
son between chlorofluoromethanes and these other substances whose sinks
are perhaps differently distributed.

That is one point that it seems to me should be made. The other
one is just a matter of information concerning this bible that I am
responsible for, and in which we were trying to put some sort of number
on what the tropospheric sink in the ocean might be, using Lovelock's
data for the atmosphere and the ocean concentration. You can make a
conservative estimate if you assume that the atmosphere and the oceans
are at near steady state, which they are probably not. But if you do,
and use a representation of the thin layer model for the transfer of
gaseous substance from the atmosphere into the surface oceans, we came
up with an estimated lifetime for a tropospheric sink of about 300 years
for fluorocarbon 11. Which is to be compared with the 50 years esti-
mated for loss by photolysis in the stratosphere. Now the effect of
that in the Academy report is to take the estimated value of 7-1/2 per-
cent ozone depletion and lower that to 6 percent. Now the 6 percent
would include some effect of that hypothetical but unknown sink that
exists in the ocean. Just as we finished these calculations, Junge
published a paper studying just exactly the same data, but with dif-
ferent solubility and with different values for the parameters in the
model, and came up with a favored lifetime for removal by that sink of
800 years. So ours is perhaps a bit more conservative than his.

**Voice in audience:**

I would like just a clarification. I would like to know how the test is made into the difference between an infinite lifetime versus whatever the 2 to 3 percent sink would mean in terms of decreased lifetime.

**F. Kaufman:**

Well a 2 percent sink, which is 50 years, would cut the steady-state value in half, at least on the F-11 which is 50 years. If it were 3 percent, it's 33 years, or you take the inverses and add them and take the ratio of those rate constants.

**J. Lovelock:**

I would just like to say that that figure represents the sum total of all possible processes. I wasn't thinking of 2 percent for any particular single process.

**F. Kaufman:**

We have got to leave. Thank you all.

# SCIENCE AND PUBLIC POLICY:

# DYNAMICS OF DECISION MAKING ON THE STRATOSPHERE

SECTION I

INVITED SPEAKERS

## STRATOSPHERIC MODIFICATION AS AN
## EXAMPLE OF ENVIRONMENTAL DECISION-MAKING

Wilson K. Talley
Assistant Administrator
for Research and Development

## A. INTRODUCTION

In recent decades, environmental hazards have appeared on the scene in countless forms, often constituting grave threats to the health and well-being of all living things - including humans. We have seen our fish contaminated by phthalates, our cattle poisoned by polybrominated biphenyls, and our horses killed by dioxin. Fluorides have destroyed forest seedlings, chloramines have killed oysters, and zinc has damaged our wheat crops. And now the fluorocarbons are threatening the ozone belt.

There exist today more than 2 million different known chemicals; every year, this list grows by an estimated 25,000 new compounds. There are currently more than 30,000 chemicals in actual commerical production; every year, this list grows by some 1000 new compounds. Of the more than 2 million known chemicals, only a few hundred have been adequately tested. We know, in fact, very little about the health effects even of the 30,000 chemicals already in commercial production. It is the risk and uncertainty about these substances that make environmental decision-making such a difficult - even agonizing - task.

Take, for example, the question of stratospheric ozone reduction. The potential depletion of ozone through the release of fluorocarbons raises two types of problems: (1) the more general problem of stratospheric modification and its associated effect on human activity, and (2) the obligation to trace the ultimate fate of by-products of man's activities. From the latter, I believe we have learned that it is essential not only to measure the toxicity of substances but also to trace their long-range effects on the environment. The general question of stratospheric modification opens the door to potential significant alteration of the global environment. The possibility that man's activities may induce stratospheric changes which may alter conditions essential for the health and well-being of all living things is a source of grave concern.

With a view toward maintaining human health on a global basis, we must consider the concept of preserving the stratosphere as a global resource, especially the ozone in the stratosphere. Obviously, hazards affecting the stratosphere, originating from activities in many nations, cannot effectively be dealt with on a national basis. International machinery to coordinate strategies among nations will need to be developed to assure preservation of this resource.

It is obvious, too, that the fluorocarbons issue is not wholly contained and cannot entirely be resolved within our national boundaries. For example, we estimate that the United States accounted for 38% of

the total fluorocarbon 11 and 12 production in 1975. The Organization for Economic Cooperation and Development (OECD) member countries, which comprise the developed western nations including the U. S., constitute 89% of the total fluorocarbon 11 and 12 production. Consequently, any national effort to reduce emissions of fluorocarbons 11 and 12 will address only a portion of the problem.

International decision-making is a slow process. The first efforts to deal with this problem, then, will most likely be taken at the national level. It is very important that, from the beginning, we effectively coordinate our national research programs and establish mechanisms to communicate and discuss our analytical and regulatory efforts.

In the longer term, concerted national actions may be insufficient. I believe this meeting today can go a long way toward laying the foundation for future international cooperation.

During the past two days you have been discussing the scientific evidence for the models predicting ozone depletion. As you may know, EPA is leading an interagency research program on the biological and climatic effects of stratospheric ozone reduction. The Federal Council for Science and Technology (now the Federal Coordinating Council for Science, Engineering and Technology) recommended that the program be divided into a short-term phase for fiscal years 1976 and 1977 and a long-term phase beginning in fiscal year 1978. EPA was given the responsibility for the short-term phase of the program.

We accepted this task and immediately set up an interagency framework to assist us. This consists of an overall policy advisory group of representatives from interested agencies and three technical task groups. The task groups are comprised of technical experts from various agencies, supplemented by consultants from outside the government. The three groups currently active are: Human Health Effects, chaired by the National Cancer Institute; Biological (other than human) Effects, chaired by the Agricultural Research Service; and Instrumentation, chaired by the National Bureau of Standards. We are in the process of forming an additional task group on climatic effects. These task groups are currently developing detailed plans of approach.

A great deal of time has been given to deciding what size program would be most appropriate and where, in this period of fiscal restraint, the funds should come from. Within the last month, EPA has decided to reprogram $4 million of its own research funds to carry out the short-term effort. We are currently working out final plans for this effort and will present our recommended plan to the Interagency Policy Advisory Group September 27. We hope then to begin work shortly thereafter.

I might point out that we view this as a truly interagency effort. Most of the available expertise for conducting this type of research is outside of EPA, and we plan, therefore, to "pass-through" most of the funds to other agencies.

We feel that a number of critical issues can be addressed
effectively in the short term. However, exploring most of the basic
scientific uncertainties will take much longer. The means for funding
and managing this needed long-term research remains undetermined at this
time.

In reviewing the uncertainties in both the physical mechanism of
ozone depletion and in the prediction of effects, we feel the accumu-
lated scientific evidence indicates that the fluorocarbon/ozone hypothe-
sis is not likely to disappear and deserves some critical attention.
In addition to reprogramming $4 million to initiate the biological and
climatic effects program, EPA has undertaken several extensive economic
studies of the relevant industrial sectors to estimate the economic
impacts associated with possible fluorocarbon regulations. EPA has
also been simulating stratospheric reactions and studying tropospheric
transport of fluorocarbons.

EPA's authority to reduce fluorocarbon emissions is presently
limited in coverage to include only fluorocarbons in pesticides, which
are less than 1 percent of the problem.

However, let me emphasize that two separate legislative initia-
tives are being considered in this Congress which would expand EPA's
authority to cover all sources of fluorocarbon emissions. The toxic
substances legislation, although not specifically mentioning the fluoro-
carbon threat, would, in its broad approach to chemical hazards, pro-
vide sufficient authority to regulate fluorocarbons. On the other hand,
the Clean Air Act amendments specifically outline decision time tables
for fluorocarbons, stipulating that any regulatory action must be based
on a positive finding by the administrator of "reasonable anticipation
of harm." The senate and house bills differ slightly, but they both
basically allow for two years of continued study to narrow the uncer-
tainties. However, expedited regulations are authorized prior to the
two-year deadline if there is a reasonable basis for anticipating
public health hazards. On the basis of the report issued by the
National Academy of Sciences earlier this week, however, it appears that
acceleration of the decision before two years may not be necessary.

An examination of the emissions of fluorocarbons indicates
that aerosol spray products constitute a significant portion of the
total burden. Our estimates indicate that 1975 aerosol releases of
fluorocarbon 11 and 12 comprise approximately 76% of the total atmo-
spheric burden from all sources during that year. The U. S. aerosol
emissions of F 11 and F 12 alone constitute 37% of the total world
aerosol emissions and 28% of the world releases from all sources. Thus
regulation may be most prudently directed toward specific uses of
fluorocarbons rather than at the substances themselves. The information
needed for developing appropriate regulations are (1) scientific data
on the validity of the physical mechanism for ozone depletion and on
the health and welfare effects of a reduction in average ozone
concentration, and (2) technical and economic information on the
magnitude and distribution of costs of alternative courses of action.

Because environmental decisions are complex and the data uncertain, it is impossible to predict faithfully all the consequences of any particular decision. Thus, we are faced with the problem of making rational decisions on environmental issues restricted to the data in hand.

Let me review briefly the nature of the environmental decision problem, followed by an examination of the scientific information that is used in the assessment of a potential hazard and, finally, the problem of comparing risks and benefits.

B.    NATURE OF ENVIRONMENTAL DECISION PROBLEM

As I have said, environmental decisions are often made in the absence of reliable data with respect to public health threats and economic tradeoffs. In the ideal world, it is fair to say that the objective of most decision-makers would be to develop solutions to environmental problems which are consistent with the severity of the problems themselves. Such an objective suggests that environmental regulations should be established on a quantitative basis that allows simple comparisons of costs and benefits. In the real world, however, this approach is seldom possible. Rigorous cost-benefit analyses which attempt to consider all these elements are generally impractical.

The basic problem - and this is the main source of the difficulties in environmental decision making - is our inability to reduce all of the factors in the decision to a common denominator. Even if we had excellent data, this problem would remain. As a result of our inability to establish comparable units of measure, environmental decisions invariably involve value judgments on which the informed public, scientists, and special interest groups have widely differing opinions. Moreover, given the nature of environmental risks and the responsibility vested in regulatory agencies for the protection of public health, it is not acceptable to postpone decisions on these problems indefinitely in the hope that better data may be obtained in the future. The public interest often demands precautionary environmental regulations based on the best data available.

A second major problem is the lack of quality data. Regulatory questions many times involve low probability events with extended periods before the manifestation of effects. Thus it is difficult and very costly to obtain statistically valid results. The presence of these limitations does not mean that useful information cannot be developed. Specific types of data can be used to narrow the uncertainties raised by a particular environmental hazard.

C.    ASSESSMENT OF AN ENVIRONMENTAL HAZARD

While we cannot expect scientific data invariably to provide conclusive support for regulatory action, the data often provides compelling arguments for such action. In the analysis of stratospheric modification problems several specific types of data will, I think,

prove useful. In the case of chlorine-catalyzed destruction of ozone, EPA will need to evaluate the following:

(1) The accuracy of the ozone depletion models, the amount of ozone perturbation, and the cause of such perturbation, including the effects of halogenated compounds other than fluorocarbons. The NAS report, which was released this Monday, and the NASA report to regulatory agencies will be fundamental to EPA's evaluations.

(2) The relationship between ozone concentration and UV-B exposure or other effects such as changes in climate.

(3) The association based on epidemiological data between UV-B exposure and skin cancer.

(4) The available data on other biological and climatic effects which may result either directly or indirectly from an accumulation of fluorocarbons in the atmosphere.

As a result of the ongoing investigation in these areas, our knowledge and understanding of these problems is improving. Our effects program should measurably improve our evaluations of the effects of stratospheric modification. Nevertheless, even if we fulfill our best expectations, precise estimates of environmental effects will not be obtainable without years of additional research.

However, as I have previously mentioned, we just cannot postpone decisions on these problems indefinitely in the hope that better data may be available in the indefinite future.

D. COMPARISONS OF RISKS AND BENEFITS: EVALUATION OF AN ACCEPTABLE LEVEL OF RISK

It is in the context of scientific uncertainties and threats to human health that environmental decision makers must recognize the general and agonizing problem of balancing the perceived costs to public health, the possible financial costs to society, and the benefits of continued use of the practice in question. These tradeoffs are made, realizing that neither benefits nor risks can be accurately estimated or compared.

Of course, when risk is obviously high and benefit is low, less information may be required for environmental decision-making.

Modern techniques of decision analysis can assist in organizing all the complex factors and available information. However, cost benefit analyses cannot substitute for rational judgment.

Moreover, no acceptable method exists for placing a value on benefits that will occur in the distant future rather than immediately. The use of discounting (as in discounted cash flow analysis) has serious limitations since it implies, for example, that future lives are worth

lers than current ones. In short, it is important to recognize that environmental decisions usually can be reached on the basis of judgment combined with knowledge of the available data and the opinions of interested and affected parties.

This process is often aided by referring to congressional intent or the "sense of the Congress." Congressionally enacted statutes many times provide guidance to policy makers on both what will be regulated and which factors are to be considered in the regulatory process. For example, the House committee report on the Clean Air Act states:

(1) EPA need not produce rigorous evidence of deleterious health effects due to ozone depletion.

(2) Nor need EPA refute every hypothesis counter to the chemical models predicting ozone depletion in order to restrict fluorocarbons.

(3) And it is sufficient for EPA to rely upon reputable scientific and medical data and laboratory and field measurements to establish reasonable anticipation of harm.

Furthermore, the report continues, the EPA is to examine the "feasibility and costs" of complying with any stratospheric ozone measures. This awareness is necessary to determine what combination of stratospheric protection measures are appropriate.

In EPA's regulation development process, every effort is made to guard against the misuse of data and, where possible, to compensate for the lack of complete data. All EPA regulations aimed at implementation of environmental legislation passed by the Congress go through a complex series of intra-agency working groups, internal reviews, and interagency reviews. This sequence usually occurs two times for every regulation, once prior to proposal and again prior to final promulgation of a regulation. In addition, a public comment period is usually provided for between proposal and promulgation, and, in some cases, public hearings are held during this period.

A proposed regulation is subjected to public review and comment and to the scrutiny of various interest groups in the hope that an indication of the social significance and value of the regulation can be obtained. On the basis of this feedback and in light of the available quantitative data, the administrator of EPA makes his final decision.

Obviously, the success of this procedure depends on obtaining a balanced set of comments and reactions. Furthermore, the quality of external comment and participation in this process depends heavily on the clarity with which all available data and analyses are presented and explained by EPA prior to the public comment period. Nonetheless, in most cases, given its limitations, this process is probably the most appropriate means of dealing with the problems so often encountered in environmental issues.

And, as you may know, the administrator recently ordered an entirely new risk-benefit procedure for carcinogens which we believe will greatly reinforce this process.

E.   CONCLUSIONS

Before concluding this discussion, it is only proper to recognize that the topic of environmental decision-making is much too broad and complex to deal with definitively in such brief comments.  Rather, the objective has been to present a short but, hopefully, balanced view of the problem and the ways in which EPA has attempted to deal with it. With this point in mind, it may be useful to summarize:

First, stratospheric ozone reduction constitutes a serious environmental risk, and EPA is developing the capacity to assess the need for fluorocarbon regulations.

Second, if regulations are necessary, international initiatives may be required to assure protection of the stratosphere since global problems deserve global solutions.

Third, because of methodological and data constraints, rigorous cost-benefit analysis for decision-making is often impractical - and may not be needed.

Fourth, as a consequence of these constraints, it is necessary to rely partially on nonquantitative methods of decision-making.  EPA has adopted an elaborate public review process which draws upon the views of a variety of interest groups whose conflicting opinions must be confronted openly, thus balancing a variety of preferences in reaching a decision.

Let me say, in conclusion, I hope I don't leave the impression that we believe our approaches are beyond improvement.  Continued expenditures on environmental research will certainly improve the scientific basis of regulatory decisions.  However,  a regulator's decision is ultimately subjective, and he must weigh his judgments against what he perceives to be the intent of Congress and the best interests of the public.  The regulator's pursuit of factual certainty should not overshadow his agency's responsibility for the protection of public health. A regulatory philosophy which strictly adheres to certainty for decisions is, in effect, dictating that the only acceptable manner of demonstrating that a risk exists is to prove - by actual "body counts" - that a source of danger exists.  I am convinced that the public interest demands precautionary environmental regulations, based on the best data available, early enough to assure that no such "body counts" are ever needed.

## MAN-MADE ALTERATION OF THE ENVIRONMENT—
## CONSUMER PROTECTION ISSUES

### R. David Pittle
### Commissioner, U. S. Consumer Product Safety Commission

I would like to begin this talk with a brief explanation followed by a quick disclaimer.  The United States Consumer Product Safety Commission is an independent regulatory agency created by the U S. Congress and charged with protecting consumers from illnesses and injuries associated with consumer products.  Decisions concerning the need for product standards, recalls, or bans are made, as I will discuss a bit later, by vote of a majority of the Commissioners (nominally five - at present there is one vacancy) acting on the basis of material and information supplied to the Commission by its staff and by interested outside persons.  Regulatory decisions made by the Commission may be reviewed and, if improperly made, can be reversed by the courts.

What products fall within the definition of a consumer product is a little more difficult to explain.  At the time the Commission was created, a number of Federal agencies were already regulating the safety of some products such as automobiles, drugs, and cosmetics.  Congress therefore excluded those products from the Commission's jurisdiction. Nevertheless, the Commission was left with a wide range of products to regulate, products that run the gamut from toys to televisions.

In directing the Commission to look at illnesses as well as injuries associated with consumer products, Congress plunged the Commission directly into the morass of complex decisionmaking that typifies the linking of cancer and other chronic diseases with their causes.  My comments today will reflect my experiences with deciding difficult and uncertain issues such as the relationship between chlorofluoromethane (CFM) release and skin cancer.

Before proceeding, let me state my disclaimer.  Because cosmetics are excluded from the Commission's jurisdiction, we do not have authority to regulate CFM propellants used in hair spray and underarm deodorants. However, the Commission does have jurisdiction over those propellants when they are used in household cleaning products.  Furthermore, because automobiles are excluded, the Commission may lack jurisdiction to regulate auto air conditioning systems.  However, it does have authority over household refrigerators and air conditioning systems.  To add to the confusion, Congress has directed this Commission to defer to the Environmental Protection Agency whenever that agency can take action under the Clean Air Act to reduce or eliminate a risk of injury or illness.  Amendments presently pending before the Congress may well give the EPA this authority for risks associated with CFM release and thus may remove the Commission's authority in this area.

Nonetheless, the fluorocarbon controversy has raged before the Commission for almost two years since the Natural Resources Defense Council first petitioned the Commission to ban the use of CFM propellants in aerosols.  My interest in this problem is and remains a strong one

both as a regulator and as one who in the past has done extensive research on modeling the structure of the lower atmosphere.

Ordinarily when the Commission regulates a product, injuries associated with it are directly and easily traceable to some defect in either the design or the manufacture of the product. For example, a bicycle manufactured with a structural weakness in its frame could fail, thus causing a child riding it to fall and break an arm. To obtain the evidence it needs to establish the risk of injury associated with those bicycles, and other products, the Commission maintains nationwide surveys of injuries reported to hospital emergency rooms and investigates a sample of the reported injuries to determine their causes and to look for recurring patterns. The Commission also has engineers on its staff who are able to test products for defects and predict, based on their tests, whether the product contains a defect that is likely to cause injuries. If the Commission does not have or cannot develop the necessary knowledge itself, it may contract with outside experts.

Let me not oversimplify. Even this analysis of ordinary cause and effect can be difficult. For example, fire often destroys the evidence of its cause. But more often the difficult question the Commission must answer in the case of the direct and immediate injuries is not the relationship of cause and effect, but whether the risks that it can establish are unreasonable - that is, should the Commission act to reduce these known risks? Answering this question usually involves complex judgments of policy.

Where injuries and illnesses are remote in time and place from their causes, however, the establishment of causation becomes a principal difficulty. The problem that haunts all government officials charged with protecting the public health - and it is a question that faces all the people of the world - is how can we determine whether today's activities will cause tomorrow's illnesses?

In resolving the question of causation two basic issues must be addressed. The first is how do we ensure that regulatory decisions are founded on the most complete and accurate scientific information possible? The second concerns the degree of scientific certainty required before regulatory action should begin. Separating these two issues is often difficult in practical applications because they are so closely related. Nevertheless the attempt must be made since one is largely a question of fact and scientific method while the other is mainly a policy judgment.

Some scientific agreement that a problem exists is a prerequisite for governmental action. This is so because of the legal need to establish a factual precedent for regulation. Some rational basis for government interference in the marketplace must be shown before that intervention can take place. Moreover, if government regulation is to have any credibility, the citizens of this country must be able to understand the reasons why regulation is necessary. This is not to say that regulation must await the resolution of all disagreement. If that were the case, public health agencies might just as well close down.

Rather I mean only that the theoretical underpinnings of a regulation must be clear, convincing, and explicable.

Various means are currently used to attain a measure of scientific certainty as to the causes of problems in the public health and environmental areas. Two such methods have been used in the present controversy. One was the formation of an intergovernmental task force, made up of representatives of all agencies with expertise in the area, to examine the available data and make recommendations for further government action. The second was the referral of the same material, together with the report of the government task force, to a panel of the National Academy of Sciences (NAS) to review the conclusions in light of some new studies to be performed.

A third method of scientific review has also been suggested by some as appropriate to this problem. That is the formation of a scientific "court of inquiry" to "adjudicate" opposing points of view on complex questions, e.g., the need for regulation of aerosol propellants. In a moment I will touch briefly on some emerging issues concerning that court.

It is extremely important to point out that these methods of review of the scientific evidence are usually made use of during the initial phases of an agency's investigation of a problem, i.e., while the regulatory agency is still attempting to determine whether action is necessary. Once an agency such as the Commission decides that sufficient evidence exists to form the basis for governmental regulation, then certain further steps are legally required. The agency must, at a minimum, publish a proposal in the Federal Register in which it outlines the action it proposes taking and why it believes such action is necessary, including a summary of the scientific evidence upon which the action is based. The public, including the industry proposed to be regulated, is then free to comment in writing on any part of the proposal. An oral hearing may be permitted or, in some cases, required. Before making the regulation final, the agency must respond publicly to the comments it receives. Thus, the law provides a further opportunity for independent scrutiny of the agency's scientific case.

If, after reviewing the comments it receives, the agency decides that it should take the course of action it proposed, the process is not necessarily complete. Upon request by interested parties the courts will scrutinize the action to determine not only that it is within the agency's legal authority but also to see that the agency has adequately assessed the evidence before it and chosen a reasonable course based on that evidence.

I stress these legal requirements for notice and comment and judicial review for two reasons. First, they provide an explicit opportunity to challenge the scientific validity of an agency's assumptions and to obtain an impartial review of the agency's conclusions. In this way the law has provided a brake to help guard against impulsive agency action not adequately grounded in fact or law. Second, as a braking process these steps take considerable time. Two or three years, for example,

would not be uncommon in a matter as legally and factually complicated as the issue of ozone reduction.

Consequently, in determining the certainty needed to propose regulatory action, sight must not be lost of the fact that a proposal is only the first of three steps. If near unanimity of scientific opinion could be achieved during the investigatory phase, this consideration would, perhaps, be less important. In theory at least, the scientific agreement would result in few comments on the agency proposal and less impetus to seek the judicial review. In practice, however, such unanimity is rare - particularly when the agency action will have an adverse effect on powerful economic interests.

I believe that agencies should generally use less formal means to test the soundness of its scientific conclusions. Open meetings with outside experts, or informal hearings at which expert scientists are invited to testify, are approaches which should be frequently used. Papers prepared by staff experts and circulated for peer review is another. The procedures permitting comment on a proposed regulation is a third. By keeping the mechanisms informal and unstructured, the agency can obtain an assessment of the relative strengths and weaknesses of its case without spending time unnecessarily in implementing formal, procedurally complex methods of obtaining the same scientific comment.

However, I do strongly support one addition to the informal data gathering and weighing techniques that are used by agencies in assessing the existence and scope of a problem. I believe there is a need to make funds available to the public, including interested scientists, so that independent technical knowledge is available in agency deliberations. Congress is considering a variety of legislation in this area such as the Agency for Consumer Advocacy and legislation sponsored by Senator Kennedy to compensate public participants, including expert witnesses, in agency proceedings. I have been a regulator for nearly three years and each passing day of my term makes me realize more strongly the need for adequately funded public participation in agency proceedings.

Where an agency is faced with a high degree of scientific uncertainty there may be a need for some more formal method of scientific peer review in order to assure the correctness of agency decisions. However, in this connection I reemphasize the distinction that I drew earlier between the method of assessing the degree of certainty and the separate judgment that sufficient certainty is present to commence regulation. The latter question involves examination of the agency's mandate in order to determine the level of certainty intended by Congress. The degree of certainty required prior to action may vary from agency to agency or may vary within an agency, depending upon the particular statute under which regulation is proposed. Moreover the decision that regulation is needed in the face of some uncertainty is not a scientific judgment but a social one that requires regulators to weigh the degree of potential future illness and misery against the potential harm of economic disruption and unemployment and the restrictions on consumer choice that arise from changing or removing products from the market.

Peer review mechanisms should, therefore, be limited to assessment of the available data and the weight it should be given in view of facts as yet unknown and theories as yet untested. Ideally, it would also include a full description of how to reduce uncertainty by specific amounts, and the costs in time and resources for that reduction.

The National Academy of Sciences report on the fluorocarbon controversy is an ideal example of what in my view are both the good and bad aspects of peer review. Thus, on the one hand the report does provide a lucid assessment of the uncertainties remaining with regard to the effect of the release of CFMs on the environment and on man. This assessment will be extremely helpful to agencies charged with protecting consumers from the environmental and health risks of CFM release.

But the report goes further and enters into the domain I believe belongs more properly to the regulatory agencies. The NAS panel calculated the expected increment of ozone reduction that would result from a two-year delay and found that increment to be small. It therefore recommended a two-year delay in the commencement of regulatory proceedings in order to obtain results from additional studies. NAS believes these studies would further reduce uncertainties regarding both ozone reduction and climatic changes. According to NAS, reduction of uncertainty would enable the regulatory agencies to better determine the extent to which fluorocarbon usage should be curtailed. For example, agencies will be in a better position to address the need to restrict the use of fluorocarbons in automobile and building air conditioning systems as well as in aerosol containers.

While recognizing the general mandate of the National Academy of Sciences, I find it difficult to accept the issuance of a policy judgment that we can afford to delay the commencement of regulatory action for two years. Moreover, this judgment carries with it added credibility simply because NAS made it and consequently it sets a strong public mood.

Not only is this public pronouncement confining to me as a regulator, but I also believe NAS has ignored two critical considerations in arriving at this conclusion. The first of these is the extent to which the law permits, and Congress intended, regulatory action that is precautionary in nature. This is action taken, not on the basis that injuries and illnesses will occur with certainty but rather on the basis that there is a risk that illness or injury may occur. In the case of the Consumer Product Safety Commission, the trigger for regulatory action is a finding by the Commission that a risk exists and that the risk is unreasonable in nature. In the House Report accompanying the Consumer Product Safety Act, Congress directed the Commission to determine whether a risk associated with a product is unreasonable by balancing "the probability that risk will result in harm and the gravity of such harm against the effect on the product's utility, cost and availability to the consumer."

This balancing test can be translated to the hazards of ozone reduction by stating that the Act requires the Commission to assess the probability that the ozone reduction theory is accurate and that continued release of CFMs into the atmosphere will eventually result

in an increased incidence of skin cancer. This is balanced against the utility of and the necessity for the aerosol container that makes use of fluorocarbon propellants.

I balanced these considerations in July 1975 and again in February 1976, when the Commission denied petitions requesting it to commence proceedings to ban use of fluorocarbon propellants in consumer products. I disagreed with those Commission decisions not to take action and voiced my dissent in opinions in which I stated my belief that the ozone layer was being adversely affected by the release of CFMs. I stated then that I did not believe the commencement of regulatory action should be delayed merely to refine the precision of our assessment of the problem.

It seemed to me then that the proposed NAS study was likely to produce only evidence that would further substantiate the conclusions of the IMOS task force. And, indeed, in my judgment this has been the case. Based on additional evidence, NAS substantially corroborates the IMOS figures for predicted ozone reduction. Beyond this it finds greater substantiation for the relationship between malignant melanoma and ultraviolet exposure, a finding that substantially increases the severity of the risk of cancer. Moreover, the NAS also concluded that release of CFMs creates a serious risk of climatic changes. The presence of additional supporting evidence and findings that indicate an increased magnitude of risk lead me to seriously question a recommendation for an additional two years research as a condition precedent to the commencement of regulatory action. I particularly question this delay as it seems highly unlikely that the additional studies will result in a recommendation that the use of CFMs as aerosol propellants not be banned.

Earlier I discussed the time needed to complete regulatory action from the date of its commencement, and suggested two to three years as a likely time frame in a complicated question such as this. Apparently this inherent time lag between proposal of a regulation and final disposition of court challenges was not considered in the report. The incremental certainty that might be gained from additional research will be useful, but in view of the apparent necessity for a ban of at least those CFMs used as aerosol propellants, and in view of the two to three years that administrative and legal proceedings are likely to consume, I believe regulatory proceedings should begin now.

As I mentioned earlier, beyond the consideration accorded the ozone reduction problem by IMOS and the NAS, some people have suggested that this issue might be appropriate for the convening of a "science court." As I understand the general concept, it calls for a panel of scientific experts who would hear and judge cases presented by opposing scientific advocates. The cases would concern current problems facing regulatory agencies, and other governmental bodies, where there was substantial disagreement on questions of science and technology. Ideally the court, which would use an adversary system, would concern itself only with technical matters and not at all with social or policy judgments.

This concept appears to answer one of the major concerns that I just expressed concerning the tendency of existing groups such as the NAS to commingle policy decisions with judgments as to the state of the scientific record. However, the creation of an entire court structure simply to attempt to remove value judgments from scientific conclusions strikes me as being somewhat akin to the left-handed use of a sledge-hammer to drive a carpet tack: it seems that the tool is much more potent than is needed and frankly it could accidentally do harm.

While I am in complete agreement with the desired goals, I have a major reservation about the need for, and utility of, a science court as a technique to aid in government decision making. The conclusions reached would have a very strong binding effect on the agencies involved simply because of the public aura that would be associated with its impressive character. More importantly, the length of time needed for this body to deliberate will hamper responsive government regulation of the public health and safety.

My reservations concerning delay introduced by the science court stem from the experiences of the Food and Drug Administration and the CPSC with the use of adjudicatory procedures to reach decisions in technical matters. These procedures are required by law in certain instances and their use has resulted in 10- and 12-year delays in the implementation of regulation while hearings are conducted. Obviously such long delays are unnecessary, but it is foolish to ignore the fact that delay is inherent in most adjudicatory procedures.

Moreover, highly complex scientific matters about which there is disagreement appear to me likely to have two natural characteristics. The first is that disagreement exists precisely because the answers are uncertain. In resolving the uncertainty, questions of policy are difficult to avoid. The second is that there will be more than two "sides" to the disagreement, thus requiring an adversary process of exponentially increasing complexity if for no other reason than to provide due process to all parties concerned.

As I stated earlier, I believe there must be experimentation as we need to improve the process of arriving at decisions in complex and uncertain matters. I believe that we should try the idea of adequately funding public participants in various informal agency processes before considering the notion of a formalized procedure such as the science court.

In leaving this subject, I believe it important to note that statements in the press that the Consumer Product Safety Commission has agreed to be a guinea pig for the science court experiment are not accurate. The matter of the science court has never been discussed or voted on by the Commission. I do not know what the Commission's decision would be if and when the matter arises.

Those of you who are still awake may be wondering at this point what magic I possess to make the best public decisions. In partial response I would like to stress that I am only one of five Commissioners charged with jointly considering and arriving at decisions that we hope

are in the best interest of the public. The Commissioners are persons
of diverse backgrounds and include at the moment a chemist, a lawyer,
an MBA, and myself, an engineer (there is one vacant seat). The
decisions that we make are constrained by the standards set forth in
the laws we administer and the evidence in the record before us. We are
accountable to the courts and to Congress for our exercise of judgment.
We can be reversed by the courts if we act arbitrarily and Congress can
cut off our funding or amend our laws if we fail to carry out Congres-
sional intent. Panels of scientists, on the other hand, whether con-
vened by the NAS or by a court of inquiry, are accountable only to
their peers. In my opinion, this is an extremely important reason
why such panels should not make decisions that go beyond the bounds
of their scientific expertise.

However, this does not mean that I think scientists should not be
permitted to express views on policy. On the contrary: I urge you all
to make recommendations to the Commission and other government agencies.
Your technical recommendations are entitled to great weight. But your
recommendations as to policy should not carry more weight than those of
any other informed and responsible citizen.

Weighing risk and reaching a decision on whether that risk is
acceptable to society is not easy when the information on which deci-
sions must be made is incomplete. Judge J. Skelly Wright of the United
States Court of Appeals for the District of Columbia in a decision
involving the Environmental Protection Agency described the dilemma
in this way.

> Man's ability to alter his environment has developed
> far more rapidly than his ability to foresee with
> certainty the effects of his alterations. It is
> only recently that we have begun to appreciate the
> danger posed by unregulated modification of the
> world around us, and have created watchdog agencies
> whose task it is to warn us, and protect us, when
> technological "advances" present dangers unappreciated
> - or unrevealed - by their supporters. Such agencies,
> unequipped with crystal balls and unable to read the
> future, are nonetheless charged with evaluating
> the effects of unprecedented environmental
> modifications, often made on a massive scale.
> Necessarily, they must deal with predictions and
> uncertainty, with developing evidence, with
> conflicting evidence, and, sometimes, with little
> or no evidence at all.

Vinyl chloride, asbestos, PCBs, CFMs, the litany of dangerous
substances grows daily. Agencies must act on the basis of as much
certainty as possible. But we cannot delay forever if we are to
adequately protect the public's health.

# STRATOSPHERIC POLLUTION - INTERNATIONAL POLICY ISSUES

### Erik Lykke
### Director General
### Ministry of Environment, Norway

The focus of discussion, nationally and internationally, has so far been almost exclusively on the scientific aspects of stratospheric pollution. In its review of the present status of knowledge this conference has clearly shown that research related to the chemistry of the stratosphere as well as effects of modification to the ozone layer should be further expanded. It seems, however, as far as I can judge, unrealistic to expect that the general scientific picture with regard to stratospheric pollution will be substantially modified in the immediate future.

Unless new hard evidence is found to reduce drastically the risk factor attached to chlorofluoromethanes (CFM's), we must expect that regulatory action against this source of stratospheric pollution will be introduced over the next few years.

In the United Kingdom the Department of Environment argues, in a paper published this year, that many of the aerosol products, particularly those used for cosmetics and toiletries, are items of convenience and not of necessity, and that there are often non-aerosol alternatives available which may be cheaper. The Department of Environment goes on to recommend that alternatives should be sought for CFM's 11 and 12 in aerosols and plastic foams, and that leakage of these substances in the manufacture and use of industrial equipment should be minimized.

In the United States, the Federal Task Force on Inadvertent Modification of the Stratosphere found, in its report in June 1975 on the basis of existing evidence, that uses of CFM's 11 and 12 should be restricted to the replacement of fluid in existing equipment and to closed systems or other uses not involving releases to the atmosphere.

The proposals in the UK and the USA seem basically to be consistent with the position taken in the US National Academy of Sciences' reports released this week.

The other specific regulatory measure for protecting the stratosphere which so far has been recommended is directed against aircraft flying at high level. In a report on "The Effects of Stratospheric Pollution by Aircraft" published by the US Department of Transportation in December 1974, it was recommended that combined operational and technical requirements for reducing pollution from stratospheric flights should be developed.

In the statement on modifications to the ozone layer issued in January this year the World Meteorological Organization predicts that a large fleet of supersonic aircraft, flying at greater altitudes than the present Tupolevs and Concordes, will have a noticeable effect on the ozone layer. The WMO advises that permissible total emission levels for

supersonic aircraft may have to be defined by international agreement.
The WMO also recommends that the trend of subsonic aircraft towards
flying at higher levels should be closely watched.

In listing the other risks to the ozone layer the WMO finds that
there is no likelihood of significant changes in the ozone layer in the
near future as a result of increased use of agricultural fertilizers,
but takes the same position as that in the USA and UK with respect to
CFM's.

The supersonic aircraft issue is, of course, especially sensitive
because of the heavy economic investments involved. A neglect of the
regulatory aspects of the problem may, however, in my view, prove to be
a mistake which may be difficult or impossible to rectify at a later date

Since a second generation of supersonic aircraft appears to be
under consideration, it would seem appropriate at this time to have the
basic environmental requirements established and agreed to, at least by
the countries most directly concerned. As stressed by the 1974 report
from the US Department of Transportation, the process of establishing
and meeting such standards should start as early as possible because of
the long lead times involved. The recommendations in that report con-
tain elements which perhaps might serve as a basis for internationally
agreed standards covering the main high level aircraft operations.

Several international organizations are at present concerning
themselves with stratospheric pollution. Experts working under the
auspices of the OECD are in the near future expected to provide up-
to-date reviews on CFM's uses, the development of substitutes, and the
economic impact of controlling the use of CFM's as propellants. The
group of advisers on environmental problems under the United Nations
Economic Commission for Europe has also expressed its concern about
the situation. The World Meteorological Organization has proposed
that there should be a coordinated international program under the leader-
ship of the WMO to monitor all aspects of the stratospheric environment
related to ozone. These and other international organizations should
be encouraged to accelerate their work and to contribute their findings
to the preparations for coordinated international actions.

The Governing Council for the United Nations Environment Program
has instructed the Executive Director of the program to convene a
meeting to review ongoing activities related to the ozone layer. This
meeting is scheduled to take place in Washington in February next year
and should, as a follow-up to the present conference, serve to clarify
the situation further and also to clarify and coordinate the role of
the various organizations.

It is, however, in my view not realistic to expect that the
international organizations could mobilize the range of expertise and
resources required for the preparation and negotiation of internationally
coordinated action for the protection of the stratosphere. The steering
of the preparatory work in this aspect should rather be undertaken by
one government working in close consultation with other governments
and the international organizations concerned.

A number of international agreements in the field of environmental protection have already been concluded. These agreements could serve as models for discussions leading to international coordination of regulatory measures for protecting the stratosphere. The main provisions in several of these agreements are not substantially different from the recommendations for protecting the stratosphere which have hitherto been developed in the US, UK and by the WMO.

For example, regulations relating to the pollution of the stratosphere by aircraft may be compared with the regulations set out in the International Convention for the Prevention of Pollution from Ships, which was signed in 1973. In fact, this convention and its annexes contain a number of technical and operational specifications for ships which go considerably beyond what may be required in the way of regulations for protecting the ozone layer against harmful impacts from high level aircraft operations.

An appropriate special convention for the prevention of strato-spheric pollution from aircraft might be negotiated under the auspices of the International Civil Aviation Organization. Alternatively, the necessary provisions might be developed in consultation with that organ-ization, and inserted in an annex to a general convention for the protection of the stratosphere.

With respect to the CFM's problem, an obvious precedent for inter-national action is a decision restricting the uses of polychlorinated biphenyls taken in 1973 by the member governments of the Organization for Economic Cooperation and Development. Experience has, however, shown that it would be desirable if restrictions regarding CFM's were more specific and of a more binding nature than the PCB decision adopted by the OECD. All parties to such an agreement should have formal assur-ance that the other parties are adopting the same measures as themselves.

The specific provisions concerning CFM's might again well be contained in an annex to a general convention for the protection of the stratosphere. By putting technical specifications in annexes to the convention, it is possible to apply a simpler and less time-consuming procedure for necessary changes than the process required for changing the convention itself. This is of particular importance when we are dealing with a subject area where further research results and tech-nological developments are almost certain to necessitate additional or adjusted regulations.

An international convention for the protection of the stratosphere would thus provide a framework for dealing with identified as well as potential threats to the ozone layer. Such a convention should contain provisions for overall supervision of the implementation of the convention and for consultations in important matters of dispute. The convention should also identify sources for scientific and technical advice and secure a measure of coordination of research and information. Some or perhaps all of these tasks may be entrusted to existing international bodies in order to avoid the creation of new international institutions.

Among the precedents for conventions containing such general
provisions and technical annexes are the marine pollution conventions
negotiated in 1971 and 1972 dealing with dumping of harmful industrial
wastes into the ocean. Many governments have become parties to these
conventions.

As things stand at present, national regulations concerning use
of CFM's are likely to be introduced before an international convention
can enter into force. If the US should take a lead in introducing CFM's
restrictions, I am pretty sure that many other governments, including
my own, would wish to support that action and introduce similar measures.

I am not arguing against this course of events, but I am convinced
that strong efforts should be made so that such a first step could be
superseded by or merged into a formal and more comprehensive interna-
tional agreement.

The situation with respect to the stratosphere is not basically
different from that of the oceans. The stratosphere is by any defini-
tion a "shared resource" and its importance is such that there can be
no valid arguments against giving it maximum protection against adverse
impacts from man's activities. A process aiming at the establishment
of a general convention for the protection of the stratosphere should
therefore be set in motion as soon as possible.

My own government, I am sure, will welcome such a development,
and seek to contribute as constructively as it can in the work ahead.

## FLUOROCARBON INDUSTRIES' RESEARCH PROGRAM

Richard Soulen
Pennwalt Corporation
King of Prussia, Pennsylvania

[Dr. Soulen outlined the fluorocarbon industries' research program on the effects of fluorocarbons on the atmosphere. A summary of this program, including the type of research activity and the laboratories involved, is available from the Manufacturing Chemists Association, 1825 Connecticut Ave., N. W., Washington, D.C. 20009, U.S.A.]

# UPPER ATMOSPHERIC RESEARCH IN THE U.S. FEDERAL GOVERNMENT

L.R. Greenwood
National Aeronautics and Space Administration
Washington, D.C.

Dr. Greenwood summarized the work of the federal organizations involved in atmospheric research, and the work of the Interagency Committee on the Atmospheric Sciences (ICAS), which was organized to coordinate these efforts (see Figure 1). The functions of ICAS are (1) to survey and evaluate the U.S. national research effort, (2) to examine the role and activities of federal agencies, and (3) to make recommendations for appropriate allocation of responsibilities.

The U.S. National Aeronautics and Space Administration has a significant role in the nation's atmospheric research effort, and a description of the NASA program on upper atmospheric research is available from NASA's Office of Space Science in Washington, D.C., U.S.A., which gives the program goals and objectives, program structure, program implementation, resources, participants, and relationships with programs in other federal agencies and in industry.
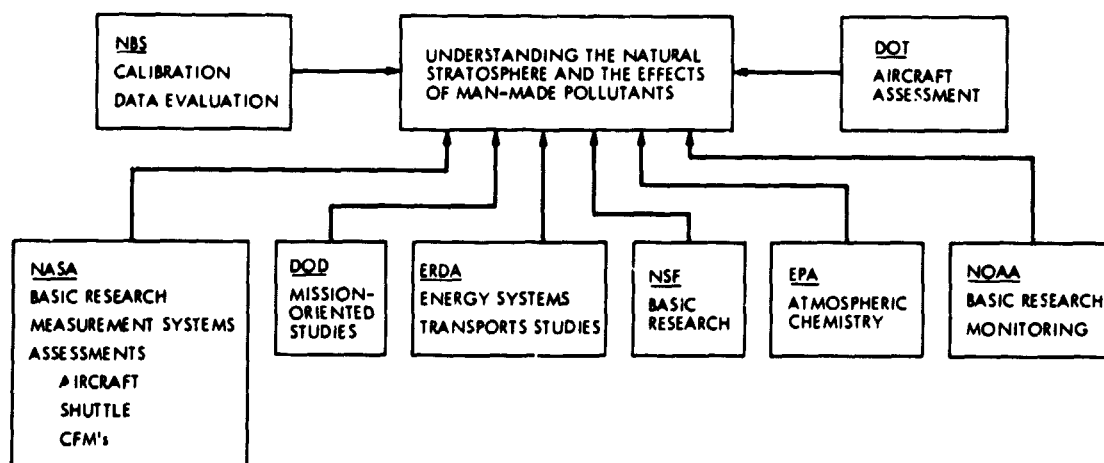


Figure 1.  U. S. federal organizations involved in atmospheric research and their responsibilities.

SECTION II

KEYNOTE SPEECH

## Opening Remarks by Carrol Bastian:

May I have your attention, please?  This morning we have the great
privelege of having with us Dr. Russell Peterson, who is chairman of the
President's council on environmental quality.  Dr. Peterson is a chemist
by background, and was in fact a chemist for Dupont for 26 years.  He
has followed a very active and outstanding public career in many posi-
tions.  He is the former governor of Delaware.  Recently, Dr. Peterson
announced his resignation from the Council on Environmental Quality,
which is effective October 1.  He is leaving to be President of New
Directions, which is a new citizens' group focusing on global problems
located in Washington, D. C.

Dr. Peterson will be giving the keynote speech for our seminar
which will tie together some of the things you heard yesterday with the
issues which will be addressed in the panel that follows.  Dr. Peterson
will be speaking on science and public policy.

ACTION IN THE FACE OF DOUBT:
ON SCIENCE AND PUBLIC POLICY

Russell W. Peterson
Council on Environmental Quality

Edmond Hoyle, the gentleman who formulated rules for card games, once advised, "When in doubt, win the trick." A century and a half later, Mark Twain counseled, "When in doubt, tell the truth." Some football quarterbacks, I understand, subscribe to the dictum, "When in doubt, punt." And some officials in industry as well as government obviously subscribe to the dictum, "When in doubt, mumble."

I offer these gleanings from some humble research because, it seems to me, the basic concern of this conference is doubt -- scientific uncertainty and the proper course of action when one is confronted by it.

In June 1974, Rowland and Molina first suggested that fluorocarbons may lead to stratospheric ozone reduction. In January 1975, Dr. Stever, the President's Science Advisor, and I formed an ad hoc task force of 15 federal organizations to study the issue and make findings and recommendations. This task force on Inadvertent Modification of the Stratosphere, better known as IMOS, issued its report in June 1975.

The IMOS study concluded the following:

(1)     Our knowleage of the chemistry of fluorocarbons and of ozone suggested a high likelihood of a reaction between them that would deplete the oxone shield.

(2)     A significant depletion of the ozone shield would increase the amount of harmful UV radiation reaching the earth.

(3)     Such increased radiation, in turn, would probably increase the incidence of skin cancer in humans, might have harmful effects on agriculture, and might affect the earth's climate.

I have carefully phrased all these propositions in the subjunctive mood. Maybe they are true. If they are true, the continued use of fluorocarbons represents an environmental hazard. The Task Force concluded that the theoretical possibility of ozone reduction by fluorocarbons was sufficiently well established to justify further research and evaluation -- fast.

Now some further research has been conducted and further evaluation has been completed by the National Academy of Sciences. The detailed scientific assessment by the Academy is remarkably consistent with that contained in the IMOS report. We still do not know that the ozone shield is being depleted by fluorocarbons. All we know is that little new evidence has been found to ease our fears about the possibility of ozone reduction and several studies to reinforce it.

So what do we do now?  Do we ban fluorocarbons on the assumption
that ozone reduction __is__ occurring, and that the health effects of such
reduction are so serious as to require immediate action?  Do we take
some less drastic step, such as limiting the production and use of
fluorocarbons, while we pursue definitive research?  Do we defer judg-
ment awaiting further study?  Or do we do nothing, recognizing that
a substantial industry is at stake here, and that we have no conclusive
scientific __proof__ for banning fluorocarbons?  What kind of action, if
any, is appropriate in the face of scientific uncertainty?

The answer to this question is of immediate interest to all of
you.  But it has an application far beyond fluorocarbons, for the prob-
lem of determining prudent public policy in the face of scientific
doubt recurs again and again as some chemicals developed for specific
purposes prove to have -- or threaten to have -- unanticipated side
effects.  Something like 2 million man-made chemicals now exist,
thousands are discovered annually, and several hundred are actually
introduced into commercial production each year.  Considering this pro-
liferation of chemicals in our society, it is clear that we cannot deal
with each on a case-by-case basis.  We must formulate some general
policies and philosophies governing them.

Until recent years, most of the health hazards we have dealt with
were characterized by direct, immediate effects.  With this type of
hazard -- food-poisoning, for example, or unshielded equipment in a
factory -- we could measure or estimate the inherent risks directly, and
act to eliminate or alleviate them.

Particularly in the last three decades, however, with the great
increase in the numbers of man-made chemicals, we have encountered a
different type of environmental risk -- one whose effects, frequently,
are not immediately obvious.  One example of such a risk is cancer
induced by chemicals; another is the fluorocarbon-ozone question.

When we are dealing with risks whose effects may occur years and
even decades after exposure to the cause, we must weigh decisions about
control on a quite different basis than with risks whose effects can be
directly observed or simulated.

First -- and this relates to the atmosphere in which a decision
is made -- the level of public concern about the risk is not usually an
accurate indication of the degree of acceptable risk.  This is especial-
ly true when the effects are not expected to occur for some time.

Second, hazards with latent effects raise fundamental questions of
justice, in that the group benefitting from the production or use of a
chemical may not be the same group whose health is placed at risk.  In
the case of fluorocarbons, we are dealing with a chemical whose first
definite effects may not be noted for another 10 to 40 years; thus the
group potentially affected by them is only in part the people who are
using them today.

Third, in the case of health hazards, characterized by a long
latency period, it is possible that a large impact may already have

resulted by the time the effects are measurable.  Measuring the effect of fluorocarbons is doubly complicated by large natural fluctuations in ozone concentrations; thus, a large, continuing effect on the **average** ozone concentration would have to take place before we could be sure that the concentration had been diminished or increased.

Finally, we must take into account the possibility that, if fluorocarbons do erode the ozone shield, the effects of past releases will continue for many years, even if we eliminate additional release immediately.

It seems to me that in judging an acceptable level of risk, the decision-maker must -- as soon as he has reasonable assurance that the predicted effects will occur -- consider the potential future effects as if they were taking place in the present.  If the hazard poses potentially serious effects, the decision-maker may not be able to wait for a measurement of the effects.  Though we must exercise great caution in reacting to relatively unsupported hypotheses, we must also be willing to act when presented with well-founded scientific theory backed up by statistically reasonable experimental evidence.

In recent years, both the Congress and the federal courts have grappled with the question of burden of proof in the chemical regulatory process.  Where does that burden lie?  Before a chemical is approved or rejected for mass production or -- as in the fluorocarbon case -- for continued use, should the government be required to prove that the compound represents an unacceptable risk to public health?  Or should the manufacturer or processor be required to demonstrate that it does not?

This question arises in all sorts of contexts.  A few months ago, while investigating a broad spectrum of environmental situations in Alaska -- ranging from the condition of wildlife habitat to the progress of the Trans-Alaska pipeline -- I met with a group of fishermen.  Their catches of salmon, they complained, had been declining in recent years. I asked them whether the dropping harvest might have been cau ˉd by overfishing on their part -- taking more salmon than could be    laced by normal reproduction.  They admitted that perhaps they had ... been as prudent as they should have been.  Even so, they argued, the principal reason for the decline of the salmon catch was not excessive harvesting, but improper timbercutting practices along the streams where the salmon spawn.

If the trees bordering a stream are cut down, the fishermen pointed out, a number of results ensue:  There is no longer any shade from the sun, so that stream-temperature rises; barriers against soil-erosion are lost, so that silt can cover the pebbles in which salmon lay their eggs; the alteration in vegetation alongside the stream changes the types of insects that normally feed there, and these insects, in turn, also feed the fish; finally, cutting down the trees bordering a stream even changes the type of algae to be found in the water.  Add all these changes together, and you wind up with a major change in a habitat depended upon by salmon.

Following my meeting with the fishermen, I talked to the loggers. Their argument, in essence, was "Nobody can prove that logging affects the catch of salmon."

Probably they were right. Unless somebody mounted a million-dollar research project, nobody could prove that cutting down the trees bordering a stream was directly responsible for the decline in the salmon catch.

But, I argued to the loggers, you're the ones who ought to be forced to prove that your activities are not hurting the fishermen. After all, salmon fishing has been going on in Alaska for several hundreds of years and, in that period, it has provided more jobs and economic benefit than lumbering. You are the people introducing a change -- and, if that change is challenged, the burden properly rests on you to prove that your activities are not responsible for local loss.

In the same way, I believe that the producers of a suspect chemical should be required to demonstrate that their product is not responsible for causing a specific, suspect change. Such proof should be regarded as one of the costs of bringing out a new product, just as R&D, advertising, packaging, and distributing are. The party that stands to benefit from the introduction of a new activity or substance should bear the cost of showing that claims of damage responsibly asserted against that activity or substance are outweighed by its benefits.

I believe firmly that we cannot afford to give chemicals the same constitutional rights that we enjoy under the law. Chemicals are not innocent until proven guilty. This, of course, should not be construed to mean a chemical is guilty or hazardous until proven safe. In fact absolute safety can seldom even be conclusively demonstrated.

By placing the burden of proof upon the manufacturer, however, it becomes his job to demonstrate that in the face of possible risk -- which may not be scientifically proven or tested -- the likely benefits of marketing of his product outweigh the anticipated risk.

Thus, the actual burden would vary on a case-by-case basis, depending upon the extent to which the chemical has been developed and used. A decision whether or not to regulate an existing product, such as fluorocarbons, also may depend upon the magnitude and type of risk inherent in waiting for a better definition of the tradeoffs. Thus, the burden of proof issue properly boils down to a risk-vs.-benefit tradeoff judgment where the manufacturer is responsible for demonstrating that the potential benefits outweigh the risks, rather than presuming a chemical is safe until outweighing risks are scientifically proven.

This leads to another point I wish to discuss -- namely the distinctio between scientific and social value judgments. Inherent in virtually every environmental or public health policy decision are two components -- scientific determination and social value judgments and we as scientists should be careful to make the distinction. There are no

individuals better qualified to make scientific judgments than scientists. But scientists are no more qualified than anyone else in making social value judgments.

Estimates of genetic parameters in levels of ozone reduction or numbers of skin cancers are scientific judgments. Similarly, monetary value of fluorocarbon production and use and the possibility for developing substitutes are economic and engineering or marketing judgments, respectively. This is not to say that these won't be debated.

The decision to regulate is the social value judgment. It answers the question, "Is the threat of risk worth the estimated economic dislocation?" This is not a scientific question but a value judgment.

Both IMOS and the National Academy of Sciences Committee came to essentially the same scientific conclusions, although much information was developed between these two reports. Each group, however, came to slightly different social value judgments.

IMOS recommended initiation of rulemaking, if its preliminary scientific assessments held up, while the Academy committee recommended up to two years' further delay in deciding upon restrictions. IMOS, therefore, concluded that the risk of ozone reduction and its effects seem to outweigh the anticipated cost of restriction. I infer from the Academy report that they made a slightly different value judgment -- namely, that the risk of not waiting for more substantial evidence likely outweighs the estimated costs of regulation in the interim. Where one comes down in such judgments depends on the individual and social value judgments. Each of us may come to a slightly different position.

There is a tendency to want to stay with the status quo when there is an uncertainty on the risk side. Some argue that we should have dead human bodies rather than rats before acting upon possible cancer-causing substances. I would argue that this is not prudent or socially responsible public policy. One should realize that there are also usually as great if not greater uncertainties as to the economic effects of actions in terms of dislocations or foregone benefits.

There are, therefore, uncertainties on both sides of the equation. And seldom will any finite amount of study on either side result in totally eliminating these uncertainties. What is needed, therefore, is as good information as can be obtained with a reasonable amount of effort in a reasonable amount of time for judgment by the reasonable decision maker.

Personally, I am very wary of risk, especially when dealing with potentially worldwide hazards that may last for many generations into the future. Thus, I concur with the value judgments made by both the Academy committee and the federal agencies on the IMOS committee when they concluded that some form of regulation seems inevitable.

I recognize the fact that with fluorocarbons we are not dealing with an imminent hazard, so there is time to develop a well-thought-out

course of action. But, we should get on with the process immediately, so that proposals can be carefully considered.

I recommend that federal regulatory agencies now commence development of proposed rules to restrict discharges of fluorocarbons 11 and 12 to the atmosphere. By starting now, the environmental and economic tradeoffs can be better ascertained and perhaps new and more desirable alternative proposals can be found. Normal rulemaking procedures are very lengthy and will allow for anticipated new scientific refinements or discoveries to be taken into account before a final decision is made.

In addition, I recommend that industry, which was alerted over 15 months ago to the likelihood of restrictions, now start voluntary phasing out of the use of fluorocarbons 11 and 12 in favor of environmentally acceptable substitutes. Such action, along with orderly rulemaking procedures, should serve to minimize any dislocation resulting from regulation. It's clear that the benefits to the consumer in using fluorocarbons for underarm spray deodorants and hair sprays do not outweigh the threat to world environment from the continued use of such propellants. Hence, I recommend that consumers stop using them and manufacturers voluntarily stop selling them.

Let me stress that we should not focus our concern merely upon aerosol uses of fluorocarbons. Only about half of current production goes to this use. The other half also gets to the atmosphere eventually and will contribute sooner or later to the problem. Thus, substitution must be considered.

Obviously this country is going to think seriously before taking any action to disturb home refrigeration. But if suitable substitute fluids or refrigeration cycles can be developed, then replacement of fluorocarbons in these systems would seem desirable.

From the pure scientific perspective, there remain valid doubts about the effect of fluorocarbons on the ozone shield. From the public-policy standpoint, however, there remains no valid reason to postpone the start of regulatory procedures.

The advice on what to do when in doubt -- to win the trick, tell the truth, punt or mumble -- is useless here. But it is unanimous on one point: when in doubt, act. And here we must act to choose the less damaging of two alternatives. In comparison with the potential health effects of uncontrolled fluorocarbon use, the potential economic losses associated with wise regulation are small. We must begin now to pay the modest costs of safeguarding the priceless health of our people and the place we live.

## Question/Answer Period:

### Question:

During your speech, as a junior apprentice in the world of politics, I felt a call of sympathy striking every time you got into the political arena, and I'm glad you introduced the new offices of the problem of indecision into this meeting because everybody seems to be seated betwixt indecisions. They seem to be unable to live with our growing ignorance, and by growing ignorance I mean the kind of awareness of the magnitude of the problem that is beginning to be appreciated by people in this field. A year or two ago it was all terribly simple, and it looked as though the answers would be forthcoming.

What I want to question is the need for regulation. And I speak as somebody coming from another country where we have different habits of government, so I modestly put this before you; not as anything more than just something to think about, because I don't expect you to have very much to say, at first. We do have a practice in Britain of always trying to settle these things by agreement between government and industry and other sectors without making regulations. To give you an example of this: When we had the DDT problem, in your country there was a 100% ban. In Britain we had a 95% cutback by agreement, which led those who absolutely depended on the use of DDT, such as the sheep farmers in Scotland, to get rid of the maggots from the backs of their sheep in summer. They got the chance to do it without risking anybody else. And this was done by agreement. I think our practice of regulating industrial pollution by consultation and agreement on a very much ad hoc basis works very well. If I may say so, it's worked sometimes well, sometimes badly, for about 100 years. So we're not talking from lack of experience at all. What I'm questioning, therefore, is the assumption that if there is a danger you must have regulation. I don't think this is a correct assumption because there are other ways of doing it. And I would suggest perhaps that there might be closer consultation between the various sides, on a less grand basis than this conference, in which people learn to see the other viewpoint. As you and I know, one has to do this in politics.

### Answer:

I think that your country and our country and the whole developed world has done a horrible job over the last 50 and 100 years in coping with the problems that we're talking about today. In fact, we had a major uprising among our people (and in your country also) a few years back about environmental matters because economic development had run roughshod over the environment with little serious concern about it and little knowledge of it. Not only the practitioners of economic development but the whole country had inadequate appreciation of what was going on. All of a sudden, we realized we were heading for tragedy if we didn't do something about it. We were really following Adam Smith's preachings, which are: free up the individual from the strengths of government and he will, even in his most selfish interest, proceed in a

way that will be in the public interest because an invisible hand will
guide him. And we've learned very well that there is also an invisible
foot that will kick us, and it's absolutely essential, I think, for
someone to worry about the public interest, not just the private and
special interests. Certainly it's wise to solve and to debate and to
listen and hear, and many times we haven't done that adequately here.
I'm sure there are examples in your country like that, also. There is
a tremendous and growing effort to increase communications. But the
basic problem still exists, that the people who want to go ahead with
an economic development are inadequately concerned about the public
interest, and we need some people standing up for the public interest
who are going to get this thing in the right balance. Furthermore, we
must appreciate the need for holistic thinking, for long-range think-
ing, for global thinking, and for interaction of variables. We are now
finally beginning to do that in a very modest way, and we need to extend
it tremendously. Chemists and physicists and electrical engineers and
lawyers, etc., I think, need to become more generous, so that they can
think and act holistically. It is absolutely essential that we have
some regulations and not just nice friendly bull sessions. The latter
will not get us to face up to the hazards coming at us.


Question:

You have spoken about the risks of Freons as though they were
something very serious. The information accumulated by the National
Academy of Science indicates that a 1% increase in the incidence of
skin cancer in the area of the United States is equivalent to a 6 mile
displacement nearer to the equator. That means that the 7% reduction
in ozone estimated by the National Academy of Science is equivalent,
insofar as UV exposure or rather incidence of skin cancer itself, to an
84-mile displacement to the south. Now if that is such a horrible
risk, we ought to rearrange real estate prices.


Answer:

We have modified our real estate prices depending upon where we
live, but to me that's kind of a silly argument. For example, at this
juncture we don't have any significant information, as you know, about
the impact of the increased radiation on plant life. We have tremendous
concerns...


Question:

Well, you know that if you bring the sun in 84 miles, you know
what that does to plant life.


Answer:

OK, let's use that; it helps me make my point. We have this
great concern globally about the production of food, and we know the

tremendous changes in food production as we go from one climatic area
to another. An 84-mile movement of some of these boundaries could
markedly affect food production. There are tremendous concerns about
changes of only a degree or so in temperature, and what that means
to food production in areas like Russia and Canada, where they're close
to the border of having a productive environment. I think that for
someone to say that a 7% reduction, with a range of 2 - 20% to cover
the uncertainty, is something that we should "pooh-pooh," and to say
that the effect of the possible impact of fluorocarbon release on climate
by the year 2000 will be equal to an increase of $CO_2$ release by 50%,
and to say that's not something we should be serious about, just bothers
me very much. I think it's something of tremendous concern, and that we
ought to be worrying about and trying to avoid it. What you ought to
put on the scale is the question of what you're gaining by going ahead
with it. Obviously, when we're talking about refrigeration, you've got
an infinitely better argument than when you're talking about spraying
Arid under your arms with a propellant and paying twice as much for it
as you can for rolling it on. In fact you can stimulate other businesses
to develop better ways of doing it.

Question:

The Academy report said that for ozone depletion in the 2 - 20%
range, reasonable people would agree that 20% would be a disastrous
depletion and reasonable people would agree that 2% is not serious.
Since I know you're a reasonable man, would you agree with those esti-
mates and with those statements about how we reasonable people should
agree?

Answer:

Obviously, there's some point where any one of us in this room
would decide that we're not going to worry about it, and that we're
willing to take that risk. And at some other point I think we'd all
agree that we're not going to take that risk. We put many talented
people, a country in effect, to work in this short interval to try to
get all the facts they could. They have now got those facts together,
and are finished with their organizations, and have brought their
social value judgments together. They have said, and I can't think of
the exact words now, that almost certainly, we're going to require
regulation, in a selective way, depending on the end use and so on.
So they considered the 7% figure, between an uncertainty of 2 - 20%,
as something that merited a very strong position, and I buy that judg-
ment. Which one do you buy: Do you buy that?

Question:

What I'm asking basically is: I do think most people agree that
a 20% depletion would be an intolerable depletion level, but I'm not
convinced that all reasonable people would agree that a 2% depletion
level would be inconsequential.

Answer:

I'm not either. One other thing when you talk about thinking holistically, one thing we must keep in mind, is that the fluorocarbon issue is just one possibility that could be interfering with our exposure to radiation. Some of them may be plus, some may be negative, many of them could be additive, cumulative. One of the big problems in the environmental area is that when we carry out a process that we've already done once or a few times, then everyone agrees that it is OK. One guy said to me one night, "If one person at the party urinates in the pool you don't get too concerned, but if everybody does you get all upset." It's the cumulative impact of the decision, and so we need to try and weigh all the things. If we're going to make changes in our environment, we need to be very concerned about that change before we launch it; not only its impact but what it does when added to others or subtracted from others.

Question:

You just mentioned that the Academy report talks about the climatic impact of Freon, and that it's about half of the $CO_2$ effect; they say it's about half by the year 2000 of $CO_2$.

Answer:

Yes. The thing that I remember is that the impact on the green-house effect from the fluorocarbons, if you continue at the 1973 rate, would be equivalent to a 50% increase in the level of $CO_2$ over today's level of $CO_2$. In other words, if we were to burn 50% more fossil fuels than we plan to burn, by the year 2000 we would have an impact on the environment equivalent to the impact expected from Freon release. Is that right?

Question:

My question is: are we doing anything about $CO_2$ regulations?

Answer:

Yes, in fact a study is under way, and there is a tremendous movement to develop other types of energy than fossil fuel energy. Mother Nature's going to help us with that because we're going to run out of fossil fuel. We've already peaked out in the United States in our production of oil and gas, and the world is going to peak out before the end of the century. But that is another problem which obviously merits discussion such as this, and concern about how we cope with it.

## Question:

Just between the two studies, it has been found that in fact some new effects [ClONO$_2$] have been discovered: that the aerosol can releases may have a consequence of increasing the ozone by 10%, rather than decreasing it by 10%. Wouldn't you adopt the attitude that that would also be bad because we've disturbing the present balance, or would you applaud the idea that we should continue not to regulate, and perhaps even encourage the use of aerosol sprays.

## Answer:

I would be very much concerned about it. But less concerned than if I had some scientists show me some connection between that and a negative impact. When we change our habitat we ought to be greatly concerned about it. I just saw a little story the other day about putting insects on the endangered species list. They talked about butterflies, for example. There are a number of species of butterflies that have disappeared, and it goes on to point out the tremendous reproductive rate of insects, the tremendous number of species, and the little apparent value of a given species to human beings. But then it went on to make the chief point, and the one that I want to make. It's not so much the disappearance of a given species of butterfly that matters. What matters is that its habitat disappeared, and we're going around changing habitat : all over the place. There's one species we're particularly concerned about, and some of these things like the depletion of the ozone layer can have a major impact on homo sapiens directly and maybe many many more times more so indirectly in ways which we don't understand today. I say we ought to run up a red flag and be concerned about it. So maybe the disappearance of insect species is a tremendous warning to us. Sort of like when the miners took the canary down in the mine with them. When the canary collapsed they decided to get out of there.

## Question:

Is it your personal opinion, or is it the CEQ opinion, that Federal regulatory agencies should start now?

## Answer:

It is the CEQ opinion and my opinion personally, both.

## Question:

I'm just a little bit concerned about how this whole matter can be put together in a logical fashion. Dr. Peterson's already indicated that he is against nuclear fuels. He is also against $CO_2$, which takes out fossil fuels . .

**Answer**:

By the way, you're saying that, and I didn't say that.

**Question**:

It looks like the world is going to get rather cold within the next few years if we're going to eliminate all these sources of fuels, and perhaps we ought to begin to use fluorocarbons at an accelerated rate in order to increase the greenhouse effect, increase the temperature of the earth, and give us more of a habitat in which we can live. Furthermore, it will produce areas to produce food and this will always get around the energy crisis.

**Answer**:

I think the audience can respond to that. Thank you.

**C. Bastian**:

Thank you very much Dr. Peterson.

SECTION III

PANEL DISCUSSION

## Opening Remarks: Carroll Bastian

We're going to have a panel discussion among some of the representatives of some of the sectors we've already heard from, and some additional ones. The structured part of the panel discussion will be followed by audience participation and exchange, so you can get in all the questions you didn't have time for with the previous speaker. I'd like to briefly tell you who we have here on the panel and then give them each a chance to speak for about 5 minutes on their point of view before we get into the discussion.

Dr. Bill Moomaw, who is a chemist and he is on the staff of Senator Dale Bunker's Senate subcommittee on the upper atmosphere, which is a subcommittee of the committee on Aeronautics and Space Sciences. Senator Moss, from whom you heard at the beginning of the conference, is chairman of the committee. Dr. Moomaw is also teaching chemistry at Williams College and is working part time with the committee.

Jim Brydon, who is chief of the Environmental Contaminants Division of the Environmental Protection Service of Canada. They're a little further along on their  ~ic substances control legislation than we are in the United States.   ʃ've already passed their legislation and Jim Brydon is charged with the problems of implementation. He's had early involvement with the fluorocarbon issue both within Canada and in the OECD.

James Merritt, President of the Cosmetic, Toiletry and Fragrance Association. We've been hearing from some of the representatives of the fluorocarbon industry, and he is a representative of some of the industries which use fluorocarbons.

Mr. Sullivan, who is science editor of the New York Times. He's had a long history of interests in atmospheric issues, as well as his other interests, particularly in the Antarctic, astronomy, plate/tectonics and the International Geophysical Year.

Ruby Compton, who is an attorney with the Natural Resources Defence Council, an environmental legal organization.

Bob Reichert, who is the director of the Government Affairs Division of the legal department of du Pont.

Ralph Cicerone, I don't know how I can introduce him to this group, I think everybody knows Ralph. He's with the Space Physics Research Laboratory at the University of Michigan and one of the more prominent scientists involved in this whole issue.

First, I'd like to call on Walter Sullivan to speak.

## W. Sullivan:

As Dr. Peterson was talking this morning, he exhorted us to think not only about ourselves and our present generation, but think ahead to

future generations, and that our actions should be determined accord-
ingly. I was reminded of what's probably an apocryphal story, but I
heard it from an Englishman. It's about the Houses of Parliament.
Apparently, somebody in Parliament was exhorting his colleagues to con-
sider posterity in making their decisions, and somebody broke in (a back
bencher) and said, "I don't see why we should do anything for posterity;
I can think of nothing that posterity has done for me."

In the consideration of this problem, it's sort of a new experi-
ence for us. As science writers we spend a lot of time writing about
charmed quarks, naked singularities, and gravitational collapse, and
somehow there's no big industry involved. There's nobody breathing
down our necks to give this or that point of view, no emotional out-
breaks in the audience, and it' quite a different experience to cover
this kind of a story although not entirely new. The CIAP debate on the
SST was sort of a nice introduction to the whole thing. It had many
parallels and it highlighted something, if we can believe the headlines
that were read to us yesterday or the day before, that has occurred
again with the Academy report. This is the wide range in which stories
like this can be handled, and many of you will recall that when the
CIAP report was first presented at a press conference in Washington,
it came out sounding as though there was no problem involving the pre-
sent fleet of SST's. At that time there was only a handful of SSTs,
but the report had found that there was indeed a cause for concern
with a full-size fleet of several hundred SST's.

We have many parallels in discussing the current subject. When
this thing first came up with the Rowland and Molina report in Nature,
some of us, including myself, held it at arm's length. It was a period
when there was a great deal of doomsday reporting, and the public and
the press were both a little bit turned off by all of these cries.
Every time you turned a corner there was something new and terrible that
was going to happen to the earth, so we were a little bit slow in pick-
ing it up. But then when we started to report on it, my own newspaper
ran a magazine piece showing a beautiful stone O, with a stone 3 down
here and a whole lot of little Gremlins, all looking very much like
aerosol dispensors, nibbling away at it and killing people right and
left.

So there was all this kind of coverage, but I maintained that if
anybody could really prove that the hypothesis was wrong, then that
would be just as good and exciting and just as wonderful a kind of a
story as proving it was right.


C. Bastian:

Thank you very much. Next we'll hear from Jim Merritt and get
some perspectives from the aerosol industry.

J. Merritt

First let me say I apologize to Carroll. I finally found her at
breakfast only just this morning. I arrived late last night and stayed

at the University Motel, and they happen to close rather early. There was no telephone service, and I did not leave word that I had gotten in. I was afraid she might have pitched and tossed all night wondering if the absent Merritt had finally shown up.

Reminded me of a story told by a cousin of mine who owned a hardware store in Eastern Ohio. When a friend walked in and said, "Harry, I want to buy a dozen alarm clocks" Harry said, "Why! I've known you 55 years and I've never known you to need one. When the dog gets up in the morning and bays, you get up and feed him." He said, "Yeah, but you know, dad died and left me a little money and I bought the motel over here on the highway, and I figure Bess can take care of the rooms and I can run the front office. But some guy some night is going to ask me to come in and leave a wake-up call for the next morning and I'm going to hand him an alarm clock, cause there ain't no use both of us laying awake all night wondering if I'm going to get him up in the morning."

Well the University motel was a little bit that way. They had no wake-up calls before 7:30 either. I arrived this morning and I was sitting to the right of the microphone when the distinguished director (Russell Peterson) spoke about punting. He came from the state of Delaware; that state which has the great small college football champions, the University of Delaware. I was also sitting to the left of the man at the right end of this group. He's from the University of Michigan and I'm from Ohio State, which thinks its better than both, and the man talks about when in doubt punt, and then I hear him try to punt some of our products right out of the stadium.

Yesterday, as we got in the plane at La Guardia and taxied out to the end of the runway, the rain was pelting down and the captain came on and said, "I'm sorry we're going to have about a 50- to 55-minute delay." The man across the aisle spoke up very loudly and said, "Now I know what a hijackee feels like."

I'd like to throw out an idea this morning. It's an idea which arises from the experience we've had in technical scientific toxicity research, and I would like to call for a supreme court of science; a supreme court which could handle not only questions like the one which has just gone to the National Academy, but the others which have come along. And coupled with this supreme court I would like to call for a science computer data bank into which all scientific research which applies to various questions could be put. I hear some snickers in the audience, and it's interesting because some of you perhaps have not had the problems we've had. We've signed contracts with university academics, and we're accused and criticized for being a little hard nosed about what we're doing and what we're requiring. We admit it because as you start at the lower left hand of the payment chart to those Universities, you find our payment line includes first a bulge in the payment then it drops to a maintenance for the conducting of the research so that the payment becomes relatively constant. At the end of that line is another bulge, and I'm on a first name basis with the business manager of a university because I won't pay that last bulge, and that last bulge says that before they get paid they issue a report and

they submit a summary of it to a technical journal for publication and send us a copy of that. Mr. Sullivan will tell you it's a lot easier to get the guy in the rewrite room or on the city desk to pick up the story and run it if it's sensational. It's difficult, much more difficult to write a story with positive data, an affirmative story and get someone to put it in the paper. We want a total bank of data so that as the scientists convene they will have access to all data both negative and positive and can then make the scientific decisions which Dr. Peterson called for, with the availability of all data.

I was interested in his comments about air conditioning, or refrigeration. I consider air conditioning a part of refrigeration. I happen to live in Washington D.C., in a rather strange place, it's a non-access place. I'm concerned about those who feel that eventually we might lose some of the fluorocarbons which are used in air conditioning. I think this scientific data bank can be utilized just as lawyers today use their legal banks into which they put every decision, so that as they write their brief they can prepose the strongest possible case. The wheels of justice in legal matters grind slowly at times. They do in scientific matters too. But don't forget that as the knowledge grows, the scientific decisions which are based on that knowledge, in our opinion, will become more effective. We're concerned about chemicals which are being considered guilty until proven innocent. We recognize that it's possible on the basis of current knowledge to declare a chemical innocent, and later with an advancement of knowledge to then declare a chemical guilty, but let's do it rationally, let's work together, let's develop a cooperative effort of government, of industry, of academics, of independent scientists, and of many others. We're all working to serve consumers, who in effect are mankind.


### J. Brydon:

I'd like to make a couple of points. First, about international approaches to the stratospheric ozone problem, and second some comments about our situation in Canada.

When the fluorocarbon issue first arose in 1974, it was obvious to us that this was a truly global problem. Senator Moss made the same point yesterday, or Wednesday, and as Mr. Lykke put it yesterday, the stratosphere is a shared natural resource. There's one further factor that I would like to put to you today, and that is that when any persistent environmental chemical enters the environment, either for the first time or in unusual quantities, there is no escape. This is true with the fluorocarbons, with PCB's, or even with $CO_2$. And maybe I might make an analogy which I think is quite apt. I used to smoke, and after smoking for 19 years the British medical association decided that if I smoked for another year I'd get lung cancer. So I quit, I escaped; that was my escape. If you're in a roomful of people, and everybody else is smoking, your escape is to leave the room; you have that opportunity. If you live in a city with smog, you have the opportunity of moving from that city. There is that escape, but if the entire global universe is contaminated with a persistent environmental

chemical, there is no escape from whatever potential problem there might be.

Yesterday, Mr. Lykke proposed an international convention on the prevention of stratospheric damage. He deserves to be heard seriously, because he's had a lot of experience in the international field, and he has a good track record. He mentioned a number of international organizations currently involved with the fluorocarbon question: OECD, UNEF, ECE, WMO, EXCU; sort of an alphabet soup. He passed them over in favor of his recommendation for a convention. In a sense he destroyed my morning because I was going to advocate the OECD as a practical vehicle for international action. However, I am going to continue to try to make my point and I invite him to respond. In 1972, the OECD environmental committee made a collective assessment that PCB's were a threat to the environment. They also agreed that all dissipated use of those substances should be banned. In 1973, the OECD council took the decision to the effect that member countries should prohibit or regulate certain factors associated with the dissipated use. They also stated that member countries shall report on their progress annually, and that, in my mind, is the key.

Perhaps the prohibitions didn't go far enough, but they were all agreed, and that was the first step. More serious, however, is that member OECD countries, with a few exceptions, did not have the appropriate legislative power, and therefore regulatory action has been slow in coming. Now that's true to some extent today and is relevant to the fluorocarbon issue. Nevertheless, as Canada's representative to the OECD chemicals group, I suggested in 1974 that the fluorocarbon issue might be part of their program, and I still believe that the OECD could provide a practical vehicle to concerted action for the control of the fluorocarbons. The OECD has underway a detailed evaluation of product and consumption of the fluorocarbons. It is embarking on a technological and economical evaluation of selective bans and alternative products. I remain optimistic that an appropriate agreement can be reached for concerted action upon the 24 OECD nations, who account for I believe 89% of the world's consumption. That is not to discount the importance of a world-wide agreement which is ideally possible under an umbrella such as an international convention.

A couple of comments about Canada: The Atmospheric Environmental Service has had a stratospheric research program going for some time in cooperation with our universities, and many of you know that there is also a great deal of collaboration with our group externally with the MCA, WMO and various U.S. agencies.

The advisory committee on stratospheric pollution noted in 1974 that the fluorocarbons appeared to pose a serious threat and encouraged further research. That group, of which Professor Schiff, Dr. Boville and Dr. Evans, who are here, are key members, is now undertaking a Canadian review.

The official Canadian position up to now on the fluorocarbon issue has been a stance of concern for the potential seriousness of the problem, coupled with a wait, watch, and see attitude. I don't

think that there's any question but that the two recent NAS reports
will have an impact on Canada and abroad.

One final point:  As Carroll mentioned, we do have the legislative
base to deal with the issue.  The environmental contaminants act cleared
Parliament last December, and has the same thrust as the U.S. toxic
substances control bill.

R. Compton:

First I thought I'd just explain what NRDC is, briefly, and what
we've done on this issue, and then our position on further actions.

The Natural Resources Defense Council is an organization of
lawyers and scientists dedicated to protecting the environment.  We're
a membership organization that's brought law suits and taken other
action to force the government to take certain actions to protect the
environment.  And one of these actions has been a petition to the Consumer
Product Safety Commission which Commissioner Pittle mentioned yesterday.
We requested that the commission propose a rule to ban aerosol consumer
products containing fluorocarbons, because we think, after reviewing
the scientific information, that that action should be taken.  Ten
states joined us in our latest petition in requesting that the commission
take this action.  As Commissioner Pittle mentioned, probably the Clean
Air Acts amendments will be passed in the next few weeks and the Commission
will no longer have jurisdiction over the fluorocarbons and consumer
products, and the EPA will have that jurisdiction.  The Natural Resources
Defense Council will probably continue their efforts as Dr. Peterson
said this morning.  We agree that it's a value judgment, that it's not
just a scientific judgment, and that our organization has made the
value judgment that the potential benefits of continued use of aerosols
particularly does not outweigh the potential risk of the increased
potential of skin cancer and potential climatic impacts and perhaps
impacts on plants and animal life.

We plan to continue pursuing this.  The NAS study unfortunately
confirmed Rowland and Melina's prediction of over two years ago that
fluorocarbons will deplete the ozone layer, and we do disagree with
the fact that the NAS took a stand and suggested when regulation should
begin.  I agree with Dr. Peterson and Commissioner Pittle that that
is a value judgment, that the academy should not have taken that position.
So we, in our efforts to represent what we consider the public interest,
will continue to push for regulation as soon as possible.  For a non-
essential product like aerosols, where there are substitutes, we think
the economic impact will not be so great.  There may even be an increase
in GNP with the new pump-sprays and other types of containers.  There
should be regulation as soon as possible.  It's just not worth waiting.

And I just want to add to what Mr. Brydon said about this bikini
business, and moving 84 miles to the south.  It is an individual choice
whether to move or not, but it's not an individual choice if someone
else is depleting your ozone layer.  It is a global problem.  And the
other thing is the business about moving 84 miles south.  If everyone

moved 84 miles south, then there could be some serious impacts on plant and animal life and everyone would be affected.

R. Reichert:

Good morning. I'm sure you all realize that Ralph and I have some minor disagreements on some minor points, but I certainly want to point out one area that we have complete agreement on. It's a very deep mutual admiration for the press in one particular area. We are confident that all statistics and technical information and things like that were made use of by the press in arriving at their football poll in choice of the University of Michigan for number 1.

What we've all been talking about here the last couple of days is the question of whether the fluorocarbons are bad, whether they ought to be banned, whether they ought to be regulated. Some good points were made on all aspects of this thing, but I think there's one thing that is being left out of this equation, and that is the question of when is it time to regulate? Now despite the recommendations Monday of the National Academy of Sciences study committee, some components of the ozone depletion theory say that we should ban fluorocarbon products now: that we already have enough evidence to act. Well, I suggest that this is a gross over-simplification of the mechanism for problem analysis and product regulation. There's always enough information to act if it's necessary to act, however meager the information might be. Seldom, if ever, does a regulatory body have all the possible evidence, and sometimes it has very little. But when a regulatory decision must be made, it is made, inevitably, on whatever evidence there is. Basically, then, the "ban now, we have enough evidence" cry completely overlooks several major parameters in the regulatory mechanism: parameters relating to time; and when must a regulatory decision be made? Specifically, parameters omitted from the "ban now, we have enough evidence" approach are considerations and ramifications to these questions. When will more meaningful scientific information be obtained and in what time framework? What extent of damage would occur and how would it vary with time? Little or no immediate damage dictates delay. Little or no added impact by waiting dictates delay. Coupled with both of those, the ability to get more scientific answers before danger of significant damage certainly dictates delay. And further coupled with these, a great societal impact that would be lessened with proper management and forethought supports delay.

Well, how does the fluorocarbon question fit into this framework? I think the first 10 pages or so of the National Academy Study Committee Report provides the best answer for this question. The committee concludes on the basis of present information that some degree of regulation of fluorocarbons probably will be needed sometime in the future. However, the committee also notes that there are three major areas of uncertainty in this theory, where new information could substantially alter this conclusion. These involve existence of possible tropospheric sinks for fluorocarbons, possible missing chemistry which would interrupt the chlorineozone catalytic chain, and information about atmospheric transport. From this carefully qualified conclusion, the committee

went on to make several recommendations.  But I'm not going to read
these recommendations to you; you've all read them by now yourselves.
However, there are several points in these recommendations, which I'll
emphasize because they relate to the subject at hand.  The points are
five:  (1) There is no need to attempt to make a regulatory decision
now.  In fact, the committee recommends against making any such decision
now.  (2) Within another 24 months the research program being sponsored
by government and industry should provide information needed to narrow
the uncertainties associated with the theory.  (3) There's always risk
in delay, but the risk in this instance is clearly not significant.
Something on t e order of an incremental 1/6 of 1% ozone depletion.
(4) Restrictions will be required 2 years from now only if there remains
a major possibility of long-term ozone depletion of more than a few
percent.  (5) If restrictions do prove necessary, it should be implicit
in this area that the use of fluorocarbons, or any product for that
matter, should not be restricted more than necessary to accomplish
a specific goal.

My basic point, and I think a major point of the committee's
report, is that the regulatory body must not merely decide whether or
not to regulate, but equally important it must decide at what point in
time such a conclusion must be reached and implemented.  In this case,
the answer depends very little on the total ultimate ozone depletion
that might occur, whether it be 7%, 20%, or whatever the total ultimate
ozone depletion might occur if no action were taken.  As the study
committee report makes clear, the answer depends on the effect of
delaying the decision for one or two years while obtaining scientific
information that will make possible a more scientifically sound decision.
These are the kinds of questions the fluorocarbon producers took into
consideration some two years ago before announcing their position,
which incidentally was announced at the time of the very first hearing
on this subject by Representative Roger's subcommittee meeting back
in 1974.  The industry position was that the theory warrants serious
consideration, more data are needed and can be obtained in a relatively
short time, no significant harm will result from delaying this decision
for a short time, hasty regulatory actions would cause unnecessary
adverse social impact, and finally, consonant to some extent to what
Dr. Peterson said, the fluorocarbon producers announced that, if the
facts bear out the theory and the continued use of certain fluorocarbon
products could cause a health hazard through depletion of stratospheric
ozone, industry is prepared to adjust production of the offending com-
pounds to the extent required to cope with the hazard, voluntarily.
As you can well imagine, it is with some degree of satisfaction that we
learned Monday that the National Academy of Science's study committee
has reached conclusions somewhat similar to our own thoughts on the
subject.  We're very much aware of the burden placed on the two commit-
tees which have studied this matter, and we know their decisions were
difficult decisions and would have been difficult no matter how they
had come out, but we also believe that their decisions were correct
and we're optimistic that the agencies of government and the legislative
bodies concerned with this question will follow the committee's council.
In this way we insure that any necessary restrictions can be imposed in
a timely and orderly manner, at the same time protecting ourselves from

imposing possibly unnecessary restrictions and the attendant unnecessary penalties upon society.


## W. Moomaw:

Leaving bucolic western New England to go and spend a year in Congress is a very shaking experience. When I decided to accept the Congressional Science Fellowship that had been offered by the AAAS, I had many ideas of what I was going to get into. Very few of those ideas turned out to be correct. When I arrived and began looking around for a particular member's office or congressional staff on which serve, Senator Dale Bumpers was just in the process of starting the first hearings to be held in the Senate on the matters of ozone depletion. Since I am a spectroscopist and photochemist by trade, and although I don't work in gas phase systems but low temperature condensed media, this seemed like a kind of issue that I might know something about and that I might be able to learn quite a bit about; one that I might enjoy working on. Well, I think all of this turned out to be the case. The hearings, I think, were very interesting. There has been some discussion here that refers to the Academy reports as the "Bible." I think perhaps one could refer to different books in the Bible, because there have been many books published. The IMOS Report may be the book of Genesis, I'm not quite sure. There have been several other congressional committee reports, so that you can subscribe to whichever book you like. These happen to be the committee hearings that were held in the Senate Space Committee. Two hearings were held last September and many of you in this room were witnesses at those hearings. Others of you were witnesses at the additional hearings that we held around the first of March. I will save until later a detailed discussion of this, but I disagree strongly with the idea of a supreme court of science. I think that the procedure that I've seen working in Congress, in which individual scientists can come and members of industry can come and people from the government can come and make their views known in a public forum, before elected representatives, albeit an imperfect system is a better system than the idea of some sort of elite supreme court of science. I will be glad to discuss that with other members of the panel later.

I might just explain one thing to you that was not entirely clear to me before I got to the Congress, which is that in the United States, at least, I don't know how its done in most foreign countries, civics classes are taught in secondary school and tell us how our government functions and the role of our elected representatives, and this sort of thing. Well, it is indeed true that these people with the election certificates are elected. Whether or not they are representative is another matter. Among other things it would obviously be impossible to represent everyone who voted in the election. Even those who voted for them on any given issue are going to find themselves at opposite ends. We have also found many cases where a member of Congress will represent a special interest, which is not very closely related to that of his constituents. It was impressive to me to see how many people out there think of their representatives as representatives, and write and tell them about it. Congressional mail is something that you cannot believe

unless you are in an office for a couple of days and see the range of
letters and the range of people who write to their senator. They peddle
everything from the latest perpetual motion machine, and "Senator, you
can have half of the royalties if you can just get NSF or ERDA or some-
body to fund me on this," all the way through to some really heart-
breaking, crushing decisions that have been made by the bureaucracies
and the regulatory agents which are clearly unjust and unfair and there
is a need for some kind of intervention, to other kinds of special
favors and things that are being asked for. But the politician really
is more than just a representative, he is more than just a politician,
he must also, I think, perform some leadership function; he must be a
little bit out in front on issues. He must be able to take information
and formulate it into some kind of general public policy in the same way
that people in the agencies must do so. He must do one other thing, and
that is, he is a broker of competing political interests. I don't
think that we should ever forget that.

In this issue, as has been stated many times, I think that the
question of whether or not the unemployment problems that might be
caused by regulation, and the capital losses, and the issues of the
availability of certain consumer products -- that those are as much a
part of the public decision that has to be made as are the technical
scientific arguments concerning the depletion of ozone. And the poli-
tician finds himself in the position of being the broker, in a sense,
of listening to these competing arguments, deciding on the basis of
the information available to him, and placing his own value judgment on
it, whether or not there is a need to do something about it. The role
of scientists in all of this, I think, is an extremely important one,
but I think I had a somewhat naive view, and I gather in talking to
many of you that you share the view that I once had long ago, a year
ago, which is that there are issues which are essentially scientific
and if only those boobs in Washington would listen to us scientists,
the whole problem would be solved. These issues are much more compli-
cated than that, and scientific input is a crucial input, but it is
only one input. I think Dr. Talley made a similar point about cost-
benefit analysis. Cost-benefit analysis is an extremely important tool
in decision making, but there is no computer program and no amount of
data that you can put in that will tell you, yes, we should regulate on
September 14, 1979, or something in this particular case. That has to
be an additional input and a useful one, but it cannot be the whole
story.

Let me just quickly touch on a couple of aspects of the Academy
report. I know I obviously cannot speak for the entire Congress or the
entire Senate, but I think that I can give you some reaction of Senator
Bumpers to the report that may be of interest to you, since he is
perhaps the single person most intimately involved in legislation in
the Senate. I think that his general view was that the report, as
Mr. Peterson said, generally does support the preliminary findings of
the IMOS report.

While there was nothing new in the reports, it was interesting
to note some of the emphasis: the emphasis on climatic modification
in the greenhouse effect, which got much more attention than it has

gotten in the past, and the melanoma issue discussed by Dr. Fitzpatrick, which has been brought before our committee and further discussed by Dr. Urbaugh. I think that there was some concern on his part of what he viewed as the overly cautious nature of the Academy in the way in which they phrased this controversial two-year delay. I just heard from the other end here, a two-year delay? I heard people from the Academy emphasizing yesterday that it says, "Up to two years," and we should be able to resolve this. I think Senator Bumpers was somewhat concerned that it appears as though the Academy had rather ignored what was going on in Congress in terms of the deadlines and the program that was being scheduled both in the House and Senate. Both programs are fairly comparable and have had a lot of work put into them. We asked NASA, "Could you get enough information together by September of '77?" and Jim King said, "Well, can't you give us a little more time?" and various other people in NASA said, "Can't you give us a little more time?" and at first we wanted it before then, but we finally settled on September '77. It is a date with which NASA wasn't totally satisfied, Senator Bumpers wasn't totally satisfied with it, and other members of the Congress weren't totally satisfied with it, but that was the date that we came out with. January 1978 looked like a reasonable time by which we would have enough information.

Now that is within the two years that the Academy stated, and so maybe we are really quibbling over months here, but the implication is that somehow Congress may be acting precipitously, and there are those that have interpreted it that way, and I don't think that is the case at all. There have been a lot of careful discussions with the agencies and with many other people on this matter.

Finally, I would just say that the prospects for congressional legislation being enacted in roughly the form I outlined are good. I just talked with the people in the Senate yesterday, and it does look like the House has finally acted and that they will go to conference. There is going to be a big hassle over the other provisions in the Clean Air Act, but in the ozone depletion issue the differences between the two bills are not so bad that there will be a great deal of disagreement. I think there will be a lot of pretty generous give and take, political brokering if you like, between the Senate and what is euphemistically referred to in the Senate as the "other body."


### R. Cicerone:

First of all, I think that one of us should thank the organizers of this conference for the arrangements. I think we all profited from it. I didn't think the conference started very well. The other night a rather middle-aged looking gentleman introduced himself as a classmate of mine, but later in the week I saw Bob Menzies running and playing tennis and I felt a lot better.

I haven't had the opportunity of meeting at least half of you people. You don't know me, so I think its essential, in fact this should be done everywhere, to put my biases up front, as Commissioner Fittle advised. I think that is only common sense, because for us to

say that there are only purely scientific aspects, or purely social
aspects, to these problems is foolish. I think the best I can do, and
the best most people can do, is to admit our biases and then try to talk
about the facts as you see them. I think it's time to make a judgment.
And it has been time for some period past now, because I believe the
benefits of aerosol products, at least those propelled by fluorocarbons,
for the most part do not outweigh the risks. I have said that publicly
and I haven't seen anything appear in the past two-and-one-half years
to change my mind. So let me proceed now to a few scientific points
that I want to cover because I don't think they have had enough atten-
tion here.

One is very much like the lead in the middle of the candle, which
either Wilson Talley or Commissioner Pittle talked about yesterday. We
have a problem with the growing greenhouse effect because of infrared
trapping of outgoing planetary radiation that has several pieces.
Ichtiaque Rasool points out that any triatomic or polyatomic molecule
is going to have an infrared spectrum. I'm sure that was pointed out
long before he said it, but he said it to me this morning. Many of my
colleagues now look back and say, "Why didn't I do what Rahmanothen did.
I thought it would be a small effect." Well, the point is, there is a
global warming indicated by simple energy budget considerations with
the increase in cfm's in the lower atmosphere, and possibly with some of
the cfm substitutes, I should point out.

Any consideration of this problem and the ensuing climatic effects
must also take cognizance of the $CO_2$ problem. It must also take cog-
nizance of other problems that may develop, such as $N_2O$ infrared trapping.
There are other problems mentioned in the Academy report, and I encourage
people to read it, such as the possibility of a feedback due to the
ozone effect caused by the cfm's, which could increase the tropopause
concentration of water, allowing more water to reach the stratosphere.
There is also the probability that the ozone layer itself will come
down a little bit in altitude, creating another greenhouse effect.
And we have to take all these things into account, not just the skin
cancer issue, which many people feel is a red herring. I don't, but
many people do. There are other dimensions to this problem.

Another brief scientific point I would like to make is that the
Academy reports are voluminous. I think it is possible, if we sit down
and read it, to digest all of the recommendations and critical remarks,
and to then reap some satisfactory judgment on this question -- now, at
this point in time. I think most businessmen and women are prepared to
make decisions at points in time. Scientists usually aren't, and I
think we could be if we would read the report. Unfortunately, most
people never will read the report. Very few scientists will. I am
reminded of the CIAP monographs and documents. I doubt if anybody
besides the meticulous and apt Harold Johnston ever read all the pages.
And probably no public official did or ever will. Hence, we are forced
to deal with the summaries and newspaper articles. I think the Academy
should have emphasized more what pieces of data are needed, rather than
how long we should take to get them. We have to know how to reduce the
uncertainties for everyone's satisfaction, and I don't think the summary
emphasized this strongly enough.

Fred Kaufman pointed out how important the summary is in the CIAP final meeting. Okay, let me pass on then to some of the public aspects of the problem that I see.

One is, first of all, that most of the informed public will take its lead from the press, and in my brief experience in this type of problem the press all too often does not check with more than one source, scientific or otherwise. Most of the skilled and reputable reporters do, but many of them don't. Consequently, we very often have unbalanced stories. I think that the book <u>All the President's Men</u> showed me the rules that the <u>Washington Post</u> had put on Woodstein [laughter] and/or Woodward, and....small minds remember names....... [loud laughter]. There are some politicians that would be very upset at that remark. But the ground rule for journalism, and when I speak to journalism students I stress this, is to get your sources straight and pit your sources against each other before you rush to press. It is analagous to having scientific papers reviewed. I think, though, that the press has done a good job on this issue, and it is time for the public to make a decision.

I am proud and pleased at the way we operate in this country. Having visited the USSR this summer for the first time, I can't tell you how proud and pleased I am of our system of checks and balances. We do not always have capricious, arbitrary judgments. There are channels of appeal and routes through which papers will be channeled. And I can completely agree with what Dr. Moomaw said earlier about the present system. A scientific court of appeals would be an elitist, capricious arrangement, I believe. In fact, the public has started to judge the issue. We just received word this morning that one of the state legislatures has been waiting for the Academy report. Somehow it has read enough news clippings to have gone ahead and passed a bill prohibiting the sale, production, and usage of fluorocarbon propellant-driven aerosol cans as of January 1, 1978. It is the Michigan house, and the vote was 84 to 11. That's probably a significant major indication of public opinion, and the fact that the time is now to judge. My biases are out front.

I have another problem that I picked up over the last few years, which is the talk among public policy analysts of cost-benefit analysis. I read an article in this month's <u>Technology Review</u>, which Jim Friend and others know is the alumni rag of MIT. It's written by a civil engineer from MIT, who is also a lawyer, and the title of it is "Why Cost-Benefit Analyses Can Be Harmful to Your Health." [Laughter] The main points as I read it are, first, that unquantifiables are often omitted, and all of us have our own measure and ideas of what unquanti-fiables are and we don't agree on them, and, second, that it is very difficult to put figures on things like life, especially the lives of the unborn.

The last point I want to make about public issues is probably from a scientific point of view. When should a problem like this be publicized? How did Molina and Rowland decide to go ahead and submit their paper? How did the rest of us decide to release what we had?

These are questions that require, I think, some maturity and a lot of judgment. We'll never know if we did the right thing, but I have had strong disagreements with people on when to publicize the potential fertilizer problem. On the one hand, you have the potential enormity of the problem and the clash with world needs. On the other hand, we have virtually no refereed scientific papers to document this problem. In my role as a scientist who has tried to take a public position on these problems, I recognize that I am in danger of losing my objective position, and to whatever extent I've kept an objective position, I owe thanks to my immediate colleagues, George Carrigan, Tom Donahue, Andy Nagy, S. Leu, Jim Anderson, Jim Margitan, Don Steadman, friends Rich Stolarski, Bob Hudson, Paul Hayes, my continuing mentor Sid Bowhill for keeping me honest whenever I tend to get too emotional about things, and of course I owe gratitude to the funding agencies, NASA, NSF and MCA for putting out money for continuing work.

### C. Bastian:

Thank you very much. [Applause] Before we get into some general questions and answers, I am going to use my favored position as Chairman to ask a question of my own. There have been several studies, and I wish I had the citations on these because I think one of them is from the University of Michigan, but there have been several recent studies that have indicated that, at least in this country, despite the volumes of scientific and technical data that arrive every morning on the government policy-makers' desks, the large majority of government policy-makers are more influenced in their formation of opinions on significant issues by what they read in the newspaper. And, I was just wondering what some of the opinions of the panelists are. Naturally, I would like to address this to Walter Sullivan, but also I would like to know what is the experience in Canada and perhaps get the legislators' viewpoints as to whether this is true or not, and what it implies for the role that responsible scientists should take in improving the situation and how the media could be more responsible as well. I'll address it to any panel member who wants to answer.

### W. Sullivan:

I wish they were more influenced by what they read in the newspaper, and less by special pressure groups and lobbyists, and so forth and so on. But I really can't speak to it because I don't work in Washington, and obviously our senate/representative people would be ...

### W. Moomaw:

Well, I think it's clear that members of both the Congress and the Executive agency are very much influenced by what they read in the newspapers. They are very busy people, and they don't have time to read the entire CIAP report, or the entire Academy report on this. There is a syndrome in Washington of an inability to read anything that

is held together, that is more than two pages held together by a staple, because that is the briefing memo. So there is a tendency to digest these things and, unfortunately, many of the staff people are very busy, and so they digest the executive summary, or they wait, or the policy maker reads it in the, you know, where all the news is fit to print, or the Washington Post, or the .... This sounds terrible, but you know there are many people in policy making who are constantly referring to what they saw on the "Today Show," or the "Yesterday Show," as it often is, and I think they are influenced by what the media prints. They are unduly influenced, like all of us are, by the way in which the headlines come out, which is often, I understand from people I know in journalism, not their fault. There are headline writers who make up those headlines which have nothing to do with the story, in some cases.

### C. Bastian:

Thank you. I was just going to ask Dr. Brydon briefly, a lot of this seminar has unfortunately been directed at the U.S. experience because more participants have been from the U.S. I was wondering what perspectives you have on the role of public opinion in your country and in other countries. Whether it is different from here.

### J. Brydon:

Well, I would endorse generally the comments about the impact of the media on legislators at home. I haven't been as close to the legislators at home in Canada as Mr. Moomaw has, but at any rate, the media, the newspapers in particular, have a big impact on the legis- lators. Letters from constituents, and in our situation letters from other legislators to members of the cabinet, are two areas of impact. As far as the people are concerned in Canada, for some time now, back in 1974, this issue has captured the imagination of the people in Canada. There has been a lot of attention in the press paid to the views of the man on the street, and I would say that there have been a lot of letters come to the Department of Environment and the Department of Health, to Barny Boville's group in the Atmospheric Environment Service and to the Minister's office. We had to generate responses to these. I don't know what stimulated the wide public interest in Canada, but at any rate it has been there and it is waned somewhat over the past year, I would say.

### J. Merritt:

I have a comment I would like to make. I would like to thank publically panel member Sullivan for briefing me on what had happened here Wednesday. As I got on that plane at La Guardia yesterday, I picked up a copy of the Times and sat down and read it, and found a summary which I thought reached the laymen in laymens' terms concerning a very, very deep scientific question or series of questions discussed the day before. I think this imposes on scientists not only the burden of reaching valid decisions, and basing them on data, but also the burden of communication with the press. We can't rely and depend on

the press. It's our responsibility to get the data to the press in terms which the press can understand. Not everyone has the ability of Mr. Sullivan in the press field. They can't take the time to call the whole range of scientists to get all points of view. This is a tremendous burden to improve that is being imposed on science. As far as Canada is concerned, I would say that not only does the action of the press influence the Canadian government, but so does action of the U.S. government. I remember when the United States moved on bithionol, in banning it, and then Canada moved on another ingredient, and England on another. Before long we had total confusion because of the lack of communication among our governments. And this is a very important problem and a very important task which faces all of us because it can have a very detrimental effect on markets in other countries, on employment in other countries, if communication is not properly carried out by the governments and by the people involved.

## Voice:

Cyclamates.

## J. Merritt:

That's a very good example. Cyclamates is another example.

## C. Bastian:

Okay, let's have just a moment to see if there are any pressing questions the panel members wish to press on each other, and then I think we will open it to some audience participation.

## R. Compton:

I just wanted to comment a bit on the media. I think that legislators and public policy makers rely on the media not only because it is easier to read and it's shorter, and they don't have time, but because the public reads the newspapers and the public perceives of a problem as having read about it in the newspaper. They don't read the scientific journals. Public policy makers and legislators must deal with the problem in light of how the public perceives it, and must deal with it in that way, and I don't think it is just because it is more convenient. I think the media plays the important role in that aspect.

## C. Bastian:

Does anyone have anything pressing to say? Okay, I have a long list of possible questions, but I think we'll give the audience a chance before I get my next two cents worth in. Yes.

**S. Bowhill:**

I would like to ask perhaps Mr. Sullivan, and perhaps any others, if there is anything that can be done by the universities to improve the supply of top quality science writers, because I've run across a number of them and some of them are really not very good. There must be something we can do. I would like perhaps your reaction.

**Voice:**

I think Noel Hinners wants to answer the question.

**N. Hinners:**

You just triggered me. I think the universities can do an awful lot, and not with science writers but with scientists. The caliber of writing is atrocious across the board, and I think the universities must take more and more of an active roll in comprehensive technical writing for all scientists; not just science writers.

**S. Rowland:**

I think I would like to make a comment here in connection with the suggestion that the legislators get most of their information from the press, and so the implication is that the scientists somehow get it from a different source [laughter]. One of the things that certainly has impressed me in the last two years is that almost no one reads the scientific journals, and almost everybody in this room has gotten most of their information, what they know on it, not from reading the journals, but from talking to other people or reading it someplace, not from the direct scientific journal itself.

**W. Moomaw:**

Carroll, could I comment on that? One of the problems that the Congress faced in trying to keep up with an issue like this, is the traditional scientific publishing game: which is that you publish and it is refereed and it comes out nine months later, and then I read your paper and I sit around and think about it, and then I do an experiment, and then I finally get around to publishing it six months after that, and it comes out nine months after that. And that kind of slow-motion, lobbing tennis game just is not possible for this kind of an issue. I fell upon a device in this past year in trying to keep tabs on this issue, and I had to because I had a dual role. Dale Bumpers had decided that this was a serious problem, and something should be done about it. So at the staff level, I often found myself in an advocacy position. He has things to worry about like being re-elected, and that sort of thing. All that could happen to me is that I could get fired; so I had to be very careful that he didn't advocate things that were unreasonable. Every time something new came up, I always tried to call at

least a couple of people who I knew would have a different viewpoint.
I made a remark yesterday, which I gather was misinterpreted by some
people, about scientists being advocates. I didn't mean that in a
negative sense. It was tremendously helpful to us in sharpening and
keeping up with fast-moving developments. When the chlorine nitrate
thing broke, and you know the kind of coverage that was getting in the
press, it was crucial to be in a knowledgeable position at that par-
ticular time, because the legislation was either going to move or not
move, based upon people's perception of what was happening. It was
extremely valuable to be able to pick up the telephone and call people,
and I don't mean just industry versus non-industry people. There are
people within industry who disagree with each other. There are people
within the academic community who feel that the last measurement on,
well, I won't say anything because my buddy might get bent out of shape,
but whether the last measurement on some particular substance is either
too high or too low, or the measurement was contaminated, or whatever
it is, it is important for us to know. So, in effect, what I was
doing was setting up a quick referee service which could operate much
more rapidly than the journal publishing thing. And I admit that that's
imperfect. It was not done in public, which I think is crucial for
refereed journals, and that is a flaw in it, but it was the only way
I could devise to keep up with fast-moving events and statements that
some of the people in this room published in the quicky journals, such
as the New York Times, before they were published in other places.


W. Sullivan:

I just wanted to supplement what Dr. Rowland said. I think that
really, in your own field, a scientist does not learn what is going on
from the press, because there is this underground press in which they
send preprints and make phone calls, even transatlantic. So I think
in your own field, obviously. there is a whole communications system
that is hidden and never subject to peer review. It is in other fields
that the problem exists, and much as I welcome all of these remarks
about the press, I think that Science magazine, with its reinvigorated
coverage of this sort of thing, and Nature magazine, are really a
goldmine of information in this area.


J. Merritt:

Yes, I have one further comment with respect to the press, and it
is not that one that John Ashbrook used to put in the Congressional
Record repeatedly when he would reprint something in the New York Times
and describe it as "all the news that's fit to tint," but it's the way
the press often looks at industry scientists as being prejudiced, and
therefore being very skeptical about what is spoken by an industry
scientist. I think we should point out that industry is continually
looking for experts in every area, and I'm talking now not only about
those companies producing the basic chemicals, but also marketers who
are producing finished products. We're relying very heavily on the
academic scientists in consulting roles to help us, and to answer our
questions. While a report may come from an industry scientist, very

often it is actually a result of academic research. I would like to caution the press as it looks at reports, that when it comes from industry not to automatically consider it prejudiced, but to give it more consideration and evaluation before judgment is made.

## D. Hunten

My point is a little stale, but I did want to put in a plug for another important means of communication, namely, interdisciplinary conferences like this one. [Applause]

## Commissioner Pittle:

Just a personal experience. I get a number of phone calls from somebody from XYZ newspaper saying he just heard that the lead in candles is something which will result in kids breathing in death at Christmas time. "Wouldn't you say that's the case, Mr. Pittle," he says, and I say, "Well, not really...." "Well wouldn't you say that Christmastime is the time when there is death wrapped up in packages to be sold?" [Laughter] "Oh, well, if you say so." [Laughter] "Well, it depends, I mean, on the one hand, you know, and probably unnecessary lead...." "Aha, unnecessary lead." Click. [Laughter] Now, I say this not to be facetious. I get these calls all the time, and I think there is a tendency to want to print sensational stories because after all it's the grabbers that sell copy. On the other hand, a lot of these issues are just plain dull when you carry them all the way out and use all the text.

The second point I would like to make is that there is an obligation that I take upon myself -- and I think that probably anybody who is ever interviewed also has this obligation -- and that is that once you've gotten through telling it as you think it is, then name one person, just one, who disagrees with you, and tell them to go talk to that person. Just to provide a balance, because very often you are very convincing and the person writing the story will decide "This is enough. I'll go print it." And then that does tell it like it is. The first story is usually the one which makes the first imprint on the part of the brain that says "Okay" for that issue, and it is very hard to turn that around. So when you are interviewed, when you are being asked about the latest findings that you have, say, "There's a guy who disagrees with me and you might check with him." Try it. I think that will help the whole quality of the story.

## Voice:

I would like to state that I think the public has a right to a clean and protected environment if it is willing to pay for it. I think it is the duty of the scientist, and the newspaper people in particular, to give the public the information they need to make a decision that they can live with. And it is my opinion that neither of those groups have carried out that duty very well in recent years,

particularly in environmental research.  Now to get to my point.
Everyone has agreed that this question about the ozone layer has a
grave amount of uncertainty about it, and I'd certainly like to point
out that the uncertainty also falls on the benefits to be achieved
by any regulatory action taken.  In other words, there is uncertainty
on the side of regulation, and that point seems to be completely missed
by everybody who has talked.  Now to raise my question.  Do you not
think that if manufacturers are required to prove the safety of their
product before they put it on the market, regulators ought to be required
to prove the benefit of their regulation before they're forming it.
Now I'd like to have comments from all of the panel, but I think I'd
like most the answer from Mr. Merritt.

## J. Merritt:

A personal comment I would have on that goes back to the policy
of the Food and Drug Administration, in publishing its proposed regula-
tion, to publish a preamble and set forth the reasons why they do or do
not propose a regulation.  Why they do propose it in the case of a
rejection, why they've rejected it.  They are in effect adopting what
you call the justification of regulation as they proceed.  I think it
is healthy.  1 think it's helping both sides; it will help Consumer's
Union, for example, when it looks at an issue as contrasted with
industry looking at the same issue.  I know there are times when
Consumer's Union looks at me and thinks, "Gee, you've got horns," and
I've got a halo, and I look back and say, "No, they've got the horns and
I've got the halo," when it really depends on point of view.  Major
surgery is mine, minor surgery is yours.  The valid argument is mine,
the silly argument is yours.  I think we've got to get away from that
and look at things objectively, and in depth, and come up with sound,
defensible scientific conclusions that we're willing to stand by.

## Voice:

I want to ask two questions.  I believe I read in the press that
there's been something of a consumers' downcurve in the use of aerosol
products.  We've also heard several statements about what could be
termed voluntary compliance from industry.  I wonder how the various
sides of the panel want to interpret this, and how the industry plans,
if at all, to anticipate regulation before it does happen through
potential voluntary compliance.

## J. Merritt:

On behalf of the cosmetic industry, we petitioned the food and
drug administration in June, after a meeting with the deputy commis-
sioner for compliance. for a regulation requiring fluorocarbon labeling
on cosmetic products.  We heard early this week that it will be
published early next week as a proposed labeling requirement.  We have
a dictionary which sets forth all ingredients in products and sets
forth the adopted names for them, which was recognized in 1973 by the

Food and Drug Administration.  We now have another document pending for approval.  It would set forth every ingredient.  I think we tend to look at the public as gullible, and the education level is substantially higher than it was 30, 40, or 50 years ago.  The public is intelligent, and a whispering housewife can kill a product overnight.  It's the best cathartic in the marketplace.  And they're very, very savvy when it comes to making what was referred to earlier as value judgments concerning whether the roll-on is half the price of the pump, or half the price of the spray.  Consumers are making up their minds, and the consumers don't reflect trends, they make trends.

### W. Moomaw:

On this point of the decline in 1975, there is something I'd like to clarify.  Among the new journals I read is Cosmetic and Drug Industry. Earlier this summer there was a statement in there -- and I may be off on the figure but a figure does stick in my mind -- that there has been an increase in the first quarter this year over the first quarter last year of something like 38%.  Now it wasn't clear whether that was in terms of aerosol units or in the use of Freon for aerosols or what. Could you just clarify that point?

### J. Merritt:

If there had been a 38% increase it would have been reflected in the dues our members pay us, and we haven't seen that figure yet. The dues are based on volume.  I don't know of any jump of that magnitude. I might say that that editor has called me all kinds of names, so I've lost a little bit of faith in his credibility too.  But at the same time, while there may have been a drop in the total number of aerosols, I think again that the consumer, once he or she -- and someone suggested that we ought to call them E's -- when E looks at the label E can make up E's mind whether to buy it or not by looking and reading the label to determine what chemicals are in it.

### R. Reichert:

Certainly on this question of consumer restraints and consumer choice, there has been a drop in fluorocarbon usage.  We are not sure whether that is totally because of consumer dissatisfaction with the nature of the product, or whether it's economics, or some combination of both.  We suspect the latter because that was at a time of some economic dislocation.  In answer to your question, are we in a spot to respond to this?  Certainly we're in a spot to respond to it if the volume of sales goes down.  Naturally, our volume of production follows it.  I think also inherent in that question is that if something were to happen to diminish that volume to zero, are we in a spot to in some way cope with that eventuality?  I would have to say that on the question of alternate propellants to maintain an aerosol type package, if this were to happen tomorrow, the answer is definitely no; we could not supply the market.  Certainly we have at du Pont (and I'm sure all

of our competitors have also) the full range of products that would seem
to be possible candidates for propellant usage. We've found some that
have physical properties that look pretty good, and I'm sure our com-
petitor's have also. We also found one or two that really looked
excellent, but by the time we had put them through the rat inhalation
test and looked at some of the rats' livers, that wasn't such a good
idea either. So the answer to the basic question is, if we had to go
tomorrow on this, we certainly would not be in a position to supply the
industry. If we have to go sometime in the future, in two years or
whatever it might be, I can't tell you if we'd be in a spot to do it.
It depends a lot on how long-term velocity toxicological tests and
various other types of tests turn out. So, I can say that we are
hopeful and guardedly confident that if necessary we could move to a
product. I don't know whether the marketplace would buy it from choice
or from price, and I think that's about where we are at du Pont at this
stage of the game.


R. Compton:

Going back to responding to public interests, and public response
to the issues: Contrary to public opinion, we don't sit in little
cubbyholes at Washington and think up nasty law suits to put industry
out of business. We do respond to the public calling us, and scientists
calling us. This particular issue has probably gotten more interest,
and we've received more calls and more response to this issue in urging
us on to take action; asking us which products contain fluorocarbons
and which don't, and asking for a lot of information we don't have. We
tell them to call industry, and they say, "Well, they told us to call
you." Our organization tries to reflect public interest in this way by
acting to the issues that they think are of major concern.


J. Merritt:

Getting back to the point of alternate propellants, the suggestion
was made earlier this morning during the first session that perhaps it
might be appropriate for industry and government to sit down and decide
how it's going to phase out, as has been done perhaps in other coun-
tries. I'd like to point out that we have antitrust laws in the United
States which prohibit us sitting down and deciding on this basis that
we will phase out from these particular propellants to others, because
that sort of action ends up restraining trade, reflecting price of
products, and will basically be held, I think, to be a violation of the
antitrust laws. So we have to make, in this country, independent
company decisions.


J. King

When I came to Washington I began to hear a lot of mumbling about
the credibility of scientists and what has happened to the credibility
of scientists as regards the whole fluorocarbon issue, but particularly
how the chlorine nitrate issue was handled, and I was wondering whether

anyone had any ideas about whether the credibility of science and scientists has been adversely affected in both the social and political arena?

C. Bastian:

Who wants to answer that?

J. Merritt:

If that was a curve and you threw it at me, I just struck out.

W. Moomaw:

OK, I think there was a problem of credibility concerning that. Trying to follow these quick zigs and zags in the amount of ozone depletion is tough enough, but when you get something that is of that magnitude -- I mean little wiggles people pretty much ignore, but something as big as the chlorine nitrate thing looked particularly devastating since there were those who claimed that it not only dropped the depletion to zero but might actually lead to an increase in the amount of ozone by a couple of percent, and then to have counterstatements made left the public and I think some members of Congress a little confused. The only thing that I could recommend to Senator Bumpers was just to lie low until things damped out a bit. That I think turned out to be the better thing to do, although even today we've heard at this meeting claims made that in fact the Academy number, assuming various things about chlorine nitrate, was too conservative and that basically instead of a mean figure of 7% that the figure ought to be 10 - 11%. Needless to say I'd be glad to hear from the advocates on either side, because there will be people in Washington who will want to know how much credibility to place in the higher or the lower figure.

W. Sullivan:

I would hope that the chlorine nitrate situation would have been educational, rather than turning people off on science. That's the way science works. The proposal was made and was reported as just a hypothesis, and it has been analyzed and modified. And finally it turns out to be not as much of a problem as it originally seemed to be. I'm sure there are some people here who remember the CIAP meeting at which somebody got up and read an editorial from some Pennsylvania newspaper that appeared after that famous press conference on the CIAP report. The editorial said that we would just never be able to believe scientists again; here they've been talking about this ozone layer, and now it turns out that the whole thing was just a fraud. It was just a way for scientists to go and play their games in their laboratories. That certainly did work to the disadvantage of science.

## C. Bastian:

I can speak from being in the government structure when the chlorine nitrate thing came out. When that first hit the press, there were a lot of policy officials who reacted to the way it was presented in the newspapers, and who did not check with the scientific community, who could have told them it was all very preliminary and it might switch back the other way. Those officials immediately started running around saying, "What are you talking about, there's no ozone problem anymore?" and they had to be educated slowly but surely.

Yes, Commissioner Pittle.

## Commissioner Pittle:

I wonder if I can take a moment and comment on something Mr. Merritt said which deserves support and a little bit of challenge. The idea about putting labels on things, such as listing the ingredients, I support fully because I think that lets people know what's in the product. But as a means of saying it will let the consumer look at that label and decide whether or not he wants the spray because it might affect the ozone layer -- I submit to you that once the gossip stops, no one will look for that word. But more importantly, and this came up yesterday, consumers are not very stupid, as you say, but they are ignorant. They do not have the technical knowledge to assess the literally hundreds of things that different industries and different agencies would like them to exercise when they buy their product. I've done a lot of research in this area, I'll tell you, and I'd be glad to discuss the details later, but if you ask consumers what they think about when they buy a product, they'll tell you price, color, and what my neighbor thinks. That's what's important. That's what they use to assess their decision making. If you ask them if safety's important, they'll say "Yes, safety's important, but I don't think about it when I buy a product." If you go further and ask the question why, the answer comes back, "I don't have to think about safety, the government's already taken care of that." Not only that, Sears and Ward and Penny and everybody else that markets the product wouldn't make a product to hurt. There is a certain brand identification and image. I'm serious that there is no thought about accepting the responsibility to look for the safety aspects of the product, and I can guarantee you that the majority of consumers in this country and in this room are very wise on some dimensions of product safety and quite ignorant about other dimensions of it. People don't have the time to sit there and try to go through all the machinations of trying to tell me which product is safest. So I think that the idea about let's stick a label on there is a good one for some reasons, but it's not going to be very successful if you want to get consumers to reject that product in order to save the ozone layer.

**J. Merritt:**

Without going into detail, our label covers ingredients which may have other impacts. For example, allergies and that sort of thing.


**Commissioner Pittle:**

Oh no, I'm not complaining against that, but I've got some concern about putting fluorocarbons explicitly on the label because right now there is a much more immediately observable effect of kids puffing on stuff, and they could go through the stores and say: "That's the one that I want. That's the one that has the fluorocarbons that I can get high on." That right now is a much more immediately observable effect. [Laughter].


**Larson:**

I'm with the Environmental Protection Agency and I'm the principal science advisor. I would like to make a comment with regard to the way regulations are handled at EPA. It's done totally openly. I realize there are people here who have not interacted with EPA and who may not know this, but some who have participated still think that decisions are made behind closed doors. First of all, we are required, this is an internal requirement, to come up with what we call a criteria document, which is a total body of knowledge containing defensible scientific information. We don't document everything that has been published on the subject, because many of you know that there is research that has been proven eventually to have much error in it, but the defensible scientific information is published in a document. We are not permitted to use unpublished data. Even if our own laboratories, for example, or if any other government laboratory or even if one of our grantees has done work that is very important, it is not permissible to be used for establishment of a regulatory decision unless it has been published and has withstood peer scrutiny. Sometimes we'll delay to get that information in and get peer review. If the scientific evidence shows that there is potential harm, based on whatever the pollution level in the environment is, it is this document that is then put forward to a steering committee of which one member is a scientist, part of the research arm, and the other members are all parts of the other organizations in EPA including the general council, the program offices, economists, what have you. It covers every single aspect. They again go through the total review of the problem including everything. Certainly the effect on the environment is the initial trigger, but the review considers the effect on the consumer, the effect on industry, the effect on labor, even the effect on a single town, if that is a one-industry town. When that is all over, and if the decision is made that we think we will regulate, we then hold public hearings. We will pass the document to our own science advisory board made of outside people -- people outside EPA -- and we will even circulate it to perhaps a hundred or so active academicians throughout the country who are experts in various aspects. When these comments come back, many times there is a total rerun, and this goes on until we think we really have a handle

on what the state of knowledge is. The same thing happens with regard to the total problem through public hearings. Finally, after one or more public hearings and many rewrites, the administrator, and by law he is the one to make the decision, will make the decision to regulate or not to regulate. In order to regulate he must hold another public hearing, open to the press and to the public, and announce his decision supported by full and immediately available documentation. Even after all this there is time before the regulation is implemente . We recirculate our decision and all the documents to all the other federal agencies, and sometimes to the states, and this process takes anywhere from 6 months to 9 months or even 18 months. Although as of now we have not initiated any regulatory action within EPA concerning this problem, let's assume we were to make a decision to regulate. We would publish the scientific criteria document, and again it would be opened to the comment and scrutiny of all the scientists who have previously participated. Even the public hearings are open to anyone who wants to come: housewives, retired people, teenagers. I don't know of any other agency that really conducts its business in an open manner. Thank you.

#### C. Bastian:

Thank you very much. That answers some questions that were raised yesterday.

#### Voice:

Commissioner Pittle disagrees.

#### F. Kaufman:

As the only remaining member of the Academy committee, let me make a few random remarks. The first one is that there's no doubt in my mind that I, and all of us, will be tarred and feathered, and I would like to ask the commissioner whether there is a non-carcinogenic tar that he could recommend. [Laughter, applause]

More seriously there are a few things that should be said, that are perhaps mildly alarming, and that seem to be falling through the cracks. First of all, I'm a little appalled at the total bias thing: let's let our bias hang out. I'm sure that Ralph, when he does his model calculations does not make them come out so as to make delta ozone be as large as possible because his bias is that it should be regulated. What we do talk about is that as private citizens we have our biases, and that's fine. But, as private citizens, as Commissioner Peterson has told us, and I fully agree with him, and by the way I agree with everything that has been said by everyone [laughter], that we're not here because we're private citizens, there are 210 million others, so what blows us up so much? We are here, presumably, or many of us, because we are scientists who are working on this as scientists and I hope we try to be unbiased. At least I tried very hard in my fight with Hal Johnston over whether the $HO_2$ rate constant is low or high. It is

entirely a scientific thing.  If it's high it will make the, uh, a wait a moment.  [Laughter]  If its low it makes the fluorocarbons bad.

I also resented a little bit Sherry's remark that none of us read the literature.  How could we?  We travel a lot.  I did find the one goof in his magnificent 33-page paper in a review of Geophysics, namely that C100 was not involved in equilibrium:  it doesn't have much to do with the problem.  Now, I did read this.  [Laughter]

One thing that I find has not been pointed out at all is the great pressure that was put on the Academy, when we were told that "Well, there is this 1 January, '78 deadline and before that there is that September '77 deadline.  These are God-given.  We must have certain results by then and, well, science be damned."  My feeling as part of the committee was that first of all I went through a nervous disorder with chlorine nitrate.  It was a terrible thing.  We had a document finished which had results which were even larger, we were told, and as a result there was a large uncertainty of 13% possible long-term deple-tion, and then chlorine nitrate appeared.  Sherry had told us about chlorine nitrate last summer, in our summer study in Snowmass, but he added, and I have it in my little notebook, that it will probably photolyze in a few minutes.  And I believed that I would have said the same thing.  Who would think that a substance like chlorine nitrate would not be rapidly photolyzed?  So then there is no point putting it in the models.  Now he [Sherry Rowland] and his group have studied it and strangely enough have found that it has a very small absorption coeffi-cient.  It does not photolyze.  Then came the period in March and April, when not only was that put into the whole chemical scene but then the modellers went berserk.  All of them.  [Laughter]  And I think your own calculations, Ralph, were that there were decreases of factors of 7 pos-sible, and a factor of 4 for another model; it ranged anywhere from 2 to 7 and it even got to the point where it became negative, where the decreases became negative.  Now should that be held against either us on the committee, or the scientific public in general?  No, because that's how science works.  We put something in, we try everything, and then we finally iron things out.  The trouble is when various people, some of my great friends in the audience, button-holed me with "When are you guys going to come up with your report?  What's holding you up?  How dare you?"  I remember at the AGU meeting in April a beautiful young lady, I forgot with whom she's associated, said "Well, you know you guys should be just lined up and thrashed."  [Laughter].

In the context, particularly of the chlorine nitrate phenomenon, I became extremely gun-shy in April, when I thought, "Well, let's go home, we don't know anything, and let's go, we have until August" (when the final document was written), and I could not quite live with any notion of having said, "We now do understand it," or "Let's forget about the tropospheric sinks, etc.," or "Let's say to go ahead and regulate." Now even then, the point is not sufficiently raised that perhaps we did a poor job in writing our report.  But it is only against our feelings, certainly mine; I don't want to speak for the other members that we are in a period of rapidly increasing knowledge.  Especially as atmospheric measurements go in the stratosphere, we are in the absolute infancy of what can be done and we now know that within a couple of years,

or maybe less, we will know a lot more. I've never heard this mentioned, and it is only in that context that I felt, "Well, let's tell the public that." I was not personally in favor of going into the regulation issue at all, because I thought it was really not our province, but the report did go into it, and apparently some people on the committee thought that we should go that far. I also want to make one last statement about that 2% number. The business of a 2% depletion as something we approve of, or that a reasonable person would approve of, I find is again, unfortunate if only in the context that 2% in the steady state after an infinity of years, which means approximately 1% in 50 years or 0.02% per year, was a title in effect that did not require action immediately and that we'd wait a while and see if science has something to get under control.

## C. Bastian:

Thank you.

We're going to have to have two very quick comments and then the closing remarks or people are going to miss their transportation to the airport. Sherry?

## S. Rowland:

I would like to comment on two things. One is that Jim King said that he was worried about the credibility of science, and I don't think the credibility of science is an absolute, inviolate thing, and it ought to be no more credible than how correct they are. Now I teach a course every once in a while at the University [laughter] in scientific controversy in which one of the things I do is to take _Time_ magazine from ten years ago and give each person in that class of 50 people a science article from that magazine which is wrong. And it's no problem getting 50 articles that turn out 10 years later to be wrong. I don't think the credibility of science could be accepted as being something that's any better than it is. And the fact that Ralph Cicerone found, as everybody did, that chlorine nitrate in certain models caused a big change in ozone depletion, that's actual scientific observation. When people announce at scientific meetings that the problem is gone away, and then that doesn't hold up, I think their credibility should be impugned. And there's no reason why we should defend the credibility of scientists who have made wrong statements.

## C. Bastian:

Thank you very much. Are there any really pressing questions? OK, one last comment.

**Kenneth Moe:**

I think there's a different kind of science which is not personal at all, which every scientist has, and that is: he views the world from the point of view of his own field. To me as a physicist, the world is physics. There's a little chemistry over here and a little engineering over there. Professor Kaufman might think the world is chemistry, with a little physics over here and a little something else over there. [Laughter].

In the beginning of the CIAP program, this was 5 years ago, I remember Bob Dickinson suggested that he felt that dynamics, the mechanical motions in the stratosphere, were at least as important as the chemistry. I feel that the dynamical aspects of the stratosphere are really not represented in the modeling, and I feel that that aspect has been neglected and really requires much more investigation before I can believe in the results of the modeling calculations.

**C. Bastian:**

We're going to have a few closing remarks for the conference from Dr. Noel Hinners, the associate administrator for Space Science at NASA.

**N. Hinners:**

Thanks Carroll. The plans for this conference were initiated somewhat over a year ago for reasons which I'll go into after I retire from the federal service. [Laughter].

At that time, many of us weren't sure of where it would go, what was happening in the world of stratospheric chemistry and research, and thought, "Well, yes, there could be a lot of good come out of such a conference." I think that has been very well proven in the last few days. I personally have been exceedingly happy with the tenure of the conference, and with the science discussion. There has been ample time for the papers to be heard, discussed, and for this interaction of the public policy makers, the decision makers if you will, with the science community. I think we all have a much better feel for what the process really is that works in this area. One of the reasons for the mix here is that it's a very rapidly moving field, and the only way that all of us keep up with it is to get it firsthand and not wait for the so-called refereed literature. I think I've learned a lesson here, with the Academy report coming out and with the comments on it. As NASA goes ahead with its assessment this next year, we are determined that it will be a technical scientific assessment, and that we will go through all sorts of pains to stay away from the social judgment issues. That's been our intent all along. It's going to need cooperation and input from all of you. NASA's already been hounding you and keeping you traveling. You'll have to continue to do that, since you're our experts in this area. I'm concerned that if and when regulation does start, there will be a perception in both the OMB (the Office of Management and Budget) and the Congress that, "OK the job is done; therefore the funding that has gone into this research can now go away." This had

drastic consequence for the CIAP program. After 3 years the funding was up; it was over and done with, and all of a sudden many of you were out in the cold with good research programs having started and no obvious future. It is my very firm intent to fight very hard to show the basic research part of our ongoing stratospheric program, and I know other agencies are going to do the same, so that we can go to Congress and say we must keep this activity up at a sensible level. We must build a research base so that the next time an assessment problem comes along we are better prepared to deal with it. Again, we'll need your help in making those arguments to keep a good solid basic research program going. I expect that we'll see then, as new problems come up, a variation within the total of the amount that we can dedicate to basic research, ongoing versus the assessment. I'm not too worried about that because I think the same people are involved, but as a problem comes up, we divert you from your lab work to going out and making more field measurements. We've got to make a very strong case for continuity and ongoing efforts so that 10 years from now we're not back in the same boat.

ABSTRACTS OF THE POSTER EXHIBITIONS

SECTION I

EXPOSITION ON MODELS AND THEORETICAL STUDIES

# ATMOSPHERIC PERTURBATION BY SUPERNOVA ULTRAVIOLET RADIATION

A. C. Aikin and T. Stecher
NASA/Goddard Space Flight Center
Greenbelt, Maryland

A supernova can release $3 \times 10^{50}$ ergs of energy within a period of 20 days. If this occurs in the vicinity of the solar system (10 to 50 par-sec) as much as 2 ergs/cm$^2$/sec/A will be deposited into the Earth's atmosphere and modification of the upper atmosphere will take place. The distribution of energy from a supernova can be characterized by a flat spectrum throughout the ultraviolet and visible wavelengths. The primary effect of this radiation will be dissociation of molecular oxygen in the stratosphere, mesosphere and thermosphere. Dissociation rates in the stratosphere are equivalent to those due to the sun; the solar rate is greatly exceeded in the mesosphere. At the same time the rate of ozone photolysis is reduced causing an increase in stratospheric ozone. This is in contrast to previous computations where only supernova gamma radiation was considered. In this instance atmospheric ionization creates nitric oxide, which destroys ozone. Observed supernova such as the event of AD 1006 occurred at such large distances ($1.5 \times 10^3$ parsec) that no significant change in the atmosphere took place.

# SPECTROSCOPIC AND KINETIC PROPERTIES OF THE ClO MOLECULE

D.M. Cooper, R.L. Jaffe, S.R. Langhoff, J.O. Arnold, and E.E. Whiting
Ames Research Center
Moffett Field, California

The results of four related studies conducted at Ames Research Center on the ClO molecule and the impact on the chemistry of the stratosphere are given in Figures 1 - 3. The work includes (1) calculations of the wavefunctions and properties of the $X^2\pi$ and $A^2\pi$ states, (2) measurements of the electronic transition moment of the $A^2\pi - X^2\pi$ band system, (3) theoretical predissociation rates of the $A^2\pi$ state, and (4) calculated rate constants for the reaction $ClO + O \longrightarrow Cl + O_2$.

Multiconfiguration, self-consistent-field plus configuration-interaction calculations (MCSCF + CI) were performed for the $X^2\pi$ electronic states of ClO. The calculated dissociation energy and dipole moment of the ground state ($X^2\pi$) were found to be in good agreement with previously published experimental values.

The electronic transition moment for the $A^2\pi - X^2\pi$ band system and its variation with internuclear distance were determined both theoretically and experimentally. The measurements were made in emission behind incident shockwaves in $Cl_2 - O_2$ gas mixtures. The temperature of the radiating gas was typically 3500 K. A comparison of the calculated and measured results showed excellent agreement. Also, the photodissociation cross-section for ClO was determined from the measurements and found to be in good agreement with existing data.

| ALTITUDE (km) | PREDISSOCIATION RATE (sec$^{-1}$) | PHOTODISSOCIATION RATE[a] (sec$^{-1}$) |
|---|---|---|
| 20 | $3.7 \times 10^{-5}$ | [b] |
| 25 | $5.9 \times 10^{-5}$ | [b] |
| 30 | $1.3 \times 10^{-4}$ | [b] |
| 35 | $3.6 \times 10^{-4}$ | $4.0 \times 10^{-8}$ |
| 40 | $9.2 \times 10^{-4}$ | $4.4 \times 10^{-6}$ |
| 45 | $2.0 \times 10^{-3}$ | $1.3 \times 10^{-4}$ |
| 50 | $3.2 \times 10^{-3}$ | $5.8 \times 10^{-4}$ |

[a]THE RATES INCLUDE CONTRIBUTIONS FROM WAVELENGTHS BETWEEN 2630 AND 2250 \

[b]NEGLIGIBLY SMALL

Figure 1. Rate constants for radiative dissociation of ClO
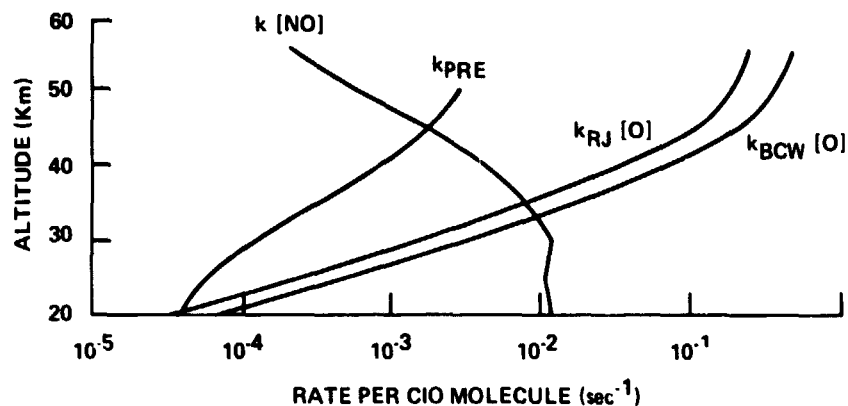
Figure 2.   Rates of different mechanisms for destruction of ClO.
The various plotted rates are for k [NO] destruction
by reaction with NO; $k_{PRE}$ destruction by radiation;
$k_{RJ}$ [O] reaction with O atoms (Jaffe theory, see
Figure 3); $k_{BCW}$ [O] reaction with O atoms using the
rate constant from Bemand, Clyne, and Watson.
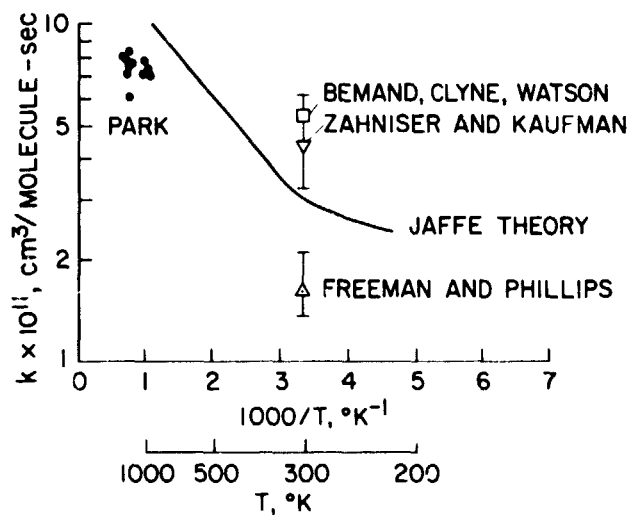


Figure 3.   Rate constants for ClO + O $\longrightarrow$ Cl + $O_2$.

A line-by-line absorption cross-section for the $X^2\pi - A^2\pi$ band system of ClO was determined from a combination of the aforementioned theoretical and experimental results. The estimated absorption cross-section was used in a radiative transport calculation with estimates of the solar flux (at a given solar zenith angle and season) to yield effective predissociation rate constants as a function of altitude (Figure 1). These rate constants were then incorporated into a one-dimensional chemical model to assess the impact of predissociation of ClO on the catalytic depletion of stratospheric ozone (Figure 2).

Finally, rate constants were calculated for the $ClO + O \longrightarrow Cl + O_2$ reaction between 220 and 1000 K (Figure 3). These rate constants, which are based on classical trajectory calculations, are slightly lower than the experimental rate data. An assessment of the importance of the above reaction in the chlorine-catalyzed ozone depletion problem was also performed.

# TOTAL OZONE TREND DETECTION CAPABILITY

William J. Hill, P. N. Sheldon, James J. Tiede

World-wide total ozone measurements have been statistically analyzed to estimate the trend detection and early warning capability provided by the data if ozone depletion theories are correct. Based on a sample of globally distributed ozone stations, a yearly global ozone change of one quarter of a percent persisting over six years would be judged statistically significant, if it were to occur, and would give an early warning equal to a 1.5% change. There is a potential for detecting even smaller changes by using data from all the current land-based stations. The analysis shows no evidence of an abnormal global trend persisting in the 1970's.

# $NO_x$/HCl DEPOSITION IN THE STRATOSPHERE
# BY THE SPACE SHUTTLE SOLID ROCKET MOTORS

B. Hwang
AeroChem Research Laboratories, Inc.
Princeton, New Jersey

The effects of the Space Shuttle solid rocket motor exhaust plumes on stratospheric $NO_x$ and HCl deposition rates are analyzed. Chamber, nozzle and plume calculations have been made which account for the coupled effects of nonequilibrium chemistry, gas/particle nonequilibrium, plume shock (including the Mach disc), and after-burning. Detailed comparisons are made between stratospheric deposition rates using the baseline SRM propellant and an "alternate" propellant which replaces ammonium perchlorate by ammonium nitrate in order to reduce the total amount of HCl in the exhaust. It was found that the total $NO_x$ deposition rate is approximately the same for each propellant, ranging from $\approx 0.02$ tons/mk at 15 km to $\approx 0.004$ tons/km at 30 km. For both propellants the ratio of $NO_x$ to total chlorine-containing species deposition rates is negligibly small, on the order of $10^{-2}$ for the baseline propellant and ranging from $10^{-1}$ to $10^{-2}$ for the alternate propellant. It is concluded that the alternate propellant, although it contains a large amount of ammonium nitrate, will not increase stratospheric $NO_x$ deposition rates.

# A ONE-DIMENSIONAL CHEMICAL MODEL OF THE STRATOSPHERE INCLUDING THE EFFECTS OF CONTINUED USE OF FLUOROCARBONS ON OZONE

Robert Kurzeja
Advanced Study Program
National Center for Atmospheric Research
Boulder, Colorado

A one-dimensional model of the stratosphere is presented which investigates the present-day and fluorocarbon-polluted stratosphere. The model includes the effects of diurnal variations and scattering on stratospheric chemistry and employs globally averaged chemical production rates to determine the distributions of transported chemicals. The calculated ozone mixing ratio was larger than the observed amount at all altitudes. In the lower stratosphere this discrepancy is probably the result of inherent limitations in the one-dimensional modeling of stratospheric transport, while in the upper stratosphere it may be due to errors in ozone observations or photochemical input data, or insufficient concentrations of nitrogen or chlorine compounds.

When $ClONO_2$ was not included in the calculations, HCl volume mixing ratios of 0.9 and 1.3 ppm were obtained at 25 and 35 km, respectively, for the present-day stratosphere. When $ClONO_2$ was included, these amounts were reduced to 0.5 and 1.0 ppm.

The time-dependent behavior of the stratosphere was studied subject to continued use of fluorocarbons. The model indicates that if present trends in fluorocarbon manufacture continue, reductions in the ozone column of 11% ($ClONO_2$ not included) and 8% ($ClONO_2$ included) by 1996 can be expected.

# STRATOSPHERIC ClO*: ITS PROBABLE ALTITUDE DISTRIBUTION
## AND POSSIBLE SIGNIFICANCE FOR CHEMISTRY
## AND REMOTE SENSING

Sheo S. Prasad
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Molecular dynamical considerations suggest that the reaction between $Cl$ and $O_3$ may produce $ClO$ with high effective vibrational temperature. Since $\omega e(N_2$ or $O_2) \gg \omega_e(ClO)$, pure V-V deactivation of $ClO^*$ by the major atmospheric constituents $N_2$ or $O_2$ could be quite inefficient. The population of $ClO^*$ will be then most probably controlled by its quenching collisions with the minor species ($O_3$, $NO$, etc.), and the deactivation through the possible formation of a $ClO$ collision complex. Thus, it is possible that sufficient amounts of $ClO^*$ may be present in the atmosphere to allow a simultaneous ground-based remote sensing of $O_3$ and $ClO$ column content as implied by Nicholl's reinterpretation of the Brewer et al. Umkehr measurements. In the absence of direct experimental data on any of the parameters involved, qualitative considerations based upon experience with similar species are used to speculate upon the probable altitude profile of $ClO^*$. The possible formation of a $ClO_3^*$ collision complex suggests that stable $ClO_3$ may be formed after stabilization by a third body. The yield of $ClO_3$ in this manner will depend upon several things, including $\Delta H_f(ClO_3)$ and the ratio S/D applicable to $ClO_3^*$. The significance of $ClO_3$ in the stratosphere may lie in its possible elimination as $HClO_4$ in the manner suggested by Samonaitis and Heicklen. Furthermore, photodissociation of $ClO_3$ could also yield odd oxygen atoms.

# TEMPERATURE RESPONSE TO STRATOSPHERIC OZONE FLUCTUATIONS

S. Stanulonis and J. W. Chamberlain
Dept. of Space Physics & Astronautics
Rice University
Houston, Texas

We have investigated the extent to which temperatures in the lower stratosphere are controlled by the absorption of solar and ground radiation by ozone. From the daily temperatures observed, a temperature-fluctuation cycle of a few days was indicated and the expected heating associated with local ozone increases was calculated. Responses at different heights are assumed to be correlated over height intervals of a few kilometers. The theoretical estimates were then compared to a regression analysis of total ozone and local radiosonde temperature at 150, 100, 50, 30. 20, and 10 mb at 13 northern hemispheric stations at the different heights. The stations ranged in latitude from Mauna Loa, Hawaii, to Resoluete, Canada. The tendency for temperature to be governed by the abundance of ozone will be discussed.

# UNCERTAINTY IN STRATOSPHERIC OZONE PERTURBATION PREDUCTIONS DUE TO UNCERTAINTIES IN REACTION RATES

R. S. Stolarski and D. M. Butler
NASA/Goddard Space Flight Center
Laboratory for Planetary Atmospheres
Greenbelt, Maryland

R. D. Rundel
NASA/Johnson Space Center
Houston, Texas

A one-dimensional steady-state stratospheric model has been used to investigate the effect of reaction rate uncertainties on the prediction of ozone perturbations due to chlorine injections and on the prediction of ambient minor constituent concentrations. This is accomplished by assigning to each reaction rate a gaussian probability distribution in log space whose half-width is the estimated one-sigma experimental uncertainty. A Monte-Carlo scheme is then used to propagate these distributions through an entire model calculation. Several hundred model runs are made with each of 48 reaction rates being simultaneously varied according to their individual probability distributions. Resulting distributions of calculated ambient concentrations, concentration ratios, and ozone perturbations due to a 1 ppb ClX injection are shown. Correlations of the variations in these parameters are made and demonstrate many of the cause-effect relationships discussed by other authors. The probability distribution for column ozone perturbation is fit with a gaussian distribution in log space on each side of the mean value. The correspondence to a gaussian is better on the high side, where a one-sigma uncertainty of a factor of 2 is found. Reduction of the uncertainties on all laboratory kinetics data to $\pm 15\%$ would reduce the ozone perturbation uncertainty to $\sim \pm 30\%$.

# A ONE-DIMENSIONAL MODEL FOR THE STRATOSPHERIC AEROSOL LAYER

R. P. Turco
R & D Associates
Marina del Rey, California

P. Hamill, O. B. Toon and R. C. Whitten
NASA Ames Research Center
Moffett Field, California

The origin, composition and general characteristics of the stratospheric aerosol layer are of considerable interest.  It is generally believed that the aerosol particles are $H_2SO_4$ - $H_2O$ solution droplets, that volcanic activity is a major influence on the layer, and that the position of the layer is closely related to tropopause height.  We have recently developed a one-dimensional model of the sulfate aerosol which predicts particle concentrations, size distributions and the position of the particle layer as a function of time and tropopause altitude.  Results (Figures 1 and 2) are in good agreement with observations.  In the model, $H_2SO_4$ is produced by gas phase reactions from $SO_2$.  The sulfuric acid vapor nucleates heterogeneously onto pre-existing Aitken nuclei and subsequently the particles grow by heteromolecular condensation and coagulation.  Eddy diffusion and gravitational sedimentation of the particles are also considered.  The model gives insight into the relative importance for the aerosol properties of condensation nuclei size distributions and concentrations, particle growth mechanisms and removal processes.  The response of the layer to volcanic activity has been modeled and results for volcanically quiescent and active periods are reported.
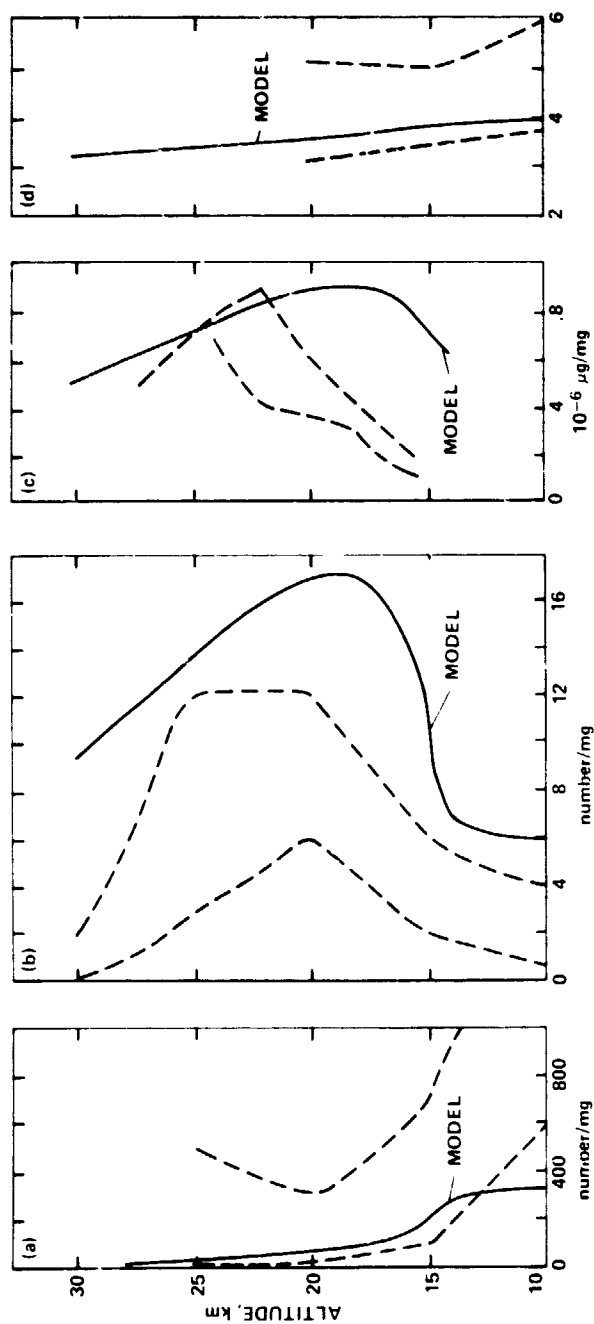
Figure 1 (a). Total number mixing ratio (particles/mg) from model (solid curve) and from observations (Kaselau et al., PAGEOPH 112, 877-885, 1974; Cadle and Grams, Revs. Geophys. 13, 475-501, 1975). (b) Mixing ratio (number/mg) for particles with radius greater than 0.15 μm from model (solid curve) and observation (Hofmann et al., J. Atmos. Sci. 32, 1446-1456, 1975). (c) Mass mixing ratio (10-6 μg/mg) from model (solid curve) and observations (Lazrus and Gandrud, J. Geophys. Res. 79, 3424-3431, 1974). (d) Ratio of number of particles with radius greater than 0.15 μm to number of particles with radius greater than 0.25 μm from model (solid curve) and observations (Pinnick et al., J. Atmos. Sci. 33, 304-314, 1976).
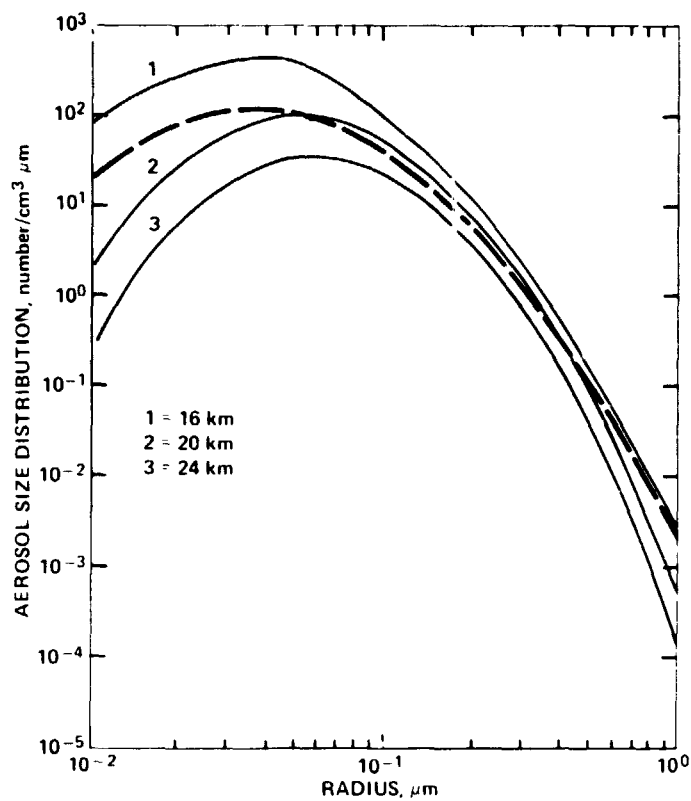
Figure 2. Model predicted size distributions at 16, 20, and 24 km. Dashed line is ZOLD curve (Toon and Pollack, J. Appl. Met. 15, 225-246, 1976) fitted to 20 km prediction at 0.05 μm.

# THE IMPACT OF ANTHROPOGENIC SOURCES OF FREONS (CHLOROFLUOROMETHANES) ON THE MERIDIONAL STRUCTURE OF THE STRATOSPHERE & OZONE DISTRIBUTION

R. K. R. Vupputuri

Atmospheric Environment Service

4905 Dufferin Street, Downsview, Canada

A zonally averaged model of the stratosphere including radiative heating and photochemistry in oxygen-hydrogen-nitrogen-chlorine atmosphere is used to investigate the effects of anthropogeneous sources of Freons on stratospheric ozone and its climate. The photochemical reactions and the reaction rate constants adopted for this particular investigation are those recommended in the NAS report on halocarbons. By specifying the lower boundary fluxes of chlorofluoromethanes based on current production rates near the earth's surface, the steady state meridional distributions of $CF_2Cl_2$ (Freon 12), $CFCl_3$ (Freon 11) and $Cl_x$ (Cl, ClO, hCl) are deduced in a self-consistent manner taking into account the main interactions among the principal trace gases ($O_3$, $HO_x$, $NO_x$ and $Cl_x$) and the feedback effects of disturbed temperature and circulation fields. Changes in the meridional distributions of ozone, $HO_x$, $NO_x$ and temperature resulting from the introduction of chlorofluoromethanes and their dissociation products are investigated in the same experiment. It is found that the chlorine compounds which result from the injection of chlorofluoromethanes into the stratosphere can lead to significant changes in the meridional distribution of ozone and temperature in the upper stratosphere. The meridional variation of the percentage decrease in the total ozone given in Figure 1 shows that the depletion of the total ozone column ranges from 7 to 10% depending upon the latitude and season, with a globally averaged value of roughly 8%. It is shown that the feedback effects of the changes in $HO_x$, $NO_x$ and the disturbed temperature and circulation fields are factors also contributing to the net total ozone depletion. The experiments also indicate that the introduction of additional chlorine compound $ClNO_3$ to the chlorine compound $ClNO_3$ to the chlorine chemistry has the effect of reducing the total ozone depletion by a factor of about 1.4.
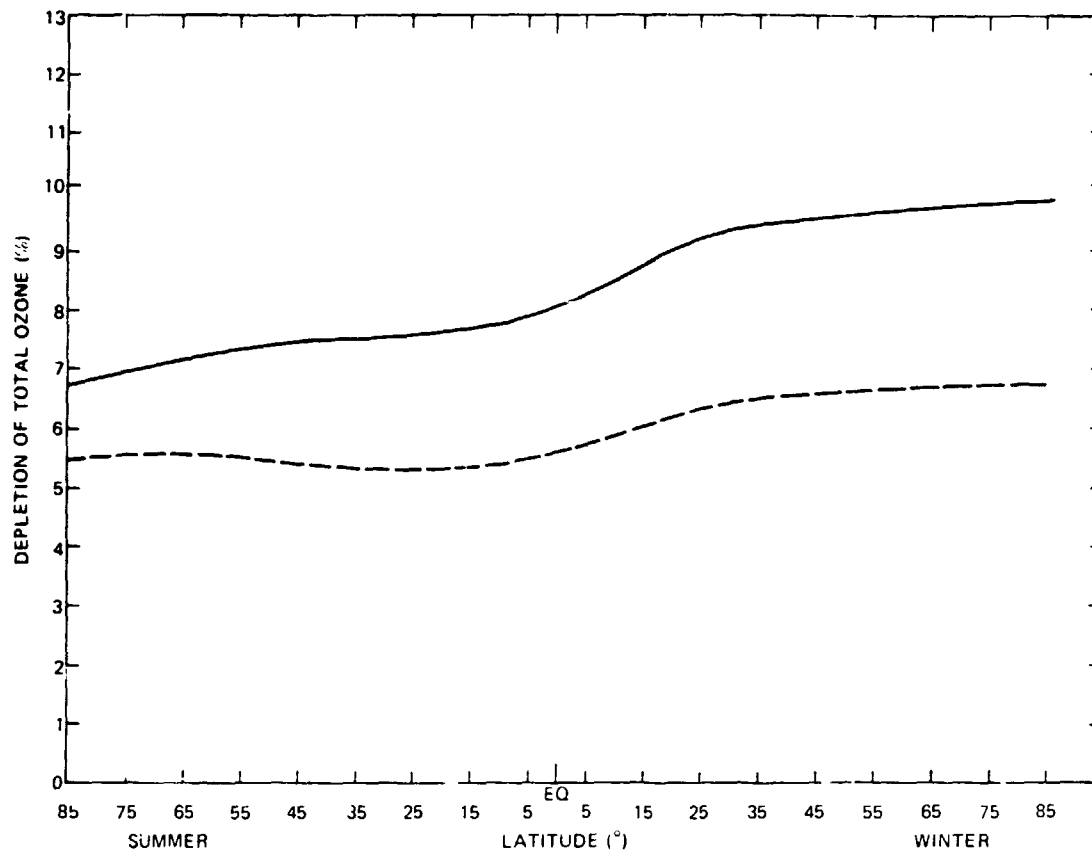
Figure 1.  Latitudinal variation of percentage depletion of
total ozone column due to the introduction of
chlorofluoromethanes and chlorine compounds
(solid line).  Dashed line represents the effect
$ClNO_3$ has on ozone depletion.

# A TWO-DIMENSIONAL MODEL STUDY OF STRATOSPHERIC TRACE CONSTITUENTS

R. C. Whitten, W. J. Borucki, and V. R. Watson
NASA-Ames Research Center
Moffett Field, California

C. A. Riegel and L. A. Capone
San Jose State University
San Jose, California

A two-dimensional model is described which simulates the merid-
ional winds and eddy transport as well as the chemistry of the odd-
oxygen, odd-hydrogen, odd-nitrogen, chlorine and carbon systems.  The
transport data have been selected such that (a) the bulk motion is in
good agreement with observed wind systems, and (b) the bulk motion and
eddy coefficient data yield tracer distributions that agree well with
observation.  The transport as well as chemical production and loss
mechanisms for odd-nitrogen, odd-hydrogen, chlorine and carbon species
are discussed.  We find that predicted seasonal and latitudinal varia-
tions of minor constituents agree reasonably well with observed data
currently available.

# LATITUDINAL AND TEMPORAL VARIATIONS OF STRATOSPHERIC TRACE GASES: IMPLICATIONS FOR OZONE PERTURBATION THEORIES

S. C. Wofsy, M. B. McElroy, and M. J. Prather
Center for Earth and Planetary Physics
Howard University, Massachusetts

Present photochemical theories provide reasonably good quantitative understanding of observations of OH, $NO_x$ and HCl distributions in the stratosphere and mesosphere. The calculations demonstrate the need for including planetary backscatter and proper diurnal integration in attempting to understand these distributions. Results are given in Figures 1 - 5 for observed and yet-to-be observed species.
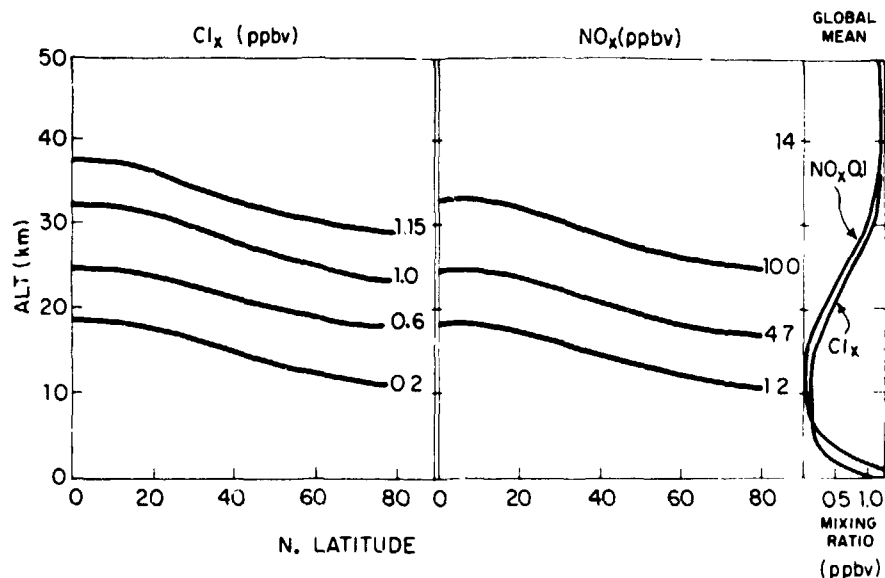


Figure 1.   The results are shown for our model with "low" values of $NO_x$ and $Cl_x$. The global mean profiles (right panel) are calculated from a 1-D transport model, then projected along the preferred mixing surfaces to obtain the 2-D profiles (left and center panels) (Wofsy, S. C., 1976: "Interactions of $CH_4$ and CO in the Earth's atmosphere," Ann. Rev. Earth Planet Sci. 4, 441-469). Nitrous oxide is the assumed precursor of $NO_x$ and $CH_3Cl$, F-11, F-12 and $CCl_4$ the precursors for $Cl_x$.

SUMMER PROFILES (NOON)
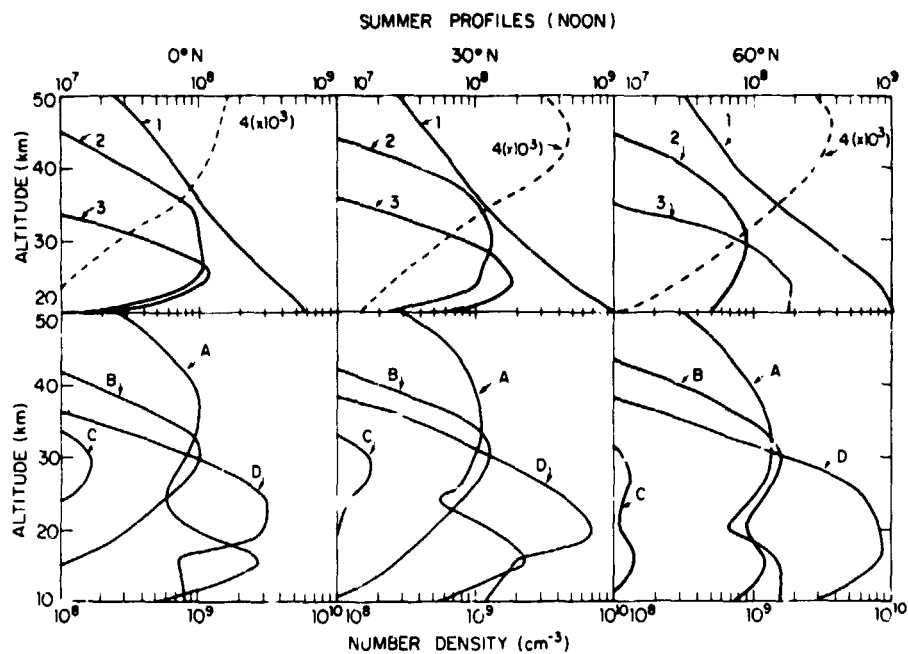
Figure 2. Summer noon profiles are shown for $NO_x$ and $Cl_x$
species. A, NO; B, $NO_2$; C, $N_2O_5$; D, $HNO_3$; 1, CH1;
2, ClO, $ClNO_3$; 4, Cl. Note the variation in shape
and magnitude of the $HNO_3$ layer, and the analogous
$ClNO_3$ layer, as a function of latitude.
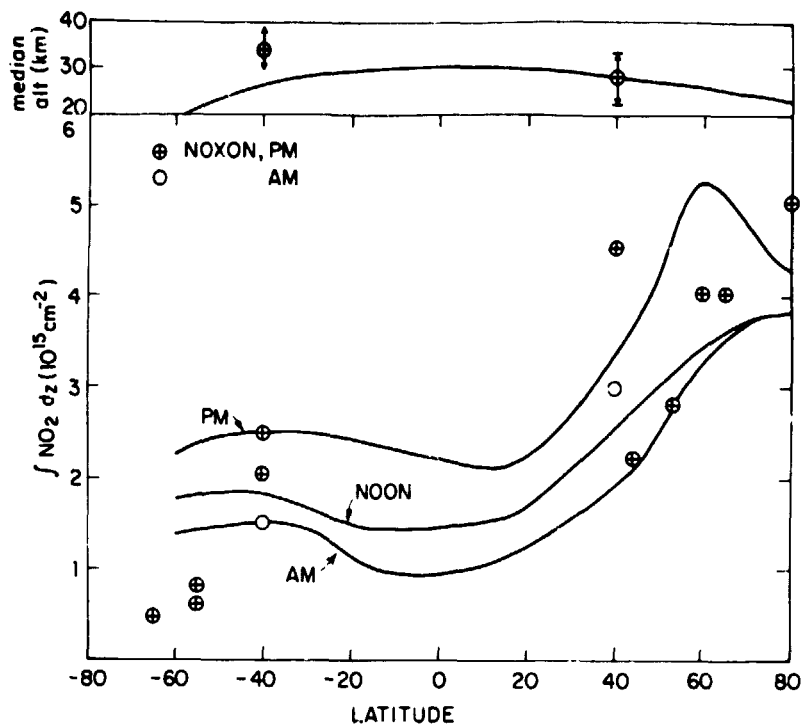
Figure 3. Latitude cross-sections are shown for NO₂
column abundance 1/2 hour before and after
sunset and at noon. Summer conditions are
well-represented by the calculations, but
winter NO₂ exhibits a sharp drop north of
40°. Most likely this is due to slow con-
version of NO$_x$ into HNO₃, which has very
long lifetimes due to the low sun angles in
this region. Noxon (1976) also has equatorial
data showing that the equatorial stratosphere
is somewhat impoverished in NO$_x$, implying that
the present mixing surfaces are inadequate in
a narrow range of equatorial latitudes.
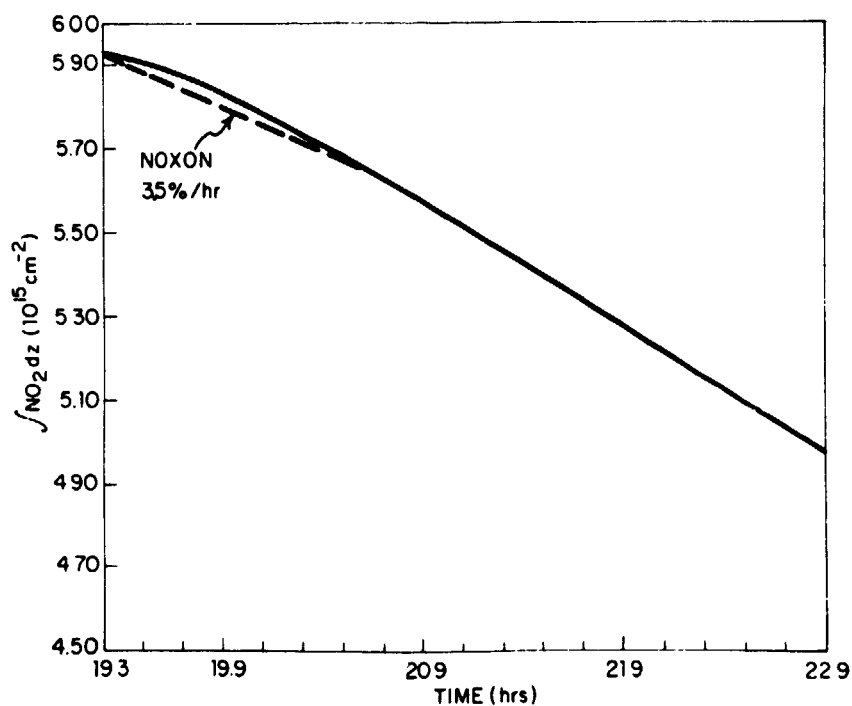
Figure 4.   The calculated night-time decay of $NO_2$ after
sunset is compared to Noxon's (1976) observa-
tions, showing excellent agreement.   The dis-
appearance of $NO_2$ is a measure of the height-
integrated rate of the slow reaction

$$NO_2 + O_3 \longrightarrow NO_3 + O_2,$$
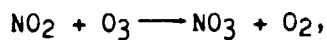
which is immediately followed by

$$NO_2 + NO_3 \xrightarrow{\text{M}} N_2O_5.$$
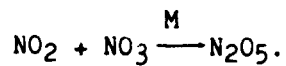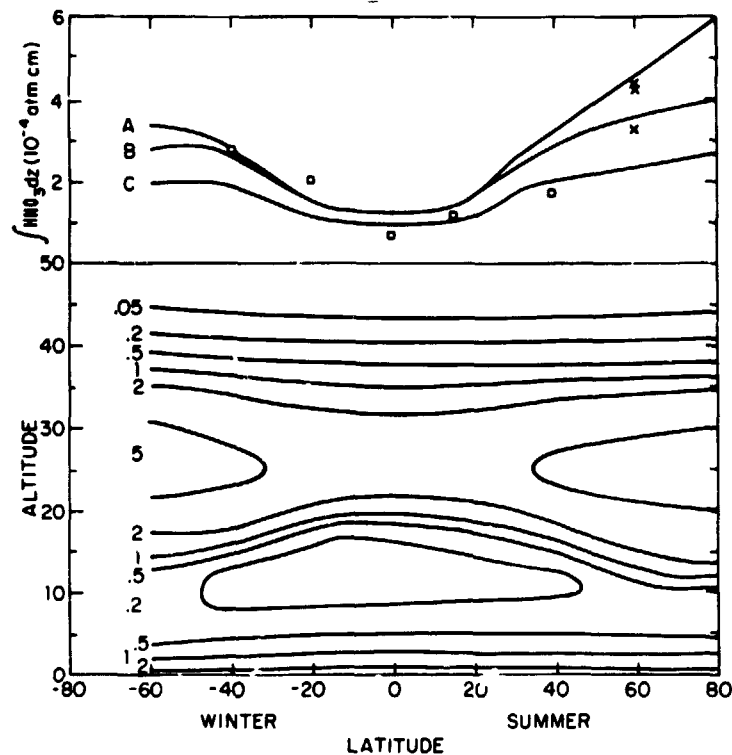
Figure 5.  Latitudinal cross sections for $HNO_3$ are shown.
In the lower panel, mixing ratio contours
(ppbv) are given.  The upper panel presents
column abundances above various altitudes:
A, whole stratosphere; B, 16 km; C, 20 km.
The squares are data by Murcray et al. (1976)
for 18 km, which should fall between B and C.
Winter high latitudes show excess $HNO_3$,probably
due to conversion of $NO_x$ into $HNO_3$.  Equatorial
data shows effect of $NO_x$-poor air where tropo-
spheric air is flowing into the stratosphere
(cf. caption to Figure 3).

# A COUPLED CHEMISTRY AND RADIATION TRANSPORT MODEL
# FOR THE TROPOSPHERE AND STRATOSPHERE

J. Zinn and C. D. Sutherland
University of California,
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

We have constructed a coupled 1D computer model of atmospheric chemistry, radiative transport, vertical expansion/contraction, eddy diffusion and precipitation, including diurnal and seasonal variations, with latitude as a parameter. The radiative transport model includes $10^5$ vibration-rotation transitions of $CO_2$, $H_2O$, and $O_3$, using an analytic approximation for the transport in individual spectral lines. The interactions between changing temperatures and changing $O_3$ concentrations are computed, as are the interactions between temperatures and precipitation rates. The rates of $HNO_2$ and $HNO_3$ removal are calculated from the precipitation rates. Tropospheric eddy diffusion coefficients are computed from computed convective neat transfer rates. Computed results are shown for the normal atmosphere and for perturbations produced by $NO_x$ enhancements.

SECTION II

EXPOSITION ON INSTRUMENTS AND STRATOSPHERIC MEASUREMENTS

# INITIAL MEASUREMENTS OF ATOMIC OXYGEN, HYDROXYL, ATOMIC CHLORINE AND CHLORINE OXIDE IN THE STRATOSPHERE

J. G. Anderson

Department of Atmospheric and Oceanic Science
Space Physics Research Laboratory
University of Michigan
Ann Arbor, Michigan

A technique employing atomic and molecular resonance fluorescence is used to determine the in situ concentration of several atoms and diatomic radicals in the region between 20 and 50 km in the earth's atmosphere. Two measurements were made of atomic oxygen on 25 November 1974 and 7 February 1975 (Figure 1), two measurements of hydroxyl on 18 July 1975 and 12 January 1976 (Figure 2), a single measurement of ClO on 15 May 1976 and a simultaneous measurement of Cl and ClO on 28 July 1976 (Figure 3). Atomic oxygen is found to decrease from $3 \times 10^9$ atoms $cm^{-3}$ at 43 km to $6 \times 10^7$ $cm^{-3}$ at 25 km. Hydroxyl is found to decrease from $3 \times 10^7$ $cm^{-3}$ at 43 km to $4 \times 10^6$ $cm^{-3}$ at 30 km. Atomic chlorine was found to decrease from $2 \times 10^6$ $cm^{-3}$ at 42 km to $4 \times 10^5$ $cm^{-3}$ at 35 km while ClO, simultaneously determined was found to increase from $3 \times 10^7$ $cm^{-3}$ at 41 km to $4.5 \times 10^8$ $cm^{-3}$ between 35 and 29 km decreasing to $1 \times 10^6$ $cm^{-3}$ at 26 km.
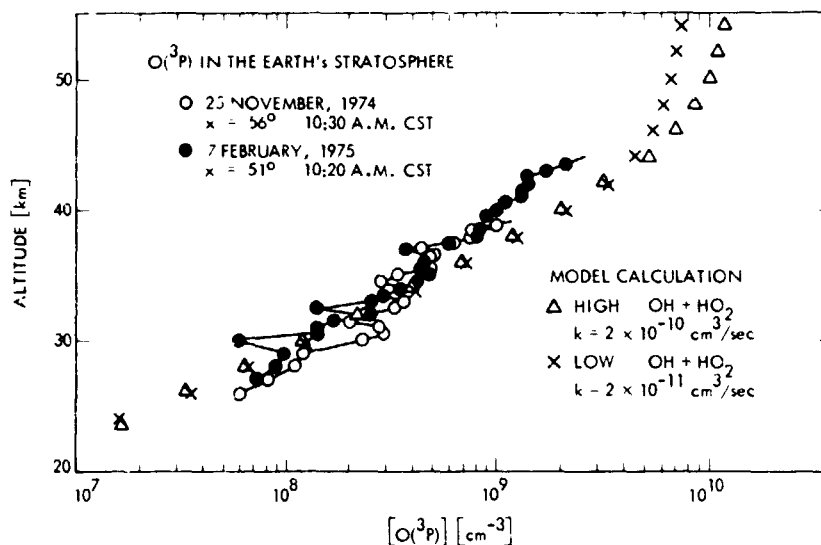


Figure 1. Two experimental measurements of $O(^3P)$ concentrations in the stratosphere compared to two model calculations using different values for the rate constant of the reaction $OH + HO_2$.
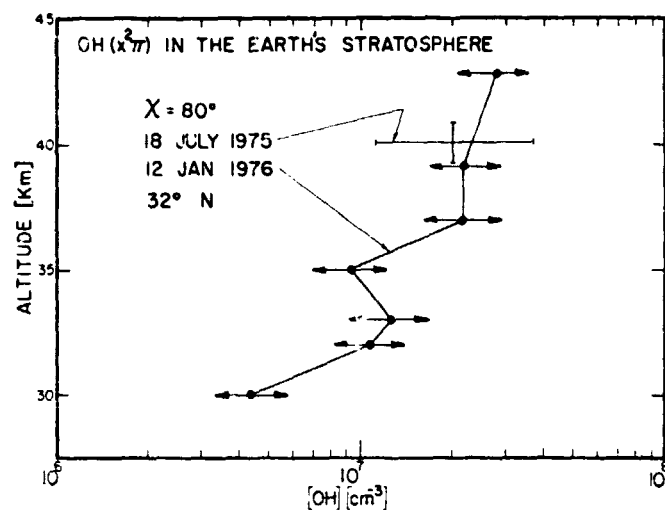
Figure 2.  Two experimental measurements of OH
concentrations in the stratosphere.
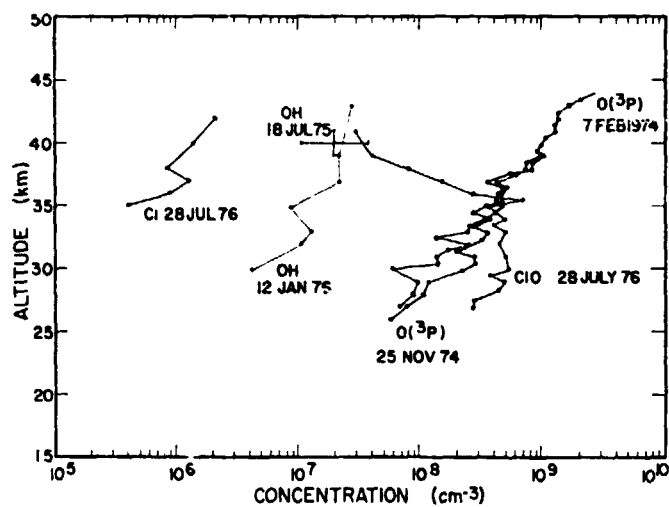


Figure 3.  Experimental measurements of $O(^3P)$, OH,
Cl and ClO concentrations plotted on the
same altitude scale.

GROUND-BASED MICROWAVE MONITORING OF STRATOSPHERIC
TRACE GAS:  A PROGRESS REPORT FROM THE
BATTELLE GROUP

P. A. Ekstrom and K. C. Davis
Battelle Memorial Institute
Pacific Northwest Laboratories
Richland, Washington

Ground-based microwave measurements of atmospheric absorption can
in principle provide a sensitive quantitative analysis of stratospheric
trace gases.  In practice, spectrometer baseline problems limit the
sensitivity for measurements made with large Cassegrain reflector
antennas.  The magnitude of the problems was clearly revealed in an
attempt to determine the amount of stratospheric ClO by an absorption
measurement against the solar continuum.  A second observing mode using
frequency-switched emission measurements at several fixed elevations
resulted in flatter baselines and has yielded an upper limit for ClO of
100 times current model predictions only after extensive data proces-
sing.  A more promising technique consists of making emission measure-
ments while rapidly beam-switching in elevation using a physically small
horn antenna.  Such an experiment is in preparation at Battelle
Observatory and promises sensitivities comparable to or less than
current model predictions.

# INSOLUBLE NUCLEI IN STRATOSPHERIC AEROSOLS

Neil H. Farlow
NASA-Ames Research Center
Moffett Field, California

Dennis M. Hayes and Homer Y. Lem
L.F.E. Corp.
Richmond, California

Collections of stratospheric aerosols have been made on special surfaces exposed from U-2 aircraft to enable isolation and detection of insoluble nuclei. These surfaces are coated with a water-soluble film that absorbs soluble portions of the particles while leaving insoluble nuclei visible on the surface. Because the soluble film does not chemically react with the liquid portion of the aerosol particles, no crystalline reaction products are formed to hamper visualization of the insoluble nuclei in the electron microscope. Conventional collecting surfaces are flown simultaneously with the soluble films to allow comparisons of unabsorbed particles with the altered ones to determine if insoluble nuclei are essential nucleating agents for stratospheric aerosols. The changing content of insoluble nuclei with time and altitude after volcanic eruptions is shown, and the association of these nuclei with individual stratospheric particles is detailed.

# EFFECTS OF THE ERUPTION OF ST. AUGUSTINE
## VOLCANO ON STRATOSPHERIC AEROSOLS

Guy V. Ferry and Neil H. Farlow
NASA-Ames Research Center
Moffett Field, California

Homer Y. Lem
L.F.E. Corp.
Richmond, California

The St. Augustine volcano on Augustine Island, Alaska, USA, erupted January 22-24, 1976. A stratospheric aerosol collection instrument flown daily on a U-2 during this period detected a change in the stratospheric aerosols 11 days after the eruption. The change was very minor in extent and duration compared to the changes caused by Volcan de Fuego which erupted in November 1974. The volume of stratospheric aerosols was doubled as a result of the St. Augustine eruption and the aerosols were much more fluid. The effects of the St. Augustine eruption were noted for only a few days. Changes in the stratospheric aerosols are reported with respect to time and altitude.

Efforts to bracket the expected increase of stratospheric aerosols caused by the St. Augustine volcano revealed the highly volatile nature of stratospheric aerosols. Changes in the collected aerosols caused by the evaporation of volatiles from the aerosols put previously published size distributions in serious doubt.

# SIMULTANEOUS MEASUREMENTS OF NITROGEN DIOXIDE AND
# NITRIC ACID IN THE LOWER STRATOSPHERE

Andre Girard, Jean-Claude Fontanella, Renee Giraudet,
and Nicole Louisnard
Office National d'Etudes et de Recherches Aerospatiales (ONERA)
92320 Chatillon, France

Simultaneous measurements of nitrogen dioxide and nitric acid (Table 1) have been performed at 15°, 45° and 65° north latitude. The equipment is an airborne grille spectrometer. For the measurements condition (at sunset) the ratio $NO_2/HNO_3$ is near 0.1 in the lower stratosphere. The validity of an estimate of the concentration of the OH radical deduced from this ratio is discussed (Table 2 and Figures 1 and 2).

Table 1. Measurements of $NO_2$ and $HNO_3$ in the lower stratosphere

| Latitude | Altitude, km | Tropopause altitude, km | Season | $NO_2$ | | $HNO_3$ | | $\dfrac{[NO_2]}{[HNO_3]}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | $mol.cm^{-3}$ | Mixing ratio | $mol.cm^{-3}$ | Mixing ratio | |
| 45 N | 15.5 | 11[a] | summer | $1.3.10^9$ | $3.5.10^{-10}$ | $10^{10}$ | $2.7.10^{-9}$ | 0.13 |
| 45 N | 11 | 10[a] | winter | $1.2.10^9$ | $1.6.10^{-10}$ | $1.1.10^{10}$ | $1.4.10^{-9}$ | 0.11 |
| 65 N | 12 | 8[b] | summer | $3.10^9$ | $4.6.10^{-10}$ | $2.8.10^{10}$ | $4.3.10^{-9}$ | 0.11 |
| 15 N | 12.6 | 15.6[a] | spring | $1.3.10^9$ | $2.2.10^{-10}$ | $2.10^9$ | $3.3.10^{-9}$ | 0.65 |

[a]Measurement (meteorological sounding)

[b]Mean value

Number densities at flight altitude

Table 2. Values used for indirect determination of OH concentrations

| Altitude, km | Troposphere | Stratosphere, km | | | | |
|---|---|---|---|---|---|---|
| | 12 | 15 | 20 | 25 | 30 | 35 |
| $k_2/k_1$ | | 0.04 | 0.05 | 0.08 | 0.13 | 0.24 |
| $10^{-6} J_3/k_1$ (a) | | 0.30 | 0.55 | 3.5 | 25 | 104 |
| [NO$_2$]/[HNO$_3$] (b) (measurements) | 0.10 | 0.10 | 0.10 | 1 | >5 | >10 |
| [OH] $\times 10^6$ (estimated) | | 4.6 | 11 | 3 | <3 | <5 |
| [OH] $\times 10^6$ (measurements) | 2 a 6$^c$ | | | | 4$^d$ | 10$^d$ |

aThese values of $J_3$ are valid for midday, mid latitude, equinox ($J_3 = 9.5 \cdot 10^{-7} \text{sec}^{-1}$ at 15 km).

bResults of the measurements of this work.

cUniversity of Maryland (October 1975).

dJ. G. Anderson. University of Michigan (July 18, 1975).

$$OH \; + \; NO_2 \; \longrightarrow \; HNO_3 \qquad (k_1)$$

$$OH \; + \; HNO_3 \longrightarrow H_2O \; + \; NO_3 \; (k_2)$$

$$HNO_3 \; + \; h\nu \; \longrightarrow \; OH \; + \; NO_2 \; (J_3)$$
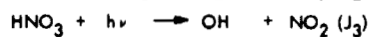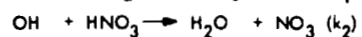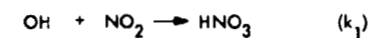
$$\frac{[NO_2]}{[HNO_3]} = \frac{k_2}{k_1} + \frac{J_3}{k_1[OH]}$$

Figure 1.  Production and destruction scheme of HNO₃
used to deduce concentrations of Oh.
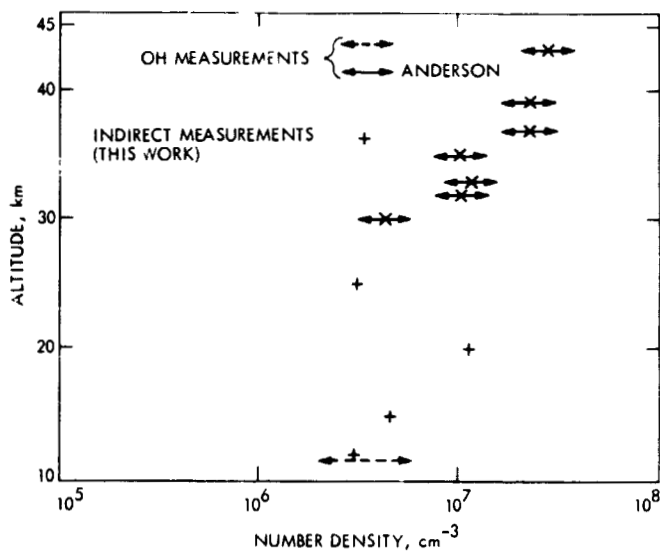


Figure 2.  Present indirect measurements of OH
concentrations compared to direct
measurements of Anderson.

# MICROWAVE TECHNIQUES FOR MEASURING STRATOSPHERIC ClO

R. K. Kakar and J. W. Waters
Jet Propulsion Laboratory
Pasadena, California

Measurement of stratospheric ClO is presently needed in order to assess the extent to which stratospheric ozone is reacting with chlorine. Because the ClO molecule has rotational spectral lines at millimeter and submillimeter wavelengths, microwave remote sensing techniques can in principle be used to measure ClO in the stratosphere. These techniques are discussed. The sensitivities for various observation modes and for both present and expected future state-of-the-art instrumentation are given.

# GEOGRAPHICAL VARIATIONS OF NO AND O$_3$ IN THE LOWER STRATOSPHERE

Max Loewenstein, H. F. Savage, and J. G. Borucki
NASA-Ames Research Center
Moffett Field, California

Nitric oxide and ozone concentrations in the lower stratosphere have been measured from a high altitude research aircraft using *in situ* measuring techniques. Results of several geographical surveys are presented here along with predictions of the Ames two-dimensional stratospheric model (Figures 1 - 6)

Meridional and zonal data were obtained in June 1974 and in June, July, and August 1975. At longitudes 122-158°W the meridional data taken between 5° and 80°N latitude show an increasing NO concentration with latitude, by a factor of 4 at 21 km altitude and a less marked increase at 18 km. The minimum NO concentration at 21 km is observed at 5°N latitude and is about $6 \times 10^8$ cm$^{-3}$. Zonal data at latitudes 22° - 38°N taken from 55° to 176°N longitude show little variation of the NO and O$_3$ concentrations with longitude.
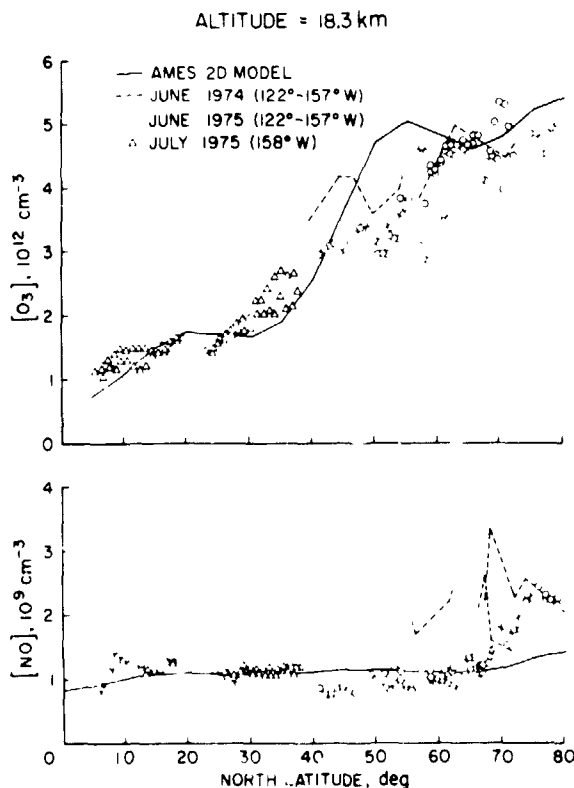
ALTITUDE = 18.3 km



Figure 1. Results of the meridional survey of O$_3$ and NO at 18.3 km altitude, 158°W longitude compared with the two-dimensional model.
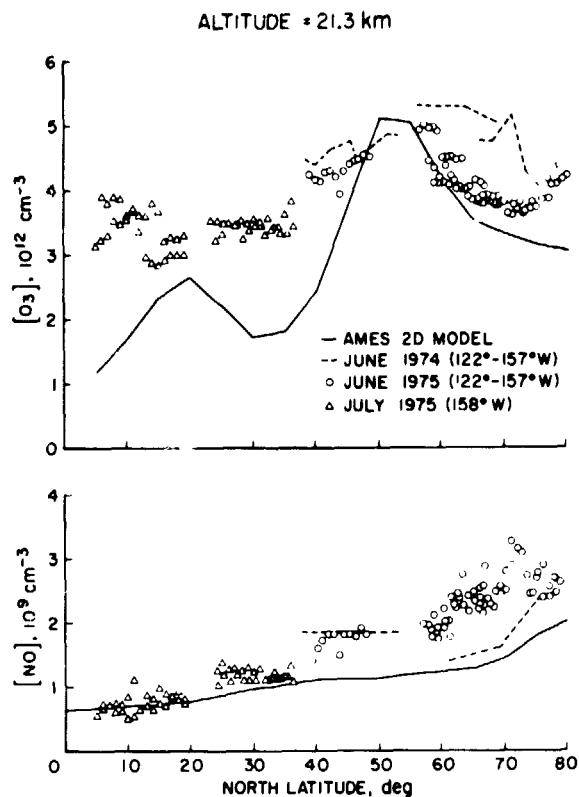
ALTITUDE = 21.3 km



Figure 2. Results of the meridional survey of $O_3$ and NO
at 21.3 km altitude, 158 W°longitude compared
with the two-dimensional model

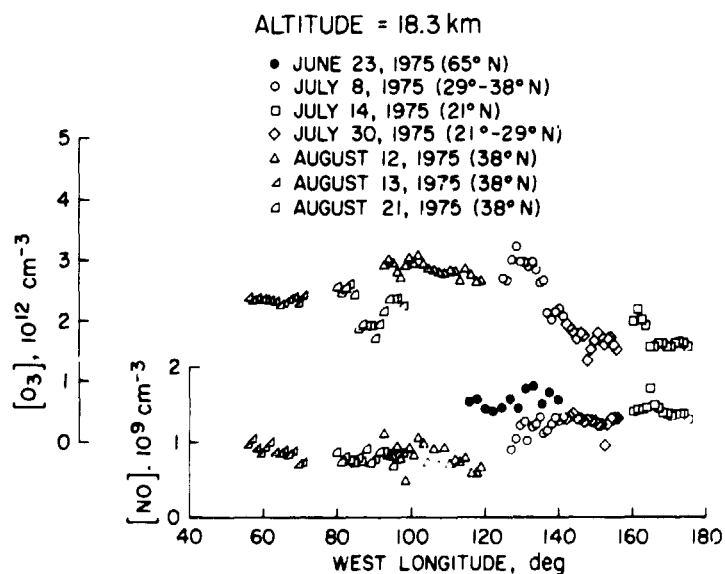ALTITUDE = 18.3 km



Figure 3. Results of the zonal survey of $O_3$ and NO at 18.3 km
altitude, at several latitudes between 21 and 65°N.

ALTITUDE = 21.3 km



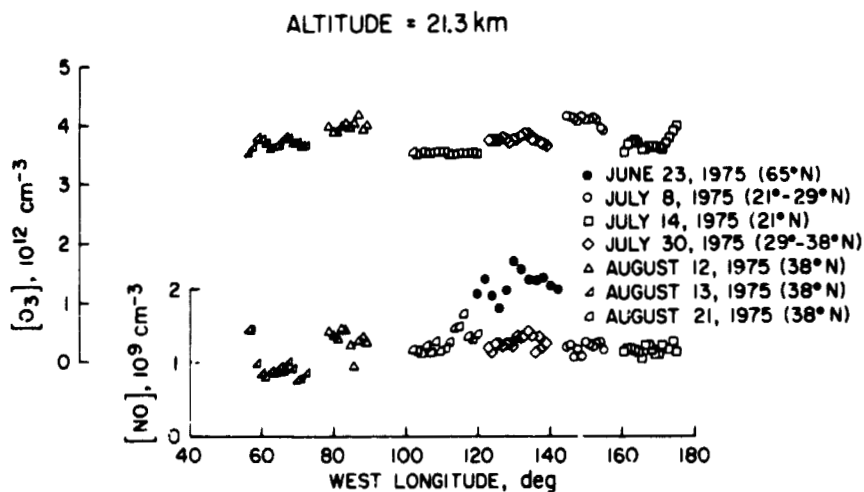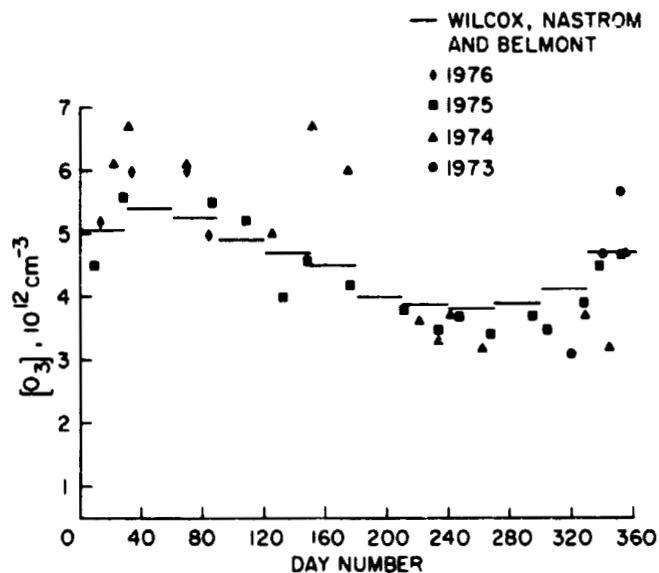Figure 4. Results of the zonal survey of $O_3$ and NO at 21.3 km altitude, at several latitudes between 21 and 65°N.



Figure 5. Ozone seasonal data (122°W, 40°N) summary at 21.3 km. The monthly mean comparison data are from an unpublished report by R. W. Wilcox, G. D. Nastrom, and A. D. Belmont, "Periodic Analysis of Total Ozone and Its Vertical Distribution," Research Report #3, CDC, Minneapolis, MN, August 8, 1975, Contract NAS2-7807.
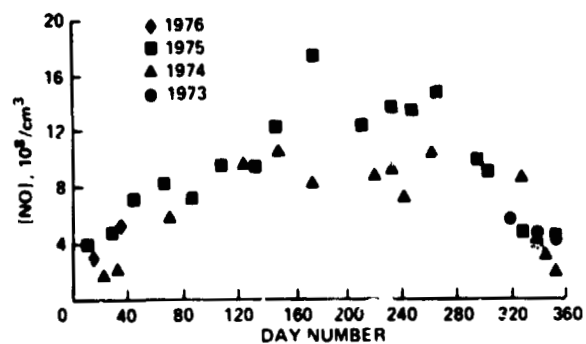
Figure 6.  Nitric oxide seasonal data (122°W, 40°N)
summary at 21.3 km.

# THE QUASI-BIENNIAL OSCILLATION IN STRATOSPHERIC OZONE

Kenneth Moe
Consulting Atmospheric Physicist
Corona del Mar, California

Before one can determine man's effect on the ozone layer, it is necessary to understand the natural variations in stratospheric ozone. Fortunately, Paetaold's balloon-borne optical ozonesonde has provided us with homogeneous data extending back for 25 years. Being made in the stratosphere, balloon measurements are free of the errors which have been shown to be introduced by aerosol scattering in the ground-based Dobson measurements of total ozone.

Various studies have shown that the total ozone column is influenced by solar ultraviolet radiation and atmospheric circulation, so one might also expect stratospheric ozone to be affected by these factors. Paetzold has already demonstrated that his balloon measurements of the integrated ozone column between 20 and 30 km are correlated with the sunspot number (hence with UV radiation). The present study examines the same data to see whether any effect of circulation can be discerned. The effect is found in the form of the quasi-biennial oscillation, with the same phase as that found for total ozone by Angell and Korshover in averaged Dobson data for Northern Europe.

Since the sunspot number and the quasi-biennial oscillation can be predicted, the naturally occurring variations in stratospheric ozone can also be predicted. Future measurements of deviations from these natural variations will be a measure of man's effect on the stratosphere.

# THE NASA U-2 AIRCRAFT AS A PLATFORM FOR HIGH ALTITUDE STRATOSPHERIC RESEARCH

Susan D. Norman
U-2 Experiments Manager
Astronautics Directorate
NASA-Ames Research Center
Moffett Field, California

In the past three years the demand for the use of the two NASA U-2 aircraft as a platform for high altitude stratospheric research has steadily increased. The rising interest in stratospheric research, as well as the favorable experimental results obtained by U-2 investigators, is largely responsible for this increase. In addition, the capability of the aircraft to maintain flight in excess of 21 km represents a capability unique in civilian aviation. Because of these factors, the number of U-2 stratospheric experiments has grown from essentially none in 1973 to seven instruments in 1976 with three more currently in the development stage.

Currently there are seven different stratospheric instrument packages operating on the U-2 with several more in the development stage (Table 1). The instruments are listed with a brief description of their objective. The aircraft performance characteristics are given in Table 2, indicating the wide variety of both in-situ and remote sensing devices which have successfully operated on the U-2.

Table 1. Existing U-2 stratospheric instrumentation

| Sensor | Description | Investigator |
|---|---|---|
| High-speed interferometer | Measure trace atmospheric species with spectral signatures in the region of 2.5 to 5.5 microns. The system is presently configured for HCL and $N_2O$ measurements with the spectral bands centered at 3.46 microns. The system can be pointed at and track the sun during sunset and sunrise and has a 1.25-deg IFOV. This system can also be reconfigured for a flight on a balloon platform. | Farmer (JPL) Raper (JPL) |
| Cryogenic air sampler | Designed to measure halocarbons with a capability to also measure methane, nitrous oxide and some hydrocarbons. The system consists of four liquid-nitrogen-cooled samplers and two whole-air samplers. Samples are analyzed in the laboratory using mass spectrometry and gas chromatography enabling concentration measurements to 0.1 ppt. | Inn (NASA-Ames) Vedder (NASA-Ames) Arvesen (NASA-Ames) |
| Infrared radiometer | Measure atmospheric nonuniformities in the 4- to 5-micron spectral region. Data will be useful for studies of convective instabilities and mixing processes in the atmosphere. The downward-looking radiometer has a rotating filter wheel which can provide six spectral bands. The IFOV is about 2.5 milliradians. | Blight (Lockheed) |

Table 1. Existing U-2 stratospheric instrumentation (contd)

| Sensor | Description | Investigator |
|---|---|---|
| Canoe CO$_2$ collector | Obtains samples of radiocarbon dioxide for use in the study of the global climate and the high-altitude environment. This is a small piggyback system. | Berger (UCLA) |
| Water vapor radiometer | Determines the total water vapor above the aircraft. It has a 2-deg FOV and measures emissions in the 18- to 35-micron region using a deuterated tri-glycerine sulfate detector. | Kuhn (NOAA) |
| Wing tank infrared spectrometer | Measures atmospheric emissions in the 7.0- to 12.5-micron and 3.0- to 4.0-micron region: The system will be flown, simultaneously with a selected lower Q-bay sensor in order to obtain simultaneous measurements of species such as ozone by different techniques. | Murcray (Univ. of Denver) |
| Wing pylon aerosol particulate sampler | Collects particles in the 0.1- to 10-micron size range. This small system (about 30 lb), is permanently mounted under the aircraft wing. Various wire meshes can be extended into the airstream for aerosol particulate collection. | Ferry (NASA-Ames) Farlow (NASA-Ames) |

Table 1. Existing U-2 stratospheric instrumentation (contd)

| Sensor | Description | Investigator |
|---|---|---|
| Lower Q-bay Airborne stratospheric in situ gas sampler | Measures $O_3$, NO, $NO_2$, and $HNO_3$ in real-time on board the aircraft. The measurements of these species are based on the chemi-luminescent reaction of NO with $O_3$. $NO_2$ and $HNO_3$ are converted to NO by a catalytic converter. | Loewenstein (NASA-Ames) |
| Filter sampler | Collects stratospheric aerosols and trace gas samples on chemically impregnated filter papers. The system has 6 filters, 16 in. in diameter. It has been used to collect data for Project Airstream and for simultaneous sampling with balloons by Dr. Allan Lazrus of NCAR. | NASA-Ames (Owned by U-2 project office) |

Table 2.  Aircraft performance characteristics

| | |
|---|---|
| Range | 2500 nm |
| Flight duration | 6.0 hr |
| Altitude | 65,000 to 70,000 ft (21.3 km) |
| Payload | Lower equipment bay   500 lb<br>Upper equipment bay   250 lb<br>Canoe   100 lb<br>Wing-mounted pods   600 lb |

# THE F-15 ZOOM-CLIMB STRATOSPHERIC AIRBORNE PLATFORM

W. A. Page
NASA-Ames Research Center
Moffett Field, California

NASA plans to acquire an Air Force F-15 high performance fighter with Mach 2.5 capability. The stratospheric zoom-climb maneuver is performed by accelerating the aircraft to supersonic speeds at high altitudes (~16 km) at which time the aircraft is zoomed upwards trading most of its kinetic energy for height. Altitudes substantially above aircraft cruise altitude can be reached (~30 km) but only for a very short time due to the near ballistic trajectory flown. The altitude capability and flight profile are shown in Figures 1 and 2, respectively. An aircraft and sensor evaluation program is planned for FY77 at Dryden Flight Research Center. In later years the aircraft will be available for deployment to other locations. Aircraft Type: F-15 (prototype #17, "Streak Eagle"). Location: Ames Research Center/Dryden Flight Research Center. Altitude Capability: 30 km. Payload weight and volume: ~800 kg and ~2 $m^3$ in several compartments.
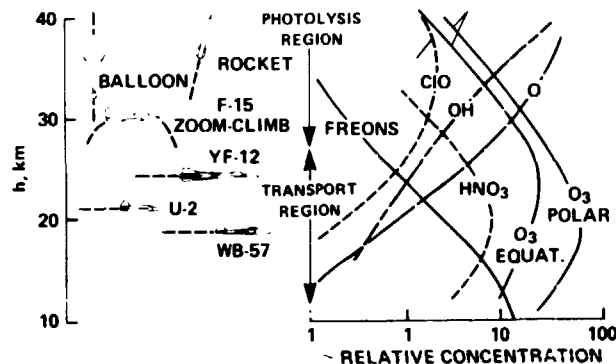


Figure 1. Altitude capability of various platforms for carrying scientific instrumentation into the stratosphere and concentration profiles of important species. Measurements are required in both the transport and photolysis regions.
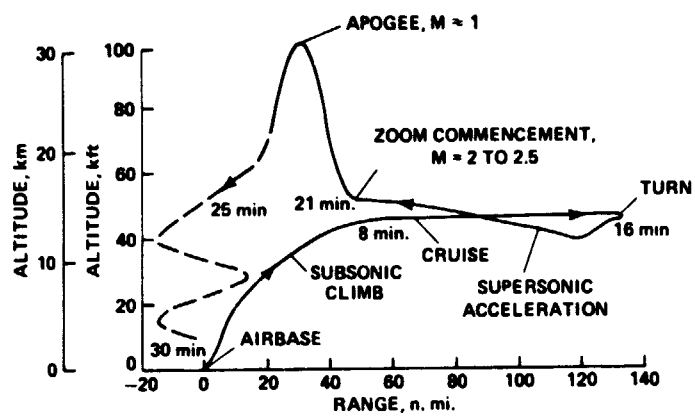
Figure 2.   F-15 zoom climb flight profile.

# THE VERTICAL DISTRIBUTION OF HCl
## IN THE 20- TO 40-km REGION OF THE STRATOSPHERE

O. F. Raper, C. B. Farmer, R. A. Toth, and B. D. Robbins
Jet Propulsion Laboratory
Pasadena, California

During the past year we have obtained two sets of stratospheric spectra covering the wavelength region from 1825 to 3600 $cm^{-1}$, using the JPL High Speed Interferometer on board a balloon-borne gondola at altitudes of 37 and 40.5 km. The wavelength interval covered encompasses transitions of all of the minor stratospheric constituents and several of the trace species of current interest in the stratosphere. Among the latter is HCl, the 1-0 transition of which is centered at 2886 $cm^{-1}$. Figure 1 is a plot of several stratospheric spectra covering that part of the HCl region in which the R-0, R-1 and R-2 rotational lines appear. We have analyzed these and other spectra for HCl, in order to extend the vertical concentrational profile of this gas in the stratosphere above that obtained earlier from U-2 observations (Farmer et al., 1976).

The present data were obtained on two separate balloon flights, the first at sunrise, September 26, 1975, and the second at sunset, May 18, 1976. Both flights were launched from -- and remained in the vicinity of -- Palestine, Texas. The spectra were taken in absorption using the rising and setting sun as the radiation source. Each interferogram was obtained in 100 seconds and, after transformation, produced a spectrum with a useful resolution of 0.18 $cm^{-1}$ and a signal-to-noise ratio of ~500/1.

The HCl data were analyzed in two stages. A preliminary concentration profile was established first using an equivalent width method described in detail elsewhere (Toth et al., 1976). The distribution thus obtained was then used in a 50-layer model atmosphere to generate synthetic spectra with the same viewing geometry as those spectra obtained during the measurements, and the HCl profile was refined until a complete match was obtained between the synthetic and the real spectra. This process is illustrated in Figures 2 and 3. Figure 2 shows the R-1 region for part of the set of stratospheric spectra obtained at 37 km on May 18, and Figure 3 contains an equivalent set of synthetic spectra generated as described above. In analyzing both sets of data, the R-1 $H^{35}Cl$ line was the principal line used, since it appears to be completely free of blending under stratospheric conditions at our resolution.

The vertical concentration profile representative of the spectra in Figure 2 is shown in Figure 4 together with our profile at lower altitudes obtained previously from the U-2 (Farmer et al., 1976) and the spectroscopic profiles of (Ackerman et al., 1976) and (Williams et al., 1976).

Within the accuracy of these measurements, the present HCl profile is consistent with that at lower altitudes and indicates that the HCl concentration continues to increase in the stratosphere, reaching a
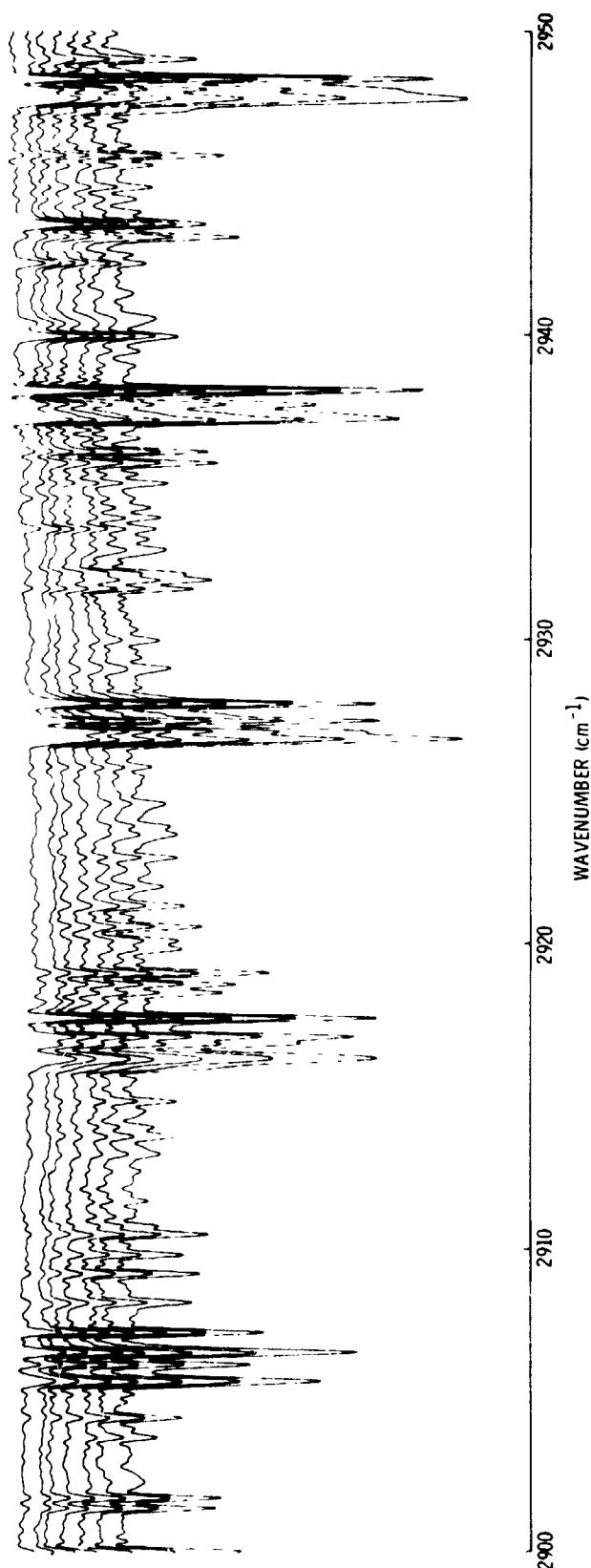
Figure 1.  Portions of a number of stratospheric spectra recorded at 37 km during sunset, May 18, near Palestine, Texas. The region shown includes the R-0, R-1, and R-2 lines of the 1-0 transition of HCl. In this figure, as well as in Figures 2 and 3, the individual spectra have been offset for clarity.
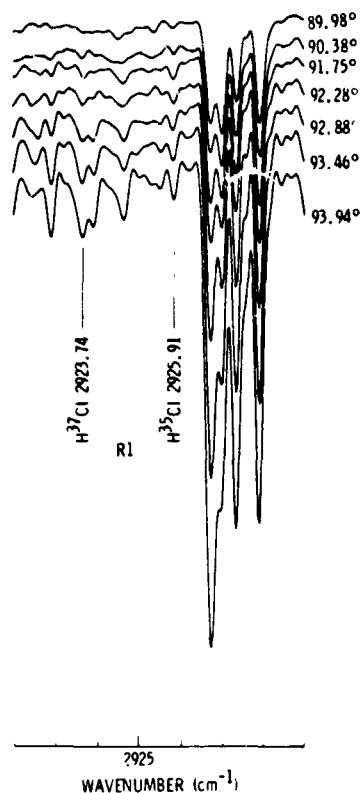
89.98°
90.38°
91.75°
92.28°
92.88′
93.46°
93.94°

H³⁷Cl 2923.74    R1    H³⁵Cl 2925.91

2925
WAVENUMBER (cm⁻¹)

Figure 2.  An enlarged version of the region of
           Figure 1 which contains the R-1 $H^{35}$
           Cl and $H^{37}$ Cl rotational lines.  The
           solar zenith angles at which the
           spectra were taken are shown at right.

maximum of ~1.7 ppbv in the 34-35 km region and falling off above that
altitude.  We see no evidence so far for seasonal variation in the
HCl concentration, since both sets of data obtained during our balloon
flights produce the same profile and both are consistent with the
profile at lower altitudes.  However, the data available to date are far
too limited to conclude that there is no secular variation in the HCl
concentration profile.

   While there is obviously some agreement among all the profiles in
Figure 4, Williams and his co-workers expressed some doubt about the
validity of their own as well as other spectroscopic measurements on
the basis of the R-5 $H^{37}$ Cl line at 2995.8 cm⁻¹, which was missing from
their data, although it is in the region of apparent window.  However,
at stratospheric temperatures the R-5 $H^{37}$ Cl line is nearly an order of
magnitude weaker than the R-1 $H^{35}$ Cl line and would probably not have
been detectable with the signal-to-noise apparent in their spectra.  In
addition, the fact that these HCl concentrations which reproduce the
R-1 $H^{35}$ Cl line also reproduce the spectral features in which the HCl
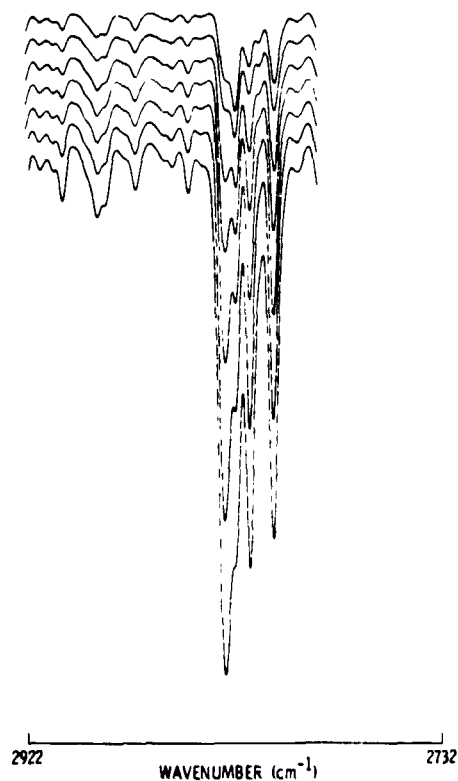
2922         WAVENUMBER (cm$^{-1}$)        2732

Figure 3.   Synthetic spectra generated with the
same solar zenith angles as those
shown in Figure 2, with the HCl profile
adjusted to match that observed in the
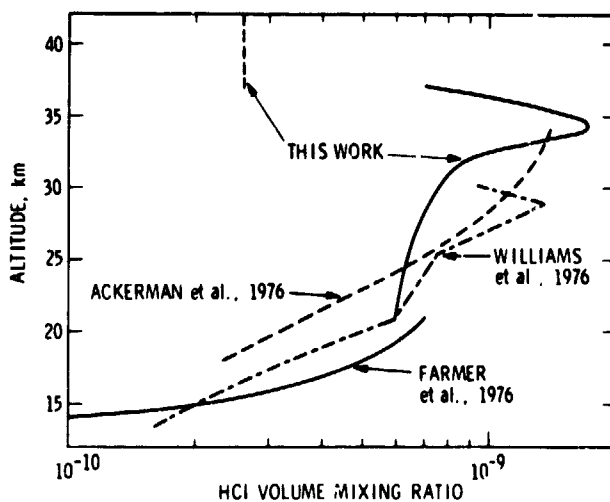real spectra (see text).

Figure 4.  The vertical concentration profile for HCl
in the stratosphere obtained during the
present and previous spectroscopic investi-
gations.

lines are blended indicates that blending of the R-1 H$^{35}$Cl line is
not a problem.

The work shown here is currently being prepared for submission to
Geophysical Research Letters.

# REFERENCES

1.  Ackerman, M., D. Frimout, A. Girard, M. Gottignies and C. Muller, Stratospheric HCl from infrared spectra, <u>Geophys. Res. Lett.</u>, 3, 81-83, 1976.

2.  Farmer, C. B., O. F. Raper and R. H. Norton, Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere, <u>Geophys. Res. Lett.</u>, 3, 13-16, 1976.

3.  Toth, R. A., C. B. Farmer and O. F. Raper, Vertical distribution of N$_2$O in the stratosphere, to be published.

4.  Williams, W. J., J. J Kosters, A. Goldman, and D. G. Murcray, Measurement of the stratospheric mixing ratio of HCl using infrared absorption technique, <u>Geophys. Res. Lett.</u>, 3, 383-385, 1976.

# VERTICAL DISTRIBUTION OF $N_2O$ IN THE STRATOSPHERE

R. A. Toth, C. B. Farmer, and O. F. Raper
Jet Propulsion Laboratory
Pasadena, California

For the past 3-1/2 years, we have measured the $N_2O$ concentration in the stratosphere from a number of airborne platforms. Some of the earlier measurements have been published by C. B. Farmer in the Canadian Journal of Chemistry, 52, p. 1544 (1974). The work shown here is a compilation of the previous results and more recent ones at higher altitudes obtained during U-2 and balloon flights which extend the $N_2O$ profile from the tropopause to 40 km. The volume mixing ratio variation with altitude which we have measured for $N_2O$ is shown in Figure 1, along with the results obtained by other investigators.

Portions of the spectra obtained during the flights and containing the bands used in the determination of the $N_2O$ profile are shown in Figures 2, 3 and 4. They are the $\nu_3$ band centered at 2224 $cm^{-1}$, the Q branch of the $\nu_1 + \nu_2'$ band centered at 1880 $cm^{-1}$, the $\nu_1 + \nu_2^\circ$ band centered at 2462 $cm^{-1}$, and the 2 $\nu_1$ band centered at 2563 $cm^{-1}$.

The work displayed here is currently being prepared for submission to Geophysical Research Letters.
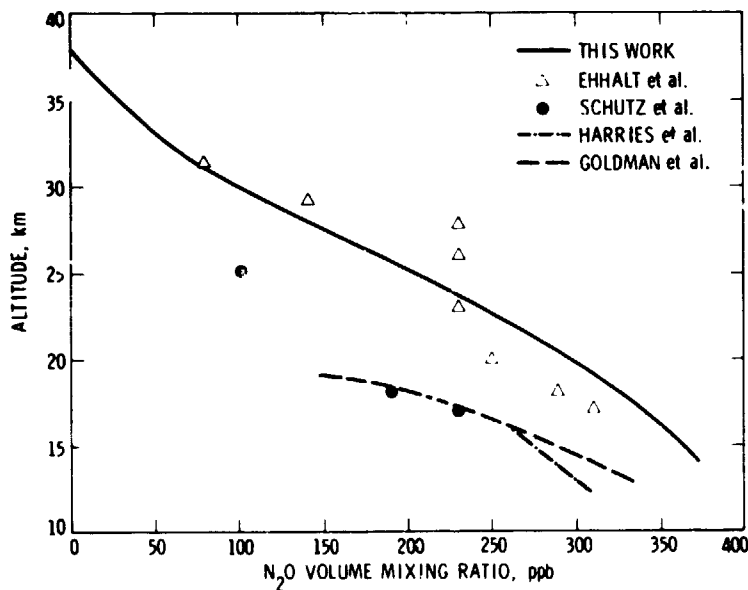


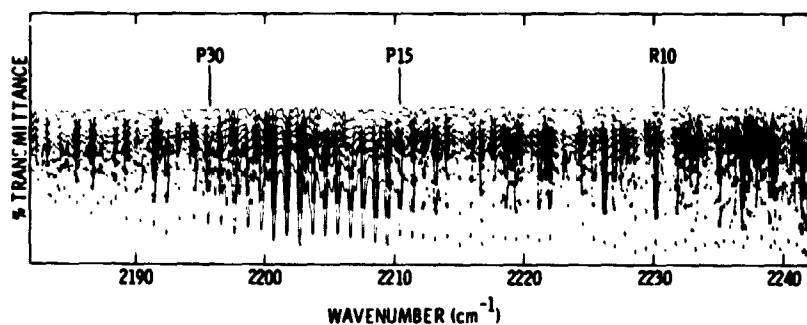Figure 1. Vertical concentration profile of $N_2O$ in the stratosphere obtained during airborne measurements.

Figure 2. Portion of a number of stratospheric spectra recorded during the balloon measurements. The region shown includes the $\nu_3$ band of $N_2O$ centered at 2224 cm$^{-1}$. In this figure and in Figures 3 and 4, the individual spectra have been offset for clarity.



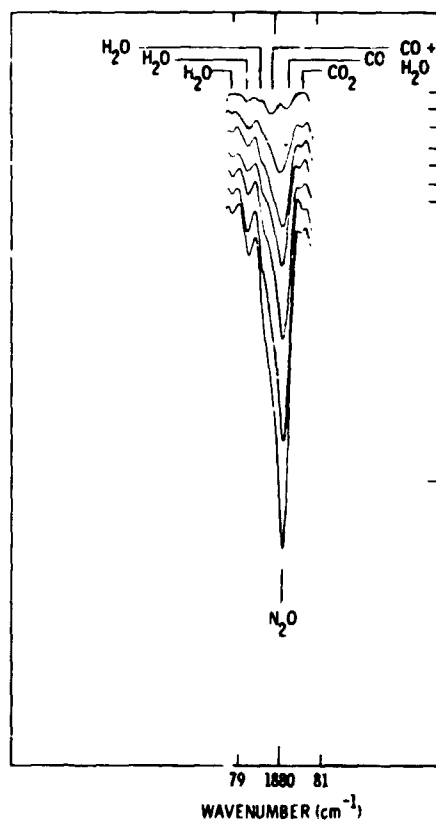Figure 3. Enlarged portion of stratospheric spectra containing the θ branch of the $\nu_1 + \nu_2$ band of $N_2O$ at 1880 cm$^{-1}$.
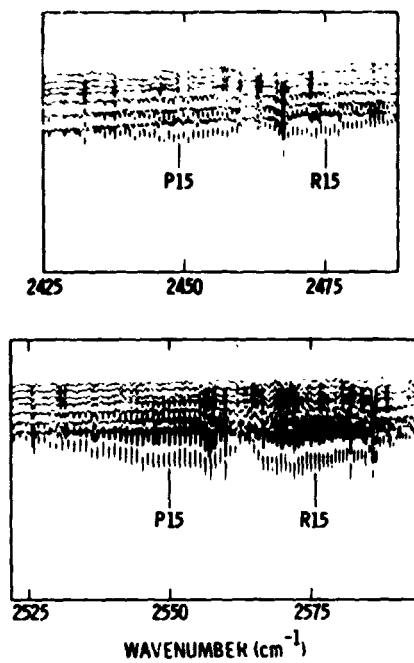
Figure 4. Additional stratospheric spectra of the regions containing the $\nu_1 + \nu_2$ band of $N_2O$ centered at 2462 cm$^{-1}$ and the $2\nu_1$ band of $N_2O$ centered at 2563 cm$^{-1}$.

# CONCENTRATIONS OF FREON 12 AND NITROUS OXIDE IN THE STRATOSPHERE

Bennett J. Tyson, Robert B. Brewer,
John A. Arvesen, and James F. Vedder
NASA-Ames Research Center
Moffett Field, California

A flow-through cryogenic collection technique has been used aboard U-2 high altitude aircraft and balloon platforms to obtain concentrated samples of air for laboratory analysis. Samples were collected at 15, 18, and 21 km using a U-2 aircraft and at 29 and 36 km using a balloon platform. The 15- and 18-km samples were collected during a rendezvous with a Washington State University Lear jet which collected samples at the lower altitudes. The rendezvous provided a unique opportunity to obtain halocarbon concentration profiles into the stratosphere.

The concentrations of Freon 12 and nitrous oxide decreased from 77 pptv to 7 pptv and from 133 ppvb to 42 ppvb respectively over the altitude range of 21 to 36 km. Other compounds were detected in the samples collected at 21 km and lower but have not yet been quantitated. Freon 11 was present in all samples but carbon tetrachloride was not detected above 21 km.

Data on the concentrations of Freon 12 and $N_2O$ at different altitudes will be presented and compared with the theoretical distributions of these species.

# A LARGE-VOLUME CRYOGENIC SAMPLER FOR STRATOSPHERIC TRACE GASES

James F. Vedder, John A. Arvesen,
Bennett J. Tyson, and Robert B. Brewer
NASA/Ames Research Center
Moffett Field, California

A liquid-nitrogen-cooled flow-through trap for condensable consti-
tuents of the stratosphere has been developed at Ames Research Center.
From aircraft and balloons, it samples large volumes of gas for labora-
tory analysis of halocarbons, hydrocarbons, and other stable trace
species. The all-metal system has a high trapping efficiency for con-
densables at 68 K at flow rates up to 25 STP l/min. Each unit consists
of a baffled cylindrical 4-liter chamber immersed in a vacuum-jacketed liquid
nitrogen reservoir. Several samplers are connected between an inlet
manifold receiving gas from an airscoop and an exhaust manifold vented
into the ambient air. A venturi tube in the exhaust line provides
mass-flow data which are recorded on magnetic tape. On the U-2 aircraft,
at 21 km altitude, ram air pressure produces sufficient flow to sample
1000 STP liters of gas in less than one hour. For balloon flights,
a sorption pump provides the flow; but smaller volumes of air are sampled
because of low ambient pressures. To avoid contaminants from the bal-
loon and gondola, the latter is lowered 300 m beneath the balloon;
and the air intake is oriented into the shear wind by large cloth
vane. A typical sample primarily contains the air trapped when the
valves are closed and the $CO_2$ condensed from the flow. After a flight,
the containers are returned to the laboratory, warmed and transferred
to a gas chromotograph for analysis. With these samples from large
volumes of gas, subparts-per-trillion condensable constituents in the
stratosphere can be measured. Large samples are required for species
that may be more abundant but less easily detected by gas chromotography
and for analysis by mass spectrometry.

# SECTION III

# EXPOSITION ON LABORATORY MEASUREMENTS

# LASER DIODE SPECTROSCOPY ON THE CHLORINE
## MONOXIDE BAND NEAR 850 CM$^{-1}$

R. T. Menzies, J. S. Margolis, E. D. Hinkley and R. A. Toth
Jet Propulsion Laboratory
Pasadena, California

Laboratory measurements of chlorine monoxide absorption in the spectral region near its fundamental vibration rotation band have been made using a tunable diode laser system. The very high spectral resolution which can be obtained with this technique makes possible the direct measurement of linewidths which are nearly doppler limited. The frequencies of several absorption lines have been determined to within 0.02 cm$^{-1}$. Heterodyne measurements using $CO_2$ gas laser frequencies are in progress; these measurements should result in selected absorption line frequency determinations which are accurate to within 30 MHz. These data, along with line intensity measurements, should be of great importance for those who are considering the detection and measurement of stratospheric chlorine monoxide concentrations using high resolution infrared spectrometers.

# UV PHOTOABSORPTION CROSS SECTIONS FOR HALOCARBONS

Donald E. Robbins
NASA-Lyndon B. Johnson Space Center
Houston, Texas

Measurements of ultraviolet photoabsorption cross sections in the wavelength region from 174 to 270 nm are reported for 12 halocarbons (Figure 1 and Table 1). The list of compounds includes Freons 11, 12, 21, 22, 114, 114B2, 115, as well as carbon tetrachloride, methyl chloride, methyl bromide, chloroform and trichloroethylene. Calculations are presented which compare the importance of various halocarbons as sources of free halogen atoms in the stratosphere (Figure 2).
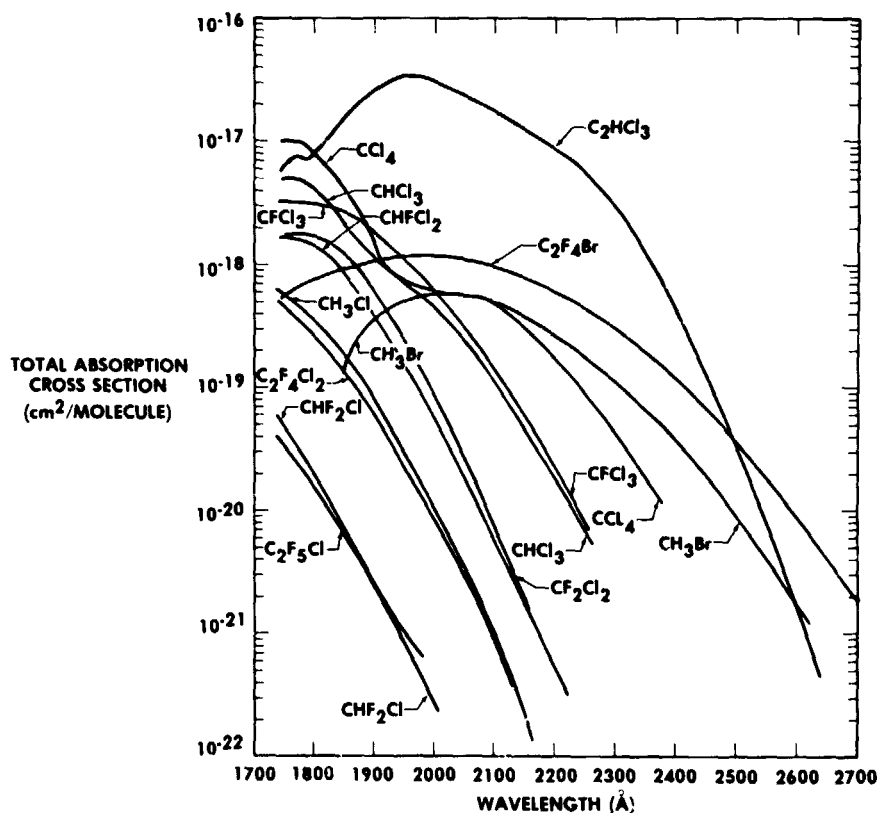


Figure 1.  Wavelength dependence of the total
absorption cross-section for a number
of halocarbons.

## Table 1.  Ultraviolet absorption cross sections
### ($10^{-21}$ $cm^2$/molecule)

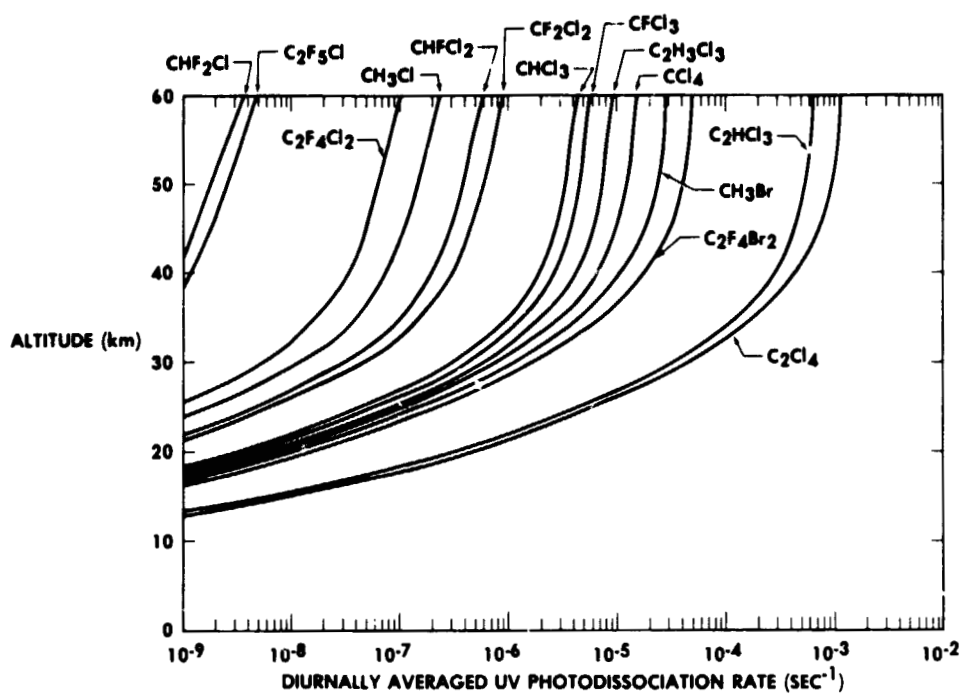| Wavelength (Å) | Carbon Tet $CCl_4$ | Chloroform $CHCl_3$ | Methyl Chloride $CH_3Cl$ | Methyl Bromide $CH_3Br$ | Freon 11 $CFCl_3$ | Freon 12 $CF_2Cl_2$ | Freon 21 $CHFCl_2$ | Freon 22 $CHF_2Cl$ | Freon 114 $C_2F_4Cl_2$ | Freon 114B2 $C_2F_4Br_2$ | Freon 115 $C_2F_5Cl$ | Trichloro-ethylene $C_2HCl_3$ | Trichloro-ethane $C_2H_3Cl_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1740 | 9950±160 | 4850±110 | 1100±18 | 5330±100 | 3140±50 | 1670±30 | 1680±30 | 59.4±1.3 | 500±7 | 549±9 | 39.6±0.7 | 5450±120 | 4280±200 |
| 1760 | 10100±180 | 5010±100 | 933±15 | 10100±200 | 3200±60 | 1760±40 | 1630±30 | 40.1±0.8 | 409±7 | 616±10 | 27.9±0.6 | 7340±130 | |
| 1780 | 9760±160 | 4750±100 | 773±14 | 12800±200 | 3130±60 | 1860±40 | 1520±20 | 28.5±0.6 | 325±5 | 698±11 | | 7130±130 | 3990±200 |
| 1800 | 7220±110 | 3900±80 | 635±11 | 391±8 | 3180±60 | 1760±40 | 1350±20 | 19.9±0.5 | 249±5 | 777±12 | 14.6±0.3 | 8260±140 | |
| 1820 | 5690±90 | 3160±70 | 465±8 | 197±5 | 2980±50 | 1590±40 | 1160±20 | 13.0±0.3 | 196±3 | 844±13 | 10.3±0.2 | 11100±200 | 3110±120 |
| 1840 | 4500±70 | 2610±50 | 347±6 | 211±5 | 2740±50 | 1360±40 | 917±16 | 8.25±0.23 | 147±3 | 900±14 | 7.72±0.17 | | |
| 1860 | 3000±50 | 1780±40 | 253±4 | 284±7 | 2470±50 | 1080±40 | 732±13 | 5.25±0.13 | 105±2 | 965±14 | 5.41±0.12 | 18500±300 | 2500±100 |
| 1880 | 1980±30 | 1410±30 | 180±3 | 226±7 | 2120±40 | 828±28 | 529±11 | 3.53±0.08 | 80.4±1.8 | 1020±20 | 3.83±0.09 | | |
| 1900 | 1340±20 | 1130±30 | 125±2 | 447±9 | 1750±40 | 593±15 | 400±8 | 2.38±0.07 | 59.7±1.4 | 1080±20 | 2.67±0.08 | | 1850±50 |
| 1920 | 965±16 | 915±20 | 87.6±1.6 | 544±12 | 1500±30 | 427±14 | 263±5 | 1.61±0.06 | 40.8±1.3 | 1110±20 | 1.89±0.07 | 30200±500 | |
| 1940 | 778±12 | 761±18 | 54.1±1.0 | 626±12 | 1220±30 | 296±8 | 180±4 | 1.02±0.05 | 25.4±1.0 | 1150±20 | 1.28±0.04 | | 1420±40 |
| 1960 | 711±12 | 641±16 | 38.0±0.7 | 692±12 | 1010±20 | 200±6 | 124±2 | 0.75±0.04 | 19.5±0.6 | 1170±20 | 0.88±0.03 | | |
| 1980 | 673±11 | 534±12 | 26.0±0.5 | 768±13 | 788±21 | 135±4 | 81.2±1.4 | 0.36±0.04 | 12.5±0.4 | 1190±20 | 0.63±0.05 | 33300±500 | 979±32 |
| 2000 | 661±11 | 429±10 | 16.9±0.3 | 796±13 | 657±18 | 87.1±2.8 | 50.9±0.8 | 0.27±0.04 | 8.06±0.30 | 1200±20 | | | |
| 2020 | 620±10 | 344±7 | 10.9±0.2 | 797±12 | 501±13 | 53.7±1.7 | 33.4±0.6 | 0.26±0.04 | 5.63±0.13 | 1200±20 | | | 644±18 |
| 2040 | 614±10 | 266±6 | 7.18±0.11 | 778±12 | 384±10 | 31.4±1.0 | 21.1±0.3 | | 3.76±0.07 | 1140±20 | | 24600±400 | |
| 2060 | 568±8 | 206±5 | 4.76±0.08 | 757±12 | 280±6 | 19.6±0.6 | 13.5±0.2 | | 2.44±0.05 | 1100±20 | | | 401±14 |
| 2080 | 532±9 | 148±3 | 3.02±0.05 | 695±11 | 210±4 | 11.8±0.4 | 8.63±0.13 | | 1.43±0.05 | 1040±20 | | | |
| 2100 | 471±8 | 108±2 | 1.91±0.04 | 657±10 | 147±3 | 7.75±0.29 | 5.59±0.09 | | 0.87±0.04 | 995±15 | | 17800±300 | 236±7 |
| 2120 | 396±6 | 77.9±1.6 | 1.16±0.03 | 597±9 | 108±2 | 4.71±0.18 | 3.55±0.06 | | 0.47±0.04 | 915±13 | | | |
| 2140 | 331±4 | 54.4±1.0 | 0.89±0.03 | 547±8 | 72.4±1.7 | 2.67±0.10 | 2.28±0.04 | | 0.41±0.04 | 841±13 | | | |
| 2160 | 272±4 | 37.9±0.6 | 0.47±0.03 | 476±7 | 51.7±1.2 | 1.67±0.09 | 1.44±0.03 | | | 771±11 | | 11300±200 | |
| 2180 | 216±3 | 25.6±0.4 | 0.36±0.03 | 420±6 | 34.5±0.7 | | 0.85±0.03 | | | 700±10 | | | 70.0±1.3 |
| 2200 | 169±3 | 17.5±0.3 | 0.23±0.03 | 375±6 | 24.4±0.6 | | 0.58±0.03 | | | 619±9 | | | |
| 2220 | 129±2 | 12.0±0.2 | | 310±5 | 15.1±0.6 | | 0.32±0.03 | | | 566±9 | | 7310±110 | |
| 2240 | 98.8±1.5 | 7.96±0.12 | | 270±4 | 10.7±0.6 | | | | | 496±8 | | | |
| 2260 | 74.1±1.1 | 5.45±0.09 | | 223±4 | 7.29±0.71 | | | | | 433±7 | | | 18.2±0.7 |
| 2280 | 56.0±0.9 | | | 182±3 | | | | | | 383±6 | | 3790±50 | |
| 2300 | 41.1±0.7 | | | 146±3 | | | | | | 322±5 | | | |
| 2320 | 30.5±0.6 | | | 121±2 | | | | | | 270±5 | | | |
| 2340 | 22.4±0.5 | | | 96.1±2.1 | | | | | | 242±5 | | 1490±20 | 5.39±0.14 |
| 2360 | 15.2±0.5 | | | 76.4±2.0 | | | | | | 193±4 | | | |
| 2380 | 12.5±0.6 | | | 58.7±2.1 | | | | | | 152±3 | | | |
| 2400 | | | | 44.2±1.9 | | | | | | 127±3 | | 427±6 | |
| 2420 | | | | 33.0±1.4 | | | | | | 103±2 | | | 1.23±0.08 |
| 2440 | | | | 23.8±1.2 | | | | | | 77.8±1.8 | | | |
| 2460 | | | | 18.7±0.8 | | | | | | 60.2±1.5 | | 78.6±1.4 | |
| 2480 | | | | 13.4±0.7 | | | | | | 47.1±1.1 | | | |
| 2500 | | | | 8.48±0.52 | | | | | | 35.8±0.9 | | | |
| 2520 | | | | 7.04±0.34 | | | | | | 28.6±0.7 | | 19.4±0.3 | |
| 2540 | | | | 4.95±0.22 | | | | | | 22.1±0.4 | | | |
| 2560 | | | | 3.58±0.15 | | | | | | 17.1±0.3 | | | |
| 2580 | | | | 2.60±0.09 | | | | | | 12.7±0.3 | | 3.59±0.07 | |
| 2600 | | | | 1.72±0.08 | | | | | | 9.63±0.24 | | | |
| 2620 | | | | 1.09±0.07 | | | | | | 7.36±0.21 | | | |
| 2640 | | | | 0.82±0.06 | | | | | | 5.21±0.18 | | 0.45±0.04 | |
| 2660 | | | | 0.53±0.05 | | | | | | 3.73±0.15 | | | |
| 2680 | | | | 0.34±0.05 | | | | | | 2.88±.12 | | | |
| 2700 | | | | 0.37±0.04 | | | | | | 2.14±0.11 | | 21.0±0.4 | |

Figure 2.  UV photodissociation rates vs altitude
for a number of halocarbons.