

QC
879.7
.U5
1982/
1983



Program of Research and Monitoring for Early Detection of Stratospheric Ozone Change

Report to Congress of Findings for 1982-1983

Washington, D.C.
January 1984

**U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration**

QC
879.7
.U5
1982/83



Program of Research and Monitoring for Early Detection of Stratospheric Ozone Change

Report to Congress of Findings for 1982-1983

Washington, D.C.
January 1984

U.S. DEPARTMENT OF COMMERCE
Malcolm Baldrige, Secretary

United States,

National Oceanic and Atmospheric Administration
John V. Byrne, Administrator

CONTENTS

	<u>Page</u>
PREFACE.....	v
INTRODUCTION.....	1
SUMMARY OF FINDINGS.....	3
AERONOMY LABORATORY.....	5
I. Model Calculations.....	5
II. In-Situ Stratospheric Composition Measurements.....	6
III. Laboratory Kinetics Measurements.....	6
IV. Optical Measurements.....	7
V. Atmospheric Dynamics.....	8
VI. References.....	8
AIR RESOURCES LABORATORY.....	11
I. Ozone Monitoring.....	11
A. Variations in Ozone.....	11
B. Trend in Upper Stratospheric Umkehr Ozone Profile Data.....	14
C. Dobson Spectrophotometer Ozone Monitoring.....	14
II. Stratospheric Temperature Monitoring.....	16
III. Water Vapor Monitoring.....	18
IV. Nitrous Oxide and Freon-11 and -12 Monitoring.....	18
V. Ultraviolet Radiation Monitoring.....	23
VI. References.....	23
GEOPHYSICAL FLUID DYNAMICS LABORATORY.....	24
I. Three-Dimensional Modeling of Trace Constituent Behavior.....	24
A. Atmospheric N ₂ O Experiments.....	24
B. Reactive Nitrogen in the Troposphere.....	25
C. Examination of the Classical Theory for Tropospheric Ozone.....	26
D. Tropospheric Ozone Photochemistry.....	27
E. Development of a Self-Consistent Two-Dimensional Transport Model.....	27

	<u>Page</u>
II. Modeling of the Troposphere - Stratosphere - Mesosphere System.....	27
A. Annual Mean Medium-Resolution Experiment.....	28
B. Analysis of Equatorial Waves in the SKYHI General Circulation Model.....	28
C. Generation and Dispersion of Equatorial Disturbances.....	29
D. Seasonal Cycle Medium-Resolution Experiment.....	29
E. Evaluation of Satellite Sampling of the Stratosphere.....	29
II. Physical Processes in the Middle Atmosphere.....	30
A. Radiative Transfer.....	30
B. Ozone Photochemistry.....	30
C. Seasonal March of Radiative-Photochemical Temperature.....	30
IV. References.....	31
NATIONAL ENVIRONMENTAL SATELLITE, DATA, AND INFORMATION SERVICE.....	33
I. TIROS Operational Vertical Sounder Total Ozone.....	33
II. Development and Implementation of Operational Solar Backscatter Ultraviolet Instruments.....	34
III. Reference.....	34
NATIONAL WEATHER SERVICE, CLIMATE ANALYSIS CENTER.....	35
I. Operational Stratospheric Modeling.....	35
II. Examination of Ozone Data for Trends.....	35
III. References.....	37

PREFACE

Section 126 (on Ozone Protection) of P.L. 95-95, Clean Air Act Amendments of 1977, states that "The Administrator of the National Oceanic and Atmospheric Administration shall establish a continuing program of research and monitoring of the stratosphere for the purpose of early detection and changes in the stratosphere and climatic effects of such changes. Such Administrator shall on or before January 1, 1978, and biennially thereafter, transmit a report to the Administrator [of EPA] and the Congress on the findings of such research and monitoring."

As part of its mission in Upper Atmospheric and Space Research, Global Monitoring of Climate Change, Basic Weather Analysis, and Environmental Modeling, NOAA and its predecessors have conducted programs of research and monitoring of the stratosphere for several decades. These programs were intensified and became significant components of the mandated program when national concern developed about the possible effects of chlorofluorocarbons and other pollutants on stratospheric ozone.

NOAA's stratospheric research and monitoring activities are conducted in six centers: the Aeronomy Laboratory; the Air Resources Laboratory; the Geophysical Fluid Dynamics Laboratory; the Office of Research and Applications and the Satellite Data Services Division of the National Environmental Satellite, Data, and Information Service (NESDIS); and the Climate Analysis Center of the National Weather Service.

The Aeronomy Laboratory conducts stratospheric composition measurements, laboratory reaction kinetics measurements, model calculations, and atmospheric dynamics measurements.

The Air Resources Laboratory monitors stratospheric ozone, water vapor, and temperature variations, measures erythemal ultraviolet radiation at the ground, and operates the U.S. portion of the World Meteorological Organization Global Ozone Research and Monitoring Network.

The Geophysical Fluid Dynamics Laboratory conducts mathematical modeling of the dynamical, radiative, and chemical processes of the troposphere, stratosphere, and mesosphere, giving particular attention to the effects of atmospheric and oceanic changes on global climate.

The NESDIS Office of Research and Applications develops and evaluates NOAA programs for operational satellite measurements of stratospheric properties. The Satellite Data Services Division of the NESDIS National Climatic Data Center archives the data from the operational satellites, and provides data to users and researchers upon request.

The Climate Analysis Center of the National Weather Service conducts analysis of stratospheric meteorological and ozone data from both ground-based and satellite measurement systems, utilizing data provided by all participating United States agencies.

Program of Research and Monitoring for Early Detection of Stratospheric Ozone Change 1982 - 1983

INTRODUCTION

The problem of predicting stratospheric ozone concentrations involves almost every aspect of atmospheric physics and chemistry. Ozone is formed primarily by the energy of solar ultraviolet radiation dissociating molecular oxygen, O_2 , into its component atoms in the high stratosphere, followed by rapid reactions of the O atoms with O_2 to form ozone, O_3 . The ozone diffuses down to the lower stratosphere under the influence of atmospheric turbulence, waves, and wind fields. Ozone concentration is determined by a balance between the classic source processes and various catalytic processes, involving principally the oxides of nitrogen, chlorine, and hydrogen (NO_x , ClO_x , HO_x) in which O and O_3 are converted back to O_2 .

The chief importance of ozone relative to the surface environment is its ability to absorb the potentially lethal ultraviolet radiation of the sun; this same absorption provides the major source of heat for the stratosphere. Differential heating in turn drives the wind systems of the stratosphere, which redistribute the ozone around the world and influence the tropospheric wind systems.

For many years, NOAA monitoring and research studies have been concerned with virtually every aspect of this giant global cycle. Direct in situ sampling and remote-sensing measurements are being made from balloons, satellites, aircraft, and ground-based platforms, and the necessary instrumentation developed within NOAA Laboratories. The data obtained are compared with predictions of various atmospheric models. Laboratory chemical reaction rates and atmospheric transport parameters together with observational data, are then applied to develop and improve the models iteratively.

The National Oceanic and Atmospheric Administration and its predecessor organizations began systematic measurements of atmospheric ozone in the late 1950's. Total ozone measurements were included in the regular work of the four NOAA baseline stations, beginning in the early 1960's at Mauna Loa (Hawaii) and South Pole, and in the mid-1970's at Barrow (Alaska) and Tutuila (American Samoa). A network of stations for the specific purpose of monitoring ozone was established in 1963 in Bismarck, N.D., Caribou, Maine, and Nashville, Tenn., to which was added Boulder, Colo., in 1967. (Three other stations were started which are no longer operated.) In addition, NOAA began in the early 1970's the coordination and processing of ozone measurements made by the National Aeronautics and Space Administration at Wallops Island, Va., the Army at White Sands, N. Mex., Florida State University at Tallahassee, Fla., and a cooperative station operated by the Peruvian Government at Huancayo, Peru.

A realistic assessment of the long-term effects of chlorofluorocarbons and other anthropogenic emissions on stratospheric ozone has proved to be a

considerably more elusive goal than was originally visualized. The principal reason for the prevailing uncertainty is the lack of precise knowledge of (1) the reaction rates and products of some of the important chemical reactions and (2) the properties of several key "reservoir" species. The latest calculations, made by NOAA and the National Center for Atmospheric Research in collaboration, indicate that ozone depletion is likely to be a highly nonlinear function of added stratospheric chlorine. That is, the ozone depletion may be small, or even slightly negative, for small chlorine increases, but will increase dramatically once the chlorine exceeds a "threshold" range. If the calculations are correct, the prospect for early detection of ozone trends is less encouraging than was thought originally.

SUMMARY OF FINDINGS

The NOAA program of research and monitoring for stratospheric ozone change involves remote and in situ sampling of ozone and other key trace atmospheric species, stratospheric temperature, and stratospheric water vapor. The data obtained are used to estimate global changes. Model calculations explore the coupled radiative, chemical, and dynamic processes of the atmosphere. Laboratory investigations, undertaken to specify rate reactions, cross sections, primary yields, product distributions, and temperature dependencies, lead to iterative model calculations.

The results of monitoring of ozone are summarized here. Full descriptions of all the monitoring and research activities and their findings during the 2-year period of this report are presented in the main sections of this report, organized by Laboratory.

Variations in Total Ozone

Total ozone data are being obtained and analyzed on a routine basis from the World Meteorological Organization's Global Ozone Monitoring Network. The network consists of ground-based instruments that compare the solar radiation in two adjacent wavelengths, in one of which ozone absorbs the ultraviolet radiation. These data are analyzed in terms of variation from the means of year-average total ozone for each hemisphere and for the world, in each case over the period of record, 1958 through 1982. The analyses show little evidence of a long-term downward trend.

Variations in Ozone Amounts in Different Layers of the Atmosphere

Observations of changes in the intensity of solar radiation (in adjacent wavelengths) scattered from the zenith sky as the sun rises and sets (the Umkehr technique) from about 15 stations provide average ozone data for various layers in the atmosphere. Photochemical models predict that the largest percentage decrease of ozone due to anthropogenic emissions will occur near the 40 km level, with possible increases in ozone in the upper troposphere and lower stratosphere.

In the 32-48 km layer of Umkehr measurements in the Northern Hemisphere (few Umkehr observation sites exist outside the Northern Hemisphere) there is evidence of a 2% - 3% decrease in ozone in this layer since 1970. (The effects of volcanic aerosols on the Umkehr technique, after large volcanic eruptions, have been taken into account in this finding.)

The near invariance of total ozone together with the slight decrease in stratospheric ozone implies an increase in tropospheric ozone, and there is evidence from ozonesonde data that such an increase has occurred.

Analyses of the long-term (22 years) record of Umkehr vertical ozone profile from the 13 highest quality observation sites indicates a statistically significant relation between Umkehr measurement effects and stratospheric aerosols in the upper Umkehr layers, and further, a

statistically significant negative trend of ozone in those layers after the Umkehr measurements have been corrected. The ozone changes detected by this analysis are consistent with recent theoretical photochemical model predictions and represent the first directly observed, statistically significant evidence of a downward trend in stratospheric ozone. The amount for Umkehr level 8 (38-43 km) is a change per year between 1970 and 1980 of -0.3%.

AERONOMY LABORATORY

Boulder, Colorado

I. Model Calculations

The Aeronomy Laboratory has continued its leadership in atmospheric chemical modeling, using both one-dimensional models that consider only vertical transport and two-dimensional models that also include the effects of meridional transport. Collaboration with the Geophysical Fluid Dynamics Laboratory (GFDL) has also continued, with the objective of including chemical effects in a self-consistent way in the framework of the GFDL three-dimensional model, which represents the closest approach to the real atmosphere and will ultimately lead to a fuller understanding of the influence of ozone changes on global climate.

The problem of the origin of non-urban tropospheric ozone has also been pursued, both through modeling and through ground-based measurements of ozone and its chemical precursors at a site in the Colorado Rockies, northwest of Denver. Tropospheric ozone contributes significantly to the total vertical ozone column, so that its behavior needs to be understood and predicted if the full environmental impact of ozone change is to be assessed. It now appears that most tropospheric ozone has its origin in photochemical reactions within the troposphere (Liu et al., 1980; 1983), rather than in direct intrusion from the stratosphere. The chief precursor is NO_x , originating in a variety of sources, including the upper troposphere (Noxon, 1981), lightning (Liu et al., 1983; Noxon, 1976), and urban pollution.

A new two-dimensional model has been developed in collaboration with the National Center for Atmospheric Research (Garcia and Solomon, 1983) and has been used in studies relating to the photochemistry and transport of stratospheric ozone. In particular, the model has successfully explained the observed global features of stratospheric NO_2 for the first time (Solomon and Garcia, 1983), including the steep "cliff" between middle-latitude and polar-region measurements.

The model has also been used to study the influence of the 11-year solar cycle on stratospheric composition, including the effects of variations in energetic-particle precipitation and in solar radiation. The results suggest that downward coupling from the thermosphere may increase stratospheric ozone at high latitudes.

Collaboration with scientists from the University of Colorado has led to participation in the highly successful Solar Mesosphere Explorer satellite project. The satellite, which was launched in October 1981, was instrumented to measure a wide variety of atmospheric constituents including ozone. Several solar-proton events occurred during the two years covered by this report, and the mesospheric ozone depletions caused by these events were clearly detected by instruments on the satellite. Aeronomy Laboratory model predictions based on particle data provided by the Space Environment Laboratory showed excellent agreement with the satellite observations (Solomon et al., 1983). Although these mesospheric ozone depletions have an insignificant

effect on the total ozone column, they provide a unique opportunity to test our understanding of the basic photochemistry of ozone, so the agreement is very encouraging.

II. In-Situ Stratospheric Composition Measurements

The photochemistry of stratospheric ozone is exceedingly complex, and is controlled by a large number of minor atmospheric constituents. Water vapor and its chemical by-products have major parts in the complex chemical cycle that leads to loss of stratospheric ozone. The odd-nitrogen (NO_x) and odd-hydrogen (HO_x) compounds are especially influential, and the Aeronomy Laboratory has for several years had a major program aimed at developing instrumentation to measure these constituents and their precursors and gathering data on a global basis using balloon and aircraft platforms.

An ultraviolet-photodissociation water-vapor instrument, developed by the Aeronomy Laboratory (Kley et al., 1979), and flown on many occasions, has provided information on stratospheric H_2O concentrations with a precision and height resolution never before achieved. Analysis of data from 11 flights over Panama on the NASA U-2 aircraft has been completed (Kley et al., 1982), and the results clearly show the vital role of tropical convective storms in injecting water vapor into the stratosphere. Certain localized regions of the tropics probably have a major role because of the characteristic intensity of their convective activity. Chief among these is thought to be the western Pacific, and Aeronomy Laboratory scientists are participating in planning an international experiment in that region. Data from the water vapor instrument have also shown the existence of fine structure in the height profile of H_2O , with corresponding fine structure in the ozone profile. The cause probably lies in changes in air trajectories with height rather than in photochemical change. Further study is under way.

An instrument that measures the concentrations of NO and NO_2 has been built and successfully flown in collaboration with the National Center for Atmospheric Research. Four balloon flights have been made from Palestine, Tex., and Gimli, Manitoba, and produced the first in situ measurements of NO_2 in the stratosphere. NO and NO_2 play vital roles in the photochemistry of stratospheric ozone.

A new instrument for in situ measurement of stratospheric ozone using a dual-beam ultraviolet absorption technique has been built and successfully flown. Flight data have revealed the fine structure in O_3 profiles mentioned above. The instrument participated in the NASA-sponsored balloon ozone intercomparison experiment in the summer of 1983.

A triple-beam instrument is being developed that should be able to make accurate ozone measurements at the 40-km altitude where the maximum anthropogenic depletion is predicted.

III. Laboratory Kinetics Measurements

Future trends in stratospheric ozone concentrations are assessed through model calculations. The success of the models depends to a very high degree on knowledge of the rates of the chemical reactions that take place in the

stratosphere, and these chemical reaction rates can be determined only by laboratory measurements. The Aeronomy Laboratory has for several years maintained a laboratory kinetics program that has achieved a position of international leadership through measurement of several of the key reactions that influence stratospheric ozone.

The principal technique used for neutral reaction studies is that of laser magnetic resonance (LMR), first developed in the Boulder Laboratories of the National Bureau of Standards. Ion-molecule reactions are studied with the flowing-afterglow and flow-drift techniques pioneered by Aeronomy Laboratory scientists.

Results obtained within the 2-year period of this report include low-pressure measurements of the reaction between HO₂ radicals,



In the atmosphere, the reaction is a source of hydrogen peroxide, H₂O₂, which plays an important role in stratospheric photochemistry. Work has also been carried out on the chemistry of the gaseous chlorine species themselves (Lee and Howard, 1982; Lee et al., 1982), which cause ozone depletion, and on the atmospheric chemistry of sodium, with the objective of determining the influence of metallic species of meteoric origin on stratospheric ozone. A study of the chemistry of NO₃, an important intermediate species in the stratospheric nitrogen cycle, is also under way.

IV. Optical Measurements

The use of optical (photometric and spectroscopic) remote sensing techniques for measuring atmospheric composition is an important part of the Aeronomy Laboratory program. The basic technique for stratospheric applications is very simple. It consists of measuring the intensity of sunlight or moonlight in a spectral region containing a known absorption feature of a stratospheric constituent, and comparing the intensity with that in a neighboring spectral region outside the absorption feature. The difference gives a measure of the line-of-sight column density of the constituent. The technique was first applied to NO₂ and gave the first global measurements of the stratospheric NO₂ column (Noxon, 1979, 1981; Noxon et al., 1979), delineating the prominent "cliff"--sharp gradient--in the winter hemisphere measurements.

The same technique was applied to NO₃ (Noxon et al., 1978) and gave the first measurements of this transient species, which plays a key role in stratospheric photochemistry. The study yielded some results that were contrary to theory. The molecule appears to be attacked by some unknown scavenger in the troposphere, and the unraveling of the anomalous behavior should yield fresh insight into the complexities of the atmospheric nitrogen cycle, with a direct bearing on the photochemistry of ozone.

A similar technique has been applied to measurements of the vertical column of the OH radical, and the long-term variation of the OH column. The results have shown some unexpected features, including a highly significant positive correlation with the sunspot cycle (Burnett and Burnett, 1981, 1982). The measurements and their analysis are continuing.

Collaboration with a University of Colorado group led to the inclusion of an optical NO₂ detector in the instrument payload of the Solar Mesosphere Explorer (SME) satellite, launched in October 1981. Analysis of data is now proceeding, and has revealed the possibility of studying global circulation patterns in the stratosphere by using NO₂ as a tracer.

The El Chichón volcanic explosion of April 1982 gave rise to unexpected changes in stratospheric composition, but unfortunately rendered the SME instrument temporarily incapable of measuring NO₂. The original ground-based techniques, however, showed large decreases in NO₂ associated with certain regions of the volcanic cloud. There were corresponding small increases in the column abundance of stratospheric ozone, and changes in the stratospheric OH column. Analysis of these observations has begun.

V. Atmospheric Dynamics

The problem of stratospheric ozone involves photochemistry, radiation, and dynamics. Ozone is formed photochemically mainly in the middle and upper stratosphere, and diffuses down into the lower stratosphere through the action of turbulence and wave motions. Its strong absorption coefficient for solar ultraviolet radiation then provides the principal heat source that drives the general circulation of the stratosphere.

The Aeronomy Laboratory has been investigating stratospheric dynamics for several years. The chief experimental tool has been the VHF Doppler radar (Gage and Balsley, 1978), which can measure horizontal and vertical motions over a wide range of heights. With the support of the National Science Foundation, the Laboratory constructed and is operating at Poker Flat, Alaska, the world's largest radar dedicated to clear-air studies.

The Laboratory is making important contributions to knowledge of atmospheric waves (VanZandt, 1982; Ecklund et al., 1981, 1982), turbulence, (Balsley and Carter, 1982; Larson et al., 1982) and circulation (Nastrom et al., 1982; Reid and Gage, 1981). Atmospheric motions on the scales of all of these influence the transport of minor constituents in the stratosphere, and must be included in the models used to assess trends in stratospheric ozone concentrations.

VI. References

- Balsley, B. B., and D. A. Carter, 1982. The spectrum of atmospheric velocity fluctuations at 8 km and 86 km. Geophys. Res. Lett., 9, 465.
- Burnett, C. R., and E. B. Burnett, 1981. Spectroscopic measurements of the vertical column abundance of hydroxyl (OH) in the earth's atmosphere. J. Geophys Res., 86; 5185.
- Burnett, C. R., and E. B. Burnett, 1982. Vertical column abundance of atmospheric OH at solar maximum from Fritz Peak, Colorado. Geophys. Res. Lett., 9, 708.
- Cicerone, R. J., S. Walters, and S. C. Liu, 1983. Nonlinear response of stratospheric ozone column to chlorine injections. J. Geophys. Res., 88, 3647.

- Ecklund, W. L., K. S. Gage, B. B. Balsley, R. G. Strauch, and J. L. Green, 1982. Vertical wind variability observed by VHF radar in the lee of the Colorado Rockies. Mon. Wea. Rev., 110, 1451.
- Ecklund, W. L., K. S. Gage, and A. C. Riddle, 1981. Gravity wave activity in vertical winds observed by the Poker Flat MST radar. Geophys Res. Lett., 8, 285.
- Gage, K. S., and B. B. Balsley, 1978. Doppler radar probing of the clear atmosphere. Bull. Amer. Meteor. Soc., 59, 1074.
- Garcia, R. R., and S. Solomon, 1983. A numerical model of the zonally averaged dynamical and chemical structure of the middle atmosphere. J. Geophys. Res., 88, 1379.
- Kley, D., E. J. Stone, W. R. Henderson, J. W. Drummond, W. J. Harrop, A. L. Schmeltekopf, and T. L. Thompson, 1979. In-situ measurements of the mixing ratio of water vapor in the stratosphere. J. Atmos. Sci., 36, 2513.
- Kley, D., A. L. Schmeltekopf, K. Kelly, R. H. Winkler, T. L. Thompson, and M. McFarland, 1982. Transport of water vapor through the tropical tropopause. Geophys. Res. Lett., 9, 617.
- Larsen, M. F., M. C. Kelley, and K. S. Gage, 1982. Turbulence spectra in the upper troposphere and lower stratosphere at periods between 2 hours and 40 days. J. Atmos. Sci., 39, 1035.
- Lee, Y. P., and C. J. Howard, 1982. Temperature dependence of the rate constant and the branching ratio for the reaction $\text{Cl} + \text{HO}_2$. J. Chem. Phys., 77, 756.
- Lee, Y. P., R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, 1982. Laser magnetic resonance spectroscopy of ClO and kinetic studies of the reactions of ClO with NO and NO_2 . Int. J. Chem. Kinet., 14, 711.
- Liu, S. C., D. Kley, M. McFarland, J. D. Mahlman, and H. Levy, 1980. On the origin of tropospheric ozone. J. Geophys. Res., 85, 7546.
- Liu, S. C., M. McFarland, D. Kley, O. Zafiriou, and B. Huebert, 1983. Tropospheric NO_x and O_3 budgets in the equatorial Pacific. J. Geophys. Res., 88, 1360.
- Nastrom, G. D., B. B. Balsley, and D. A. Carter, 1982. Mean meridional winds in the mid- and high-latitude summer mesosphere. Geophys. Res. Lett., 9, 139.
- Noxon, J. F., 1976. Atmospheric nitrogen fixation by lightning. Geophys. Res. Lett., 3, 463.
- Noxon, J. F., 1979. Stratospheric NO_2 : II. Global behavior. J. Geophys. Res., 84, 5067.

- Noxon, J. F., 1981. NO_x in the mid-Pacific troposphere. Geophys. Res. Lett., 8, 1223.
- Noxon, J. F., R. B. Norton, and W. R. Henderson, 1978. Observation of atmospheric NO_3 . Geophys. Res. Lett., 5, 675.
- Noxon, J. F., E. C. Whipple, and R. S. Hyde, 1979. Stratospheric NO_2 :
I. Observational method and behavior at mid-latitude. J. Geophys. Res., 84, 5047.
- Reid, G. C. and K. S. Gage, 1981. On the annual variation in height of the tropical tropopause. J. Atmos. Sci., 38, 1928.
- Solomon, S., and R. R. Garcia, 1983. Simulation of NO_x partitioning along isobaric parcel trajectories. J. Geophys. Res., 88, 5497.
- Solomon, S., G. C. Reid, D. W. Rusch, and R. J. Thomas, 1983. Mesospheric ozone depletion during the solar proton event of July 13, 1982. Part II. Comparison between theory and measurements. Geophys. Res. Lett., 10, 257.
- Van Zandt, T. E., 1982. A universal spectrum of buoyancy waves in the atmosphere. Geophys. Res. Lett., 9, 575.

AIR RESOURCES LABORATORY

Rockville, Maryland

I. Ozone Monitoring

Research and development activities have so progressed over the past several years that we now have a fairly well-defined strategy for monitoring trends in the total global ozone budget and trends in upper stratospheric ozone concentrations where the greatest percentages of depletions are expected to occur. Moreover, a global monitoring system composed of operational satellite instruments and ground-based instruments, having the necessary reliability for making the required long-term measurements, has been developed to maturity.

Advantages of the satellite system include global coverage with a single instrument and real-time data acquisition. The ground-based Dobson ozone network and the rocket and balloon ozonesonde networks continue to be needed for verification and calibration of the satellite measurements.

Parts of the system are already in use, and the key satellite monitoring instrument, the solar backscatter ultraviolet ozone monitor, will be deployed on NOAA's TIROS-N by the end of 1984. Research teams of highly competent scientists from government, universities, and private industry have been organized at NASA and NOAA to oversee operations of the ozone-monitoring system and, with the new data products, verify past scientific findings and make firmer assessments of future deleterious changes in the ozone layer.

A. Variations in Ozone

1. Variations in total ozone

It is important to monitor total ozone (the total amount of ozone in a vertical column above a point on the earth's surface) because the variations in this quantity affect the amount of solar ultraviolet radiation reaching the ground; an increase in ultraviolet radiation resulting from a decrease in total ozone could be deleterious to humans and plants. Total ozone data are being obtained on a routine basis from the World Meteorological Organization Global Ozone Monitoring Network (70 stations in the Northern Hemisphere and 20 stations in the Southern Hemisphere). Ground-based instruments are used; they compare the solar radiation in two adjacent wavelengths, in one of which ozone absorbs the ultraviolet radiation.

Figure 1 shows the variation in year-average total ozone for both hemispheres and for the world from 1958 through 1982, as estimated from the ground station data (Angell and Korshover, 1983). There is more uncertainty in the Southern Hemisphere values (greater lengths of the vertical bars) because fewer stations are represented. The data show little evidence of a long-term trend in total ozone in either hemisphere, or in the world as a whole, although the 1982 Southern Hemisphere value is the second lowest of

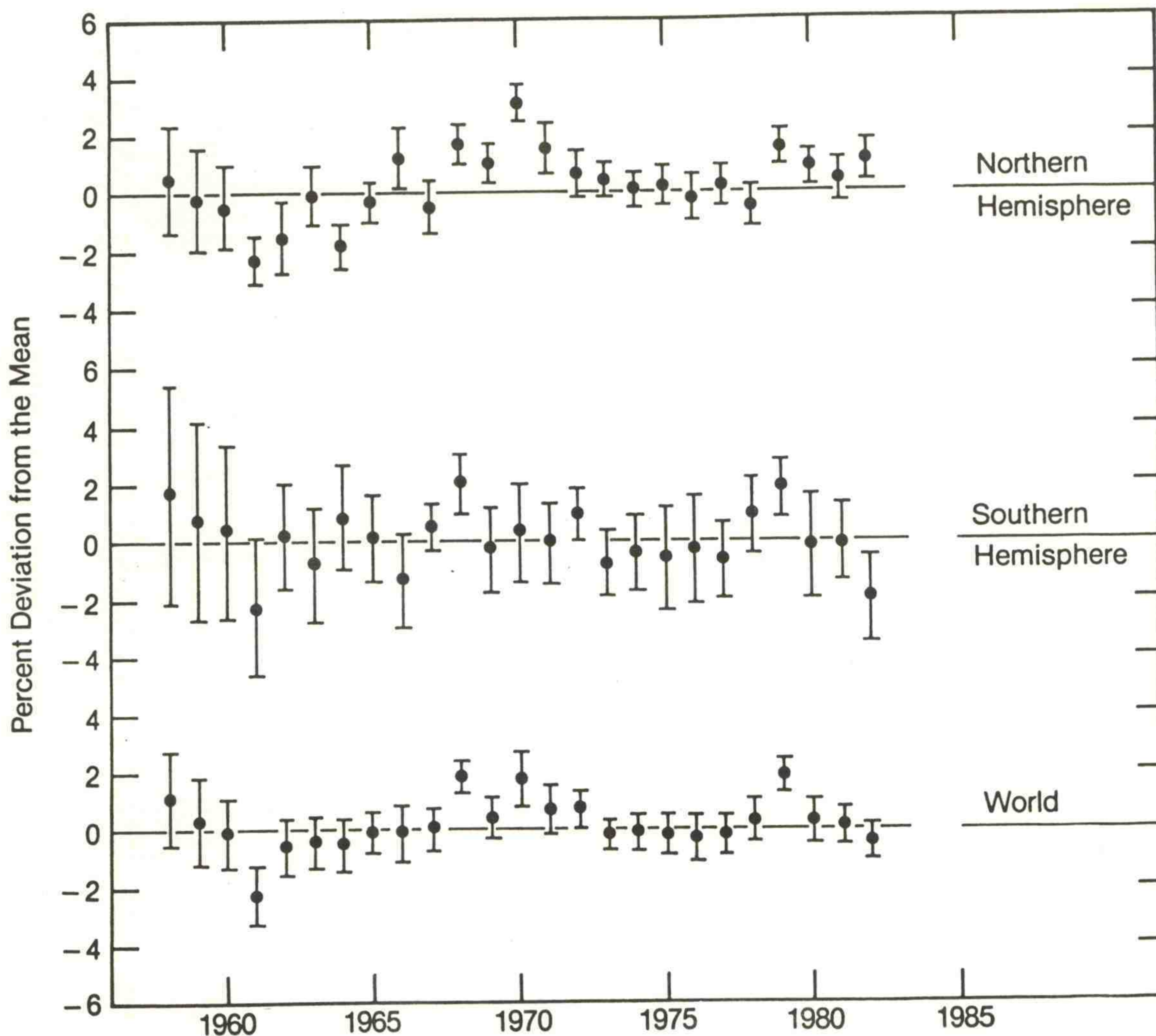


Figure 1. Variation in year-average total ozone for the hemispheres and the world, expressed as percentages of deviation from the mean. There is about a 70% chance that the true value of the annual mean lies within the limits indicated by the vertical bars.

record. Ozone amounts tended to be above average in 1958, 1968-70, and 1979, near times of sunspot maxima, but it is too early to claim a relationship.

2. Variations in ozone amounts in different layers of the atmosphere

It is important to monitor ozone variations in different layers of the atmosphere because photochemical models predict that the largest percentage decrease of ozone due to human activity will occur near the 40-km level, with possible increases in ozone in the troposphere and low stratosphere, up to a height of about 20 km. That is, there could be a change in ozone profile, with perhaps serious climatic effects, without a change in the quantity of total ozone.

Figure 2 shows the variations in year-average ozone in north temperate latitudes from 1961 through 1982, as estimated from Umkehr observations and

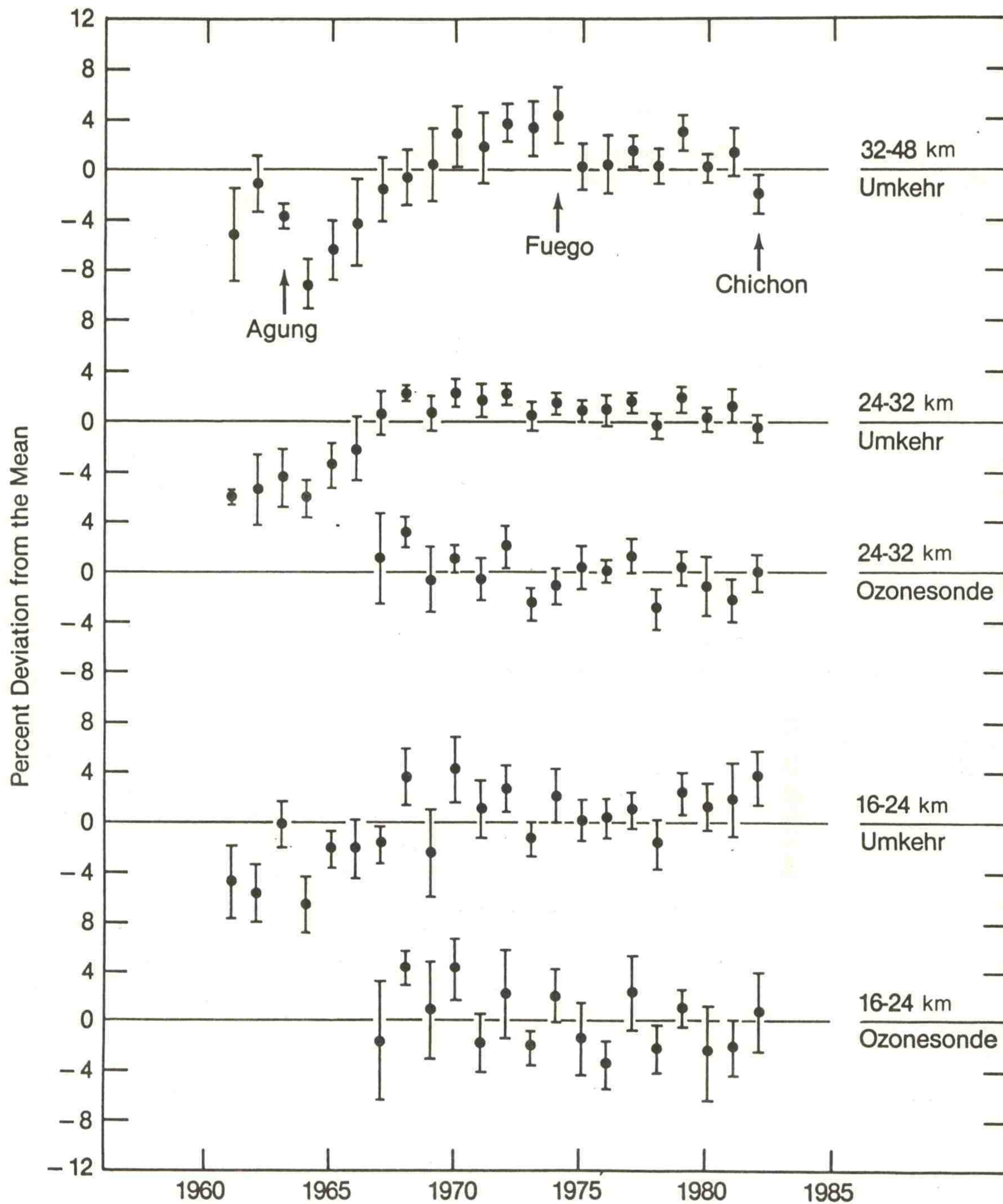


Figure 2. Variation in year-average ozone in stratospheric layers of north temperate latitudes, from Umkehr and ozonesonde measurements.

ozonesonde measurements. Umkehr observations were made by about 15 stations in the ground network and involve observations of changes in the intensity of radiation (in adjacent wavelengths) scattered from the zenith sky as the sun rises and sets. (Results are presented only for the north temperate zone because most of the Umkehr observations are in this zone.)

It is apparent that in the 32-48 km layer the ozone amount estimated by the Umkehr method has been relatively low at or following the volcanic

eruptions of Agung (Indonesia) in 1963, Fuego (Guatemala) in 1974, and El Chichón (Mexico) in 1982. These relatively low ozone values are believed to be mostly fictitious, and due to the influence volcanic aerosols in the stratosphere have on the Umkehr observations. Determination of the ozone trend in the 32-48 km layer is accordingly difficult when there are large volcanic eruptions. Even so, there is evidence of a 2%-3% decrease in ozone in this layer since 1970. It is not known at this time whether the cause of this indicated ozone decrease is natural or anthropogenic.

Umkehr data for the 24-32 and 16-24 km layers suggest only about a 1% decrease in ozone in these layers since 1970. However, ozonesonde (balloon-borne instruments making in situ measurements of ozone) data obtained from about 15 stations for 1967-1982 suggest an ozone decrease of several percent in these layers. Thus, the available evidence suggests a small ozone decrease since 1970 through most of the north temperate stratosphere. The near invariance of total ozone (Fig. 1) together with the slight decrease in stratospheric ozone (Fig. 2) implies an increase in tropospheric ozone, and there is evidence from ozonesonde data that such an increase has indeed occurred.

B. Upper Stratospheric Umkehr Ozone Profile Data: Evidence of an Apparent Downward Trend

A team of scientists from U.S. universities, the Canadian government, NASA, and NOAA investigated the heretofore neglected effect of stratospheric dust on long-term Umkehr observations of stratospheric ozone and found an apparent downward trend in ozone concentration between 35 and 45 km. Reinsel et al. (1984) analyzed the long-term (22 years) Umkehr vertical ozone profile record from 13 stations, together with the Mauna Loa atmospheric transmission data, to examine the ozone record for stratospheric dust effects. Their analysis indicates a statistically significant relation between Umkehr-measurement effects and stratospheric aerosols (originating from volcanic injections) in the upper Umkehr layers (Table 1), and further, a statistically significant negative trend of ozone in those layers after the Umkehr measurements have been corrected. Although the cause or causes of the estimated trend cannot be unambiguously determined by statistical investigation, the ozone changes detected by the analysis are consistent with recent theoretical photochemical model predictions (Weubbles et al., 1983), and represent the first directly observed evidence of a downward trend in stratospheric ozone. (See also National Weather Service, sec. II.)

For verification of the trend, it is essential that the Umkehr data be closely monitored in the future to assess whether the detected trend persists. It is equally important to improve the quality and quantity of Umkehr measurements and to obtain regular stratospheric aerosol measurements on a more extensive geographic basis. This will allow for even more accurate adjustments for aerosol effects on the Umkehr data.

C. Dobson Spectrophotometer Ozone Monitoring

During 1982 and 1983, the Air Resources Laboratories continued to monitor total ozone at ten of twelve Dobson instrument stations (Table 2).

Table 1. Ozone change between 1970 and 1980, estimated from Umkehr vertical ozone profiles corrected for the effects of atmospheric dust

Umkehr Layer (altitude)	Change Per Year (%)	95% Confidence Interval
9 (43-48 km)	-0.29	±0.39
8 (38-43 km)	-0.30*	±0.16
7 (34-38 km)	-0.22	±0.17
6 (29-34 km)	-0.00	±0.11
5 (24-29 km)	-0.04	±0.14

*This is consistent with the Weubbles et al. (1983) updated theoretical predictions of ozone depletion rate.

Table 2. 1983 U.S. Dobson ozone spectrophotometer station network

Station	Period of Record	Instrument Number	Agency
Bismarck, N. Dak.	1 Jan. 63-present	33	NOAA
Caribou, Maine	1 Jan. 63-present	34	NOAA
Tutuila Is., Samoa	19 Dec. 75-present	42	NOAA
Mauna Loa, Hawaii	2 Jan. 64-present	63	NOAA
Wallops Is., Va.	1 Jul. 67-present	38	NOAA/NASA
Barrow, Alaska	2 Aug. 73-8 Oct. 82	76	NOAA
Nashville, Tenn.	1 Jan. 63-present	79	NOAA
Boulder, Colo.	1 Sep. 66-present	82	NOAA
White Sands, N.Mex.	5 Jan. 72-29 Jan. 82	86	NOAA/Army
Tallahassee, Fla.	2 Jun. 73-31 May 79 5 Oct. 81-present	58	NOAA/Florida State U.
Huancayo, Peru	14 Feb. 64-present	87	NOAA/Huancayo Obs.
Amundsen-Scott, Antarctica	5 Dec. 63-present	80	NOAA

Observations at Pt. Barrow, Alaska were discontinued in October 1982 in anticipation of relocating that station to Poker Flat, Alaska. Observations at White Sands, N. Mex., were terminated in January 1982 when the U.S. Department of the Army could no longer support the program.

Funding was obtained in 1982 from the U.S. Environmental Protection Agency, the Chemical Manufacturers Association, the WMO Voluntary Cooperation Program, and NOAA for automating six Dobson spectrophotometers and establishing them in a global network for long-term Umkehr measurements of possible ozone changes at 40 km altitude due to the effects of anthropogenic pollutants. As of 31 December 1983, five of the instruments, as well as Ash-Dome shelters for the instruments, had been automated. Five of the instruments were installed and are operational at Haute Provence, France; Poker Flat, Alaska; Mauna Loa, Hawaii; Perth, Australia; and Boulder Colo. The remaining two instruments are awaiting host-nation clearances for Huancayo, Peru, and Pretoria, South Africa. The automated Dobson instrument at Boulder has been operational since early in 1983.

Following the eruption of El Chichón volcano in April 1982, a program was implemented at Mauna Loa Observatory to study the effects of stratospheric aerosols on Umkehr observations. Initial measurements confirmed previous observations and theoretical work indicating that the accuracy of ozone measurements near 45-km altitudes would be adversely affected. When the stratosphere was heavily loaded with aerosols in May 1982, conventional Umkehr measurements yielded erroneous negative ozone values near 45 km. As the aerosol layer became progressively thinner, the Umkehr measurements reverted to near-normal values by the end of 1982.

In 1981, seven standard lamp units were built and calibrated in the Laboratory. These were sent to the seven WMO regions of the globe for checking Dobson instrument calibrations at 5 to 19 stations in each region. Results from the majority (77) of the stations have been received, and show that 36% of the instruments require recalibration.

II. Stratospheric Temperature Monitoring

Stratospheric temperature changes affect the rates of photochemical changes that are relevant to the ozone balance. Monitoring of stratospheric temperature is also important because of the cooling of the stratosphere associated with an increase in carbon dioxide (CO₂). Since the CO₂-induced stratospheric cooling should be considerably greater than the CO₂-induced tropospheric warming, it is the stratosphere that should provide the earliest warning of a CO₂ effect.

In the Northern Hemisphere, stratospheric temperatures are being monitored from both rocketsonde and radiosonde data. Figure 3 shows variations in year-average temperature, as estimated from rocketsonde or radiosonde data (Angell and Korshover, 1983, a,b).

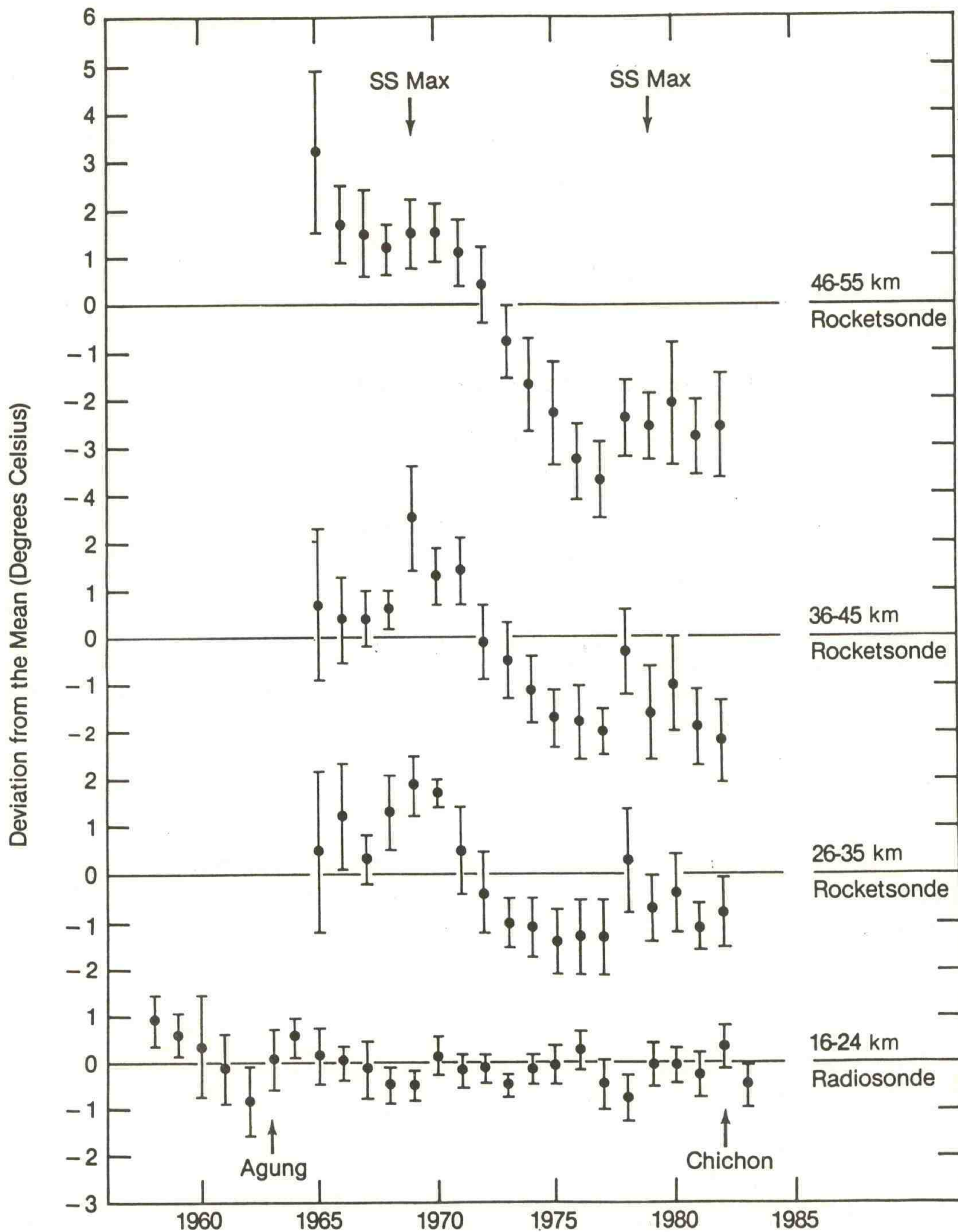


Figure 3. Variation in year-average temperature in stratospheric layers of the Northern Hemisphere. Temperatures for 46–55, 36–45, and 26–35 km layers were estimated from rocketsonde data through 1982, obtained mostly in the western quadrant of the Northern Hemisphere. Temperatures for the 16–24 km layers were estimated from radiosonde observations through 1982, throughout the Northern Hemisphere. The vertical bars represent 70% confidence limits. That is, there is about a 70% chance that the true value of the yearly mean temperature lies between the top and bottom limits. Arrows labeled SS MAX indicate years of maximum sunspot activity.

The radiosonde data for the 16-24 km layer show that there was a warming of the low stratosphere following the volcanic eruptions of Agung (Indonesia) in 1963 and El Chichón (Mexico) in 1982, but there is little evidence of a long-term trend in temperature in this layer. The rocketsonde data, however, suggest a large temperature decrease between 1970 and 1976 but little temperature change thereafter. The indicated cooling between 1970 and 1976 is much too large to be associated, in its entirety, with a CO₂ effect, and the reason for this large decrease is unknown. There is evidence from the rocketsonde data of relative temperature maxima near the times of sunspot maxima in 1969 and 1979, but it is too early to claim a relationship.

III. Water Vapor Monitoring

The radiative and photochemical properties of water vapor in the stratosphere and the role of water vapor as a tracer of exchange between the troposphere and the stratosphere are the subject of continued research. Regular soundings from Boulder are combined with earlier data from Washington, D.C., to support studies of stratospheric water vapor distribution and variations. (See also Aeronomy Laboratory, sec. II)

Below 15 km (120 mb) in the upper troposphere and lower stratosphere, seasonal fluctuations in the tropopause produce a marked annual variation in water vapor mass mixing ratio. Around 20 km (50 mb) altitude, the seasonal variations are small, rendering this region advantageous for studying variations on longer time scales. A curve fitted to the individual measurements provides evidence of a prominent quasi-biennial oscillation (QBO). This QBO suggests a modulation of the poleward transport of Hadley Cell circulation by tropical stratosphere zonal winds. A quadratic trend line fitted to the water vapor data at 20 km shows that the earlier upward trend through the 1960's became negative during the late 1970's, so that current values approximate those observed in the early 1960's.

IV. Monitoring of Freon -11 and -12, and Nitrous Oxide

Freon-11(CCl₃F) and Freon-12 (CCl₂F₂), both anthropogenic, are decomposed in the stratosphere by photolysis, causing catalytic destruction of stratospheric ozone by released chlorine atoms. Nitrous oxide (N₂O) also enters into stratospheric photochemical reactions (involving NO_x) as a significant precursor to the catalytic destruction of ozone. Nitrous oxide is emitted from land by bacterial denitrification of fixed nitrogen, as well as from combustion of fossil fuels.

The Air Resources Laboratory has been monitoring F-11, F-12, and N₂O since 1977. Data obtained at Pt. Barrow, Alaska; Niwot Ridge, Colorado; Mauna Loa, Hawaii; American Samoa, South Pacific; and South Pole, Antarctica, are shown in Figures 4-6. Results of linear regression trend analyses of the measurement data are shown in Tables 3 and 4.

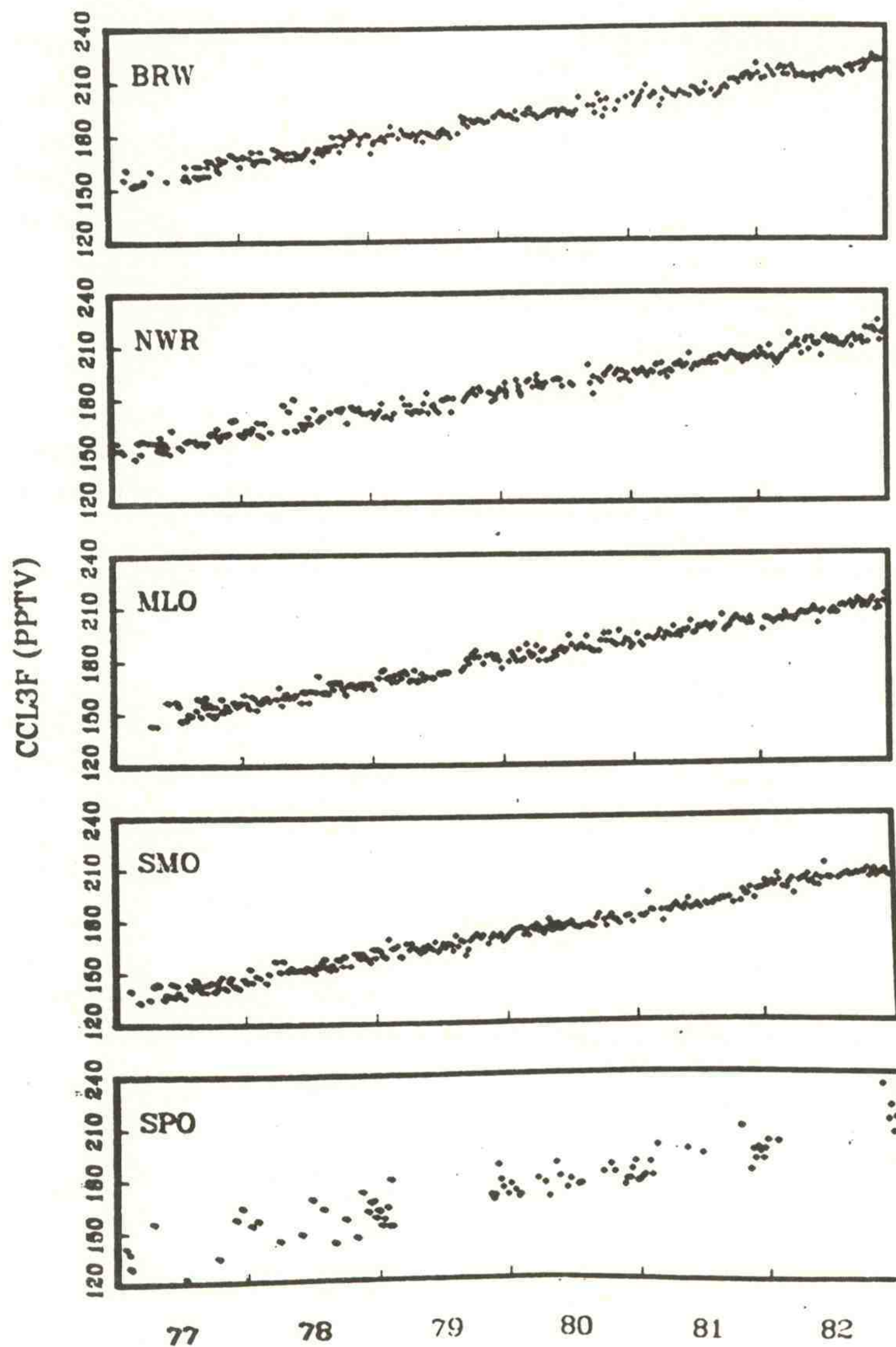


Figure 4. Freon-11 data obtained at the Air Resources Laboratory baseline observatories. (Outlying points have been removed.)

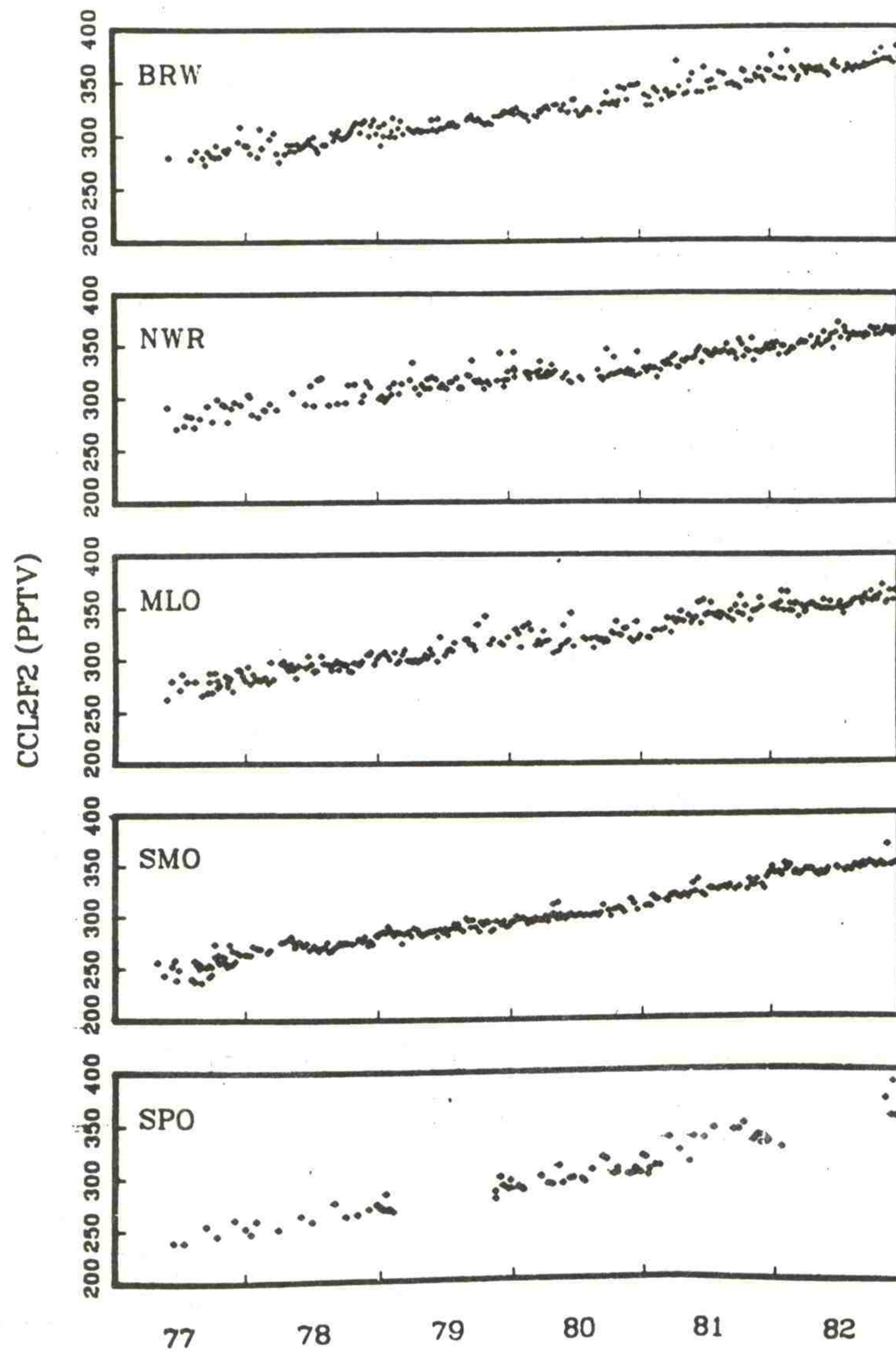


Figure 5. Freon-12 data obtained at the Air Resources Laboratory baseline observatories. (Outlying points have been removed.)

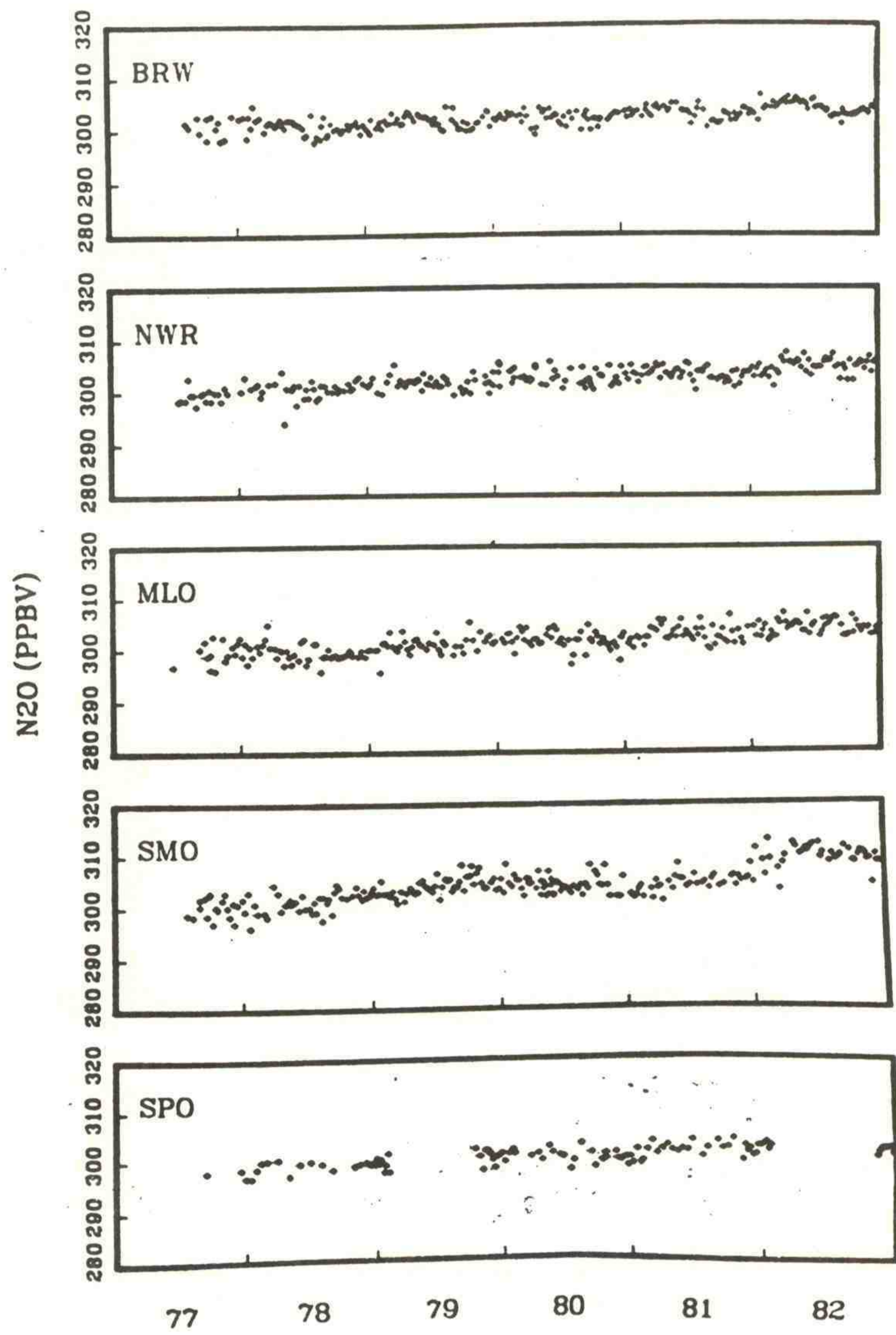


Figure 6. Nitrous oxide data obtained at the Air Resources Laboratory baseline observatories. (Outlying points have been removed.)

Table 3. Summary of CCl₃F (Freon-11) and CCl₂F₂ (Freon-12) measurement results

Station	1982 Mean Mixing Ratio (pptv)	1 Jan 1977 Mixing Ratio (pptv)*	1977-1982 Growth Rate (pptv yr ⁻¹)*
CCl₃F			
Barrow	214.9	154.1±0.40	11.12±0.11
Niwot Ridge	210.5	150.1±0.43	10.93±0.12
Mauna Loa	206.3	145.3±0.41	11.32±0.11
Samoa	202.2	134.7±0.37	12.10±0.11
South Pole	214.9	134.6±1.96	12.70±0.57
CCl₂F₂			
Barrow	362.9	270.0±0.97	16.73±0.26
Niwot Ridge	356.8	276.7±1.23	14.15±0.32
Mauna Loa	358.8	268.5±1.03	15.67±0.28
Samoa	345.8	241.8±0.76	18.39±0.22
South Pole	364.5	225.7±2.67	22.34±0.74

*Indicated uncertainties are 95% confidence internal standard errors.

Table 4. Summary of N₂O measurement results

Station	1982 Mean Mixing Ratio (ppbv)	1 Jan 1977 Mixing Ratio (ppbv)*	1977-1982 Growth Rate (ppbv yr ⁻¹)*
Barrow	303.8	300.1±0.20	0.61±0.05
Niwot Ridge	304.8	299.1±0.23	0.99±0.06
Mauna Loa	304.0	298.3±0.25	0.99±0.07
Samoa	309.3	299.1±0.31	1.59±0.09
South Pole	302.2	297.5±0.32	0.01±0.09

*Indicated uncertainties are 95% confidence internal standard errors.

V. Ultraviolet Radiation Monitoring

Ultraviolet radiation has been monitored since 1974 by the worldwide network of Robertson-Berger (RB) meter sites. During the 1982-83 period, 32 instruments were in operation, 18 of which were located in the contiguous United States. Nine of the U.S. group have continuous 10-year records, and nine have been in operation 3 to 5 years. The non-U.S. stations have periods ranging from 1 to 9 years. The network was originally established in response to perceived threats to the ultraviolet-absorbing stratospheric ozone layer through the introduction of certain anthropogenic chemicals into the environment. Any subsequent increase of ultraviolet radiation is anticipated to induce increasingly harmful biological effects such as higher human skin cancer rates.

The RB meters are operated continuously. They provide half-hourly integrals of UV radiation, which are recorded in arbitrary rather than absolute energy units. The instrument has proved to be stable and very rugged in operation, yielding data recovery rates in excess of 90% at nearly every site. Further, 13 of the U.S. locations are National Weather Service stations, which provide concomitant meteorological observations. Additionally, two stations, Bismarck and Tallahassee, also have daily total ozone measurements available for comparison purposes. In 1983, an Air Resources Laboratory scientist compared the RB meter with a double slit monochromator, establishing a method by which the RB unit of measurement may be converted to energy units.

VI. References

- Angell, J. K., and J. Korshover, 1983a. Global temperature variations in the troposphere and stratosphere, 1958-1982. Mon. Wea. Rev., 111, 901-921.
- Angell, J. K., and J. Korshover, 1983b. Global variation in total ozone and layer-mean ozone: An update through 1981. J. Climate and Appl. Meteor., 11, 1611-1627.
- Reinsel, G. C., G. C. Tiao, J. J. DeLuisi, C. L. Mateer, A. J. Miller, J. E. Frederick, 1984. Analysis of upper stratospheric Umkehr ozone profile data for trends and the effects of stratospheric aerosols. J. Geophys. Res., 89, 4833-4840.
- Weubbles, D. J., 1983. A theoretical analysis of the past variations in global atmospheric composition and temperature structure. Lawrence Livermore Laboratory Report UCRL-53423, 161 pp.

GEOPHYSICAL FLUID DYNAMICS LABORATORY

Princeton, New Jersey

Changes in atmospheric trace constituents and the climatic effect of such changes cannot be adequately predicted or understood without a firm knowledge of the processes that maintain or alter the normal state. Research to improve simulation and understanding of the atmosphere (including the stratosphere) has been under way at the Geophysical Fluid Dynamics Laboratory (GFDL) for more than 25 years. The middle atmosphere research effort was accelerated in 1970 when a commitment was made to investigate the chemistry, radiation, and dynamics of the stratosphere. Stratospheric research performed at GFDL since January 1982 builds on the considerable research base established earlier.

I. Three-Dimensional Modeling of Trace Constituent Behavior

Since 1979, GFDL has explored problems relating to transport and chemistry of trace constituents, using one of the GFDL global three-dimensional (3-D) general circulation models (GCM) (e.g., Manabe et al., 1974; Manabe and Mahlman, 1976). This model provides self-consistent, time-dependent winds as input to a separate model to study many aspects of trace constituent transport and chemistry (for model details, see Mahlman and Moxim, 1978; Levy et al., 1982).

A. Atmospheric N₂O Experiments

Nitrous oxide (N₂O) is well recognized to be the most important precursor gas controlling the ozone amount in the atmosphere. This gas has mainly biological sources at the earth's surface, is essentially inert in the troposphere and lower stratosphere, and is destroyed photochemically in the middle stratosphere. A small but important part of that photochemical destruction leads to the formation of "reactive nitrogen" in the form of nitric oxide (NO). This gas and its photochemical companion, NO₂, form the major catalytic ozone destruction cycle in the lower and middle stratosphere. Thus, a firm quantitative understanding of N₂O is essential for a thorough understanding of ozone and its change.

Analysis has been completed on a number of 3-D model experiments exploring the structure and variability of N₂O from various surface sources. In addition to the previously reported results, predictions are offered on the real behavior of tropospheric N₂O, which await observational testing: (1) a significant (~1%) excess of N₂O in the Southern Hemisphere middle troposphere (assuming no significant anthropogenic sources); (2) magnitudes of spatial and temporal variability of N₂O in and away from the boundary layer; and (3) conditions under which the empirical "Junge rule" should be inapplicable (Levy et al., 1982).

Work has also been completed on a series of experiments designed to test various photodestruction hypotheses. The results strongly suggest that more photochemical destruction of N₂O is required than the model allows

through use of current absorption cross section data. (Recent measurement work [Frederick and Mentall, 1982] showing reduced O_2 cross sections indicates that a portion of the difference may be identified.) Especially useful is the finding that properly calculated global-average 1-D eddy diffusion coefficients should be applicable to a wide range of long-lived trace gases. The analysis also predicts that all horizontal maps of the vertical "topography" of time-mean mixing ratio surfaces will be essentially the same for a rather wide class of long-lived trace constituents.

This relationship is predicted to hold as long as the stratospheric chemical destruction time scale is long compared with an appropriate meridional transport time scale. It has allowed development of a simple theory that predicts the temporal tracer variability in terms of time-mean spatial gradients and non-conservative effects (Mahlman et al., 1984). These two predictions will be tested against available observational data.

B. Reactive Nitrogen in the Troposphere

In recent years it has been recognized that understanding of tropospheric ozone requires a quantitative understanding of the tropospheric budget of reactive nitrogen (e.g., Liu et al., 1980; Kley et al., 1981). However, sources of tropospheric reactive nitrogen include stratospheric injection (Levy et al., 1980), surface combustion, and possibly lightning and surface biological activity.

GFDL has completed a set of 3-D model experiments designed to investigate the possible effect of the U.S. combustion source on the global tropospheric budget of reactive nitrogen. In all experiments the combustion nitrogen is assumed to be immediately converted to HNO_3 , which is rapidly removed by both precipitation and contact at the earth's surface. This assumption should produce a lower-limit estimate of the contribution of combustion nitrogen to the global distribution of reactive nitrogen.

A series of 2-month integrations showed that even very rapid rainout (a global lifetime of ~ 2 days in the lower troposphere) is not sufficient to produce an HNO_3 profile in the upper troposphere that drops off with altitude as fast as or faster than that of H_2O , another very efficiently removed trace gas. Adding another mechanism, the selective filtering of water soluble trace gases in rising air, produced a more appropriate HNO_3 profile. However, the fundamental uncertainty in quantifying the removal processes remains a very significant barrier to complete understanding of reactive nitrogen, and thus, of ozone.

The experiment that included filtering of rising air, as well as wet and dry removal, has been integrated from January through August. The model indicates that there is no significant transport into the Southern Hemisphere, and stratospheric injection dominates down to 500 mb almost everywhere. However, there is significant transport of U.S. HNO_3 to Canada and Latin America, and episodic events carry it over the North Atlantic to Europe, up to the Arctic, and out over the eastern equatorial Pacific. Extratropical cyclones are the major mechanism for lifting combustion HNO_3 out of the boundary layer to the middle and upper troposphere where long-range transport can take over.

It is also found that the effective source to the atmosphere is significantly less than the surface emission rate for a substance such as HNO_3 that is easily removed by surface destruction. The amount depends on both the emission height and the intensity of boundary layer mixing processes.

Work is continuing on quantifying removal. More carefully posed model experiments are being planned for multiple subspecies of the reactive nitrogen group, particularly interactive NO_x ($\text{NO} + \text{NO}_2$) and HNO_3 .

C. Examination of the Classical Theory for Tropospheric Ozone

In polluted boundary layer air, ozone is clearly under strong photochemical influence; however, ozone in the "unpolluted" troposphere may or may not be, depending on the amount of reactive nitrogen present (see sec. I.B). The 3-D GFDL global tracer model has been used to explore one possibility: Tropospheric ozone might be explained by the "classical" mechanism (i.e., transport of ozone from the stratosphere, balanced by contact removal at the surface). This would be reasonable, simply because the classical processes must be present, even if an active tropospheric ozone chemistry is also involved.

The calculations use the stratospheric ozone chemistry described by Mahlman et al. (1980). The uncertainty in modeling surface removal rates is addressed by performing two separate numerical experiments, using "upper limit" and "lower limit" removal efficiencies.

Outside the continental boundary layer, the results of the calculations using upper- and lower-limit surface removal rates bracket the observed data. The model's interhemispheric and meridional gradients agree well with observations, except for the northern high latitudes, where the model shows a much stronger gradient than is suggested by the few observations available. A detailed analysis of model-generated local vertical ozone profiles and comparison with available observations show good qualitative agreement in both profile means and variances. In general, the model seasonal variations also show reasonable agreement with observations. An exception in Northern Hemisphere middle latitudes might be explained by a model transport deficiency.

The results are much less certain in the boundary layer, particularly over land. Over land, the model surface ozone values show too steep a vertical gradient, too high a variability, and no summer maximum. These deficiencies may be the result of excluding photochemistry, but they may also be due to too strong mixing in the bottom layer of the model, too weak mixing in the boundary layer as a whole, or no seasonal structure in the model surface removal efficiencies (Levy et al., 1984).

Measurement and modeling studies are needed to resolve discrepancies. The study has clearly demonstrated, however, that classical mechanisms are essential in any complete model of tropospheric ozone.

D. Tropospheric Ozone Photochemistry

The studies discussed have indicated that a detailed understanding of ozone photochemistry (in the presence of atmospheric transport) is essential. Therefore, a detailed ozone photochemical model has been developed. To test some of the previous concepts, model results, and observations, experiments with a detailed diurnal ozone photochemical model have been carried out at 500 mb for summer and winter conditions at 15° and 45° latitude (ozone, and carbon monoxide and water vapor mixing ratios are specified; methane chemistry is neglected; NO_x mixing ratios are varied systematically from 10 pptv to 1 ppbv).

The results, combined with those of the classical ozone study (sec. I.C), suggest that net photochemical destruction of ozone may take place in summer high latitudes, while some net production may occur in summer middle latitudes. These conclusions are critically dependent upon highly uncertain assumptions about the amount of NO_x present in the atmosphere (see sec. I.B.).

E. Development of a Self-Consistent Two-Dimensional Transport Model

Several atmospheric chemistry and transport problems have been profitably attacked through use of economical zonally averaged 2-D transport models. Yet it has been recognized for some time (e.g., Mahlman, 1975; Plumb, 1979) that the usual 2-D models are formulated in a manner consistent with contemporary understanding of atmospheric dynamics.

To see if fundamental improvements can be made, statistics from the 3-D tracer transport model are being used to evaluate the scientific feasibility of a self-consistent 2-D transport model. In principle, two well-posed 3-D tracer experiments provide all the transport coefficients and advective velocities required to satisfy the constraints of recent "generalized diffusion tensor" theories (Matsuno, 1980; Danielsen, 1981). Work on this problem is in the preliminary stage.

II. Modeling of the Troposphere-Stratosphere-Mesosphere System

For the past 8 years, GFDL has been developing a comprehensive, 3-D general circulation model of the radiative-chemical-dynamical structure of the atmosphere from the earth's surface to the mesopause (e.g., Fels et al., 1980). (This model is hereafter referred to as SKYHI.) A major goal has been to develop an internally consistent capability for simulating ozone amount and its changes. This involves a careful and accurate coupling of the chemistry with a self-consistent realistic transport and radiative transfer. As the model capability evolves, progressively more realistic experiments will be conducted. Recent experiments with SKYHI have been designed (and new techniques have been developed) to evaluate model performance in various aspects of circulation and transport dynamics.

A. Annual Mean, Medium-Resolution Experiment

This SKYHI experiment uses annual mean solar radiation (no seasonal cycle) and medium resolution (40 levels in the vertical and a 5° latitude horizontal grid) to evaluate aspects of the model's dynamics and associated transport. The analysis, using newly developed "Eliassen-Palm" diagnostics, shows that wave disturbances reduce the mean speed of the westerlies. The effect is particularly large in the upper mesosphere where the wave-induced zonal flow decelerative forces are large enough to "close off" the polar night jet at about 65 km. Another dramatic result is the effect of disturbances on the middle-latitude tropospheric westerlies: the mean tropospheric westerly wind shear is reduced by about $2 \text{ m s}^{-1} \text{ km}^{-1} \text{ day}^{-1}$.

The analysis also indicates wave-induced acceleration of westerly winds at heights of about 28 and 60 km over the equator, associated with local westerly wind maxima. A separate analysis has shown that the required momentum deposition at 28 km is accomplished by "traditional" equatorial Kelvin waves. On the other hand, at 60 km the momentum is mainly due to "fast" Kelvin waves with eastward phase speeds of about 80 m s^{-1} .

For middle latitudes, the conclusion of the new diagnostics about the force exerted by eddies on the zonal flow is qualitatively opposite to that provided by traditional methods. The new diagnostic conclusion was tested through a companion model experiment in which all eddy quantities were virtually removed from the stratosphere. The new diagnostics provided a far better prediction of the subsequent change in mean flow than do the traditional approaches (Andrews et al., 1983). The new diagnostics also give improved insights into mechanisms responsible for transport of ozone and other trace constituents. Such approaches have already stimulated new developments of SKYHI, which have yielded improved quantitative modeling of stratospheric transport.

B. Analysis of Equatorial Waves in SKIHI

A space-time spectral analysis of equatorial middle-atmosphere Kelvin and gravity waves, as simulated by the SKYHI annual mean insolation model (sec. II.A), produced some remarkable findings related to stratospheric dynamics and associated transport.

The model Kelvin waves are associated with zonal wavenumbers 1-2, have an eastward phase velocity, and tilt eastward with height. The lower-stratosphere "traditional" Kelvin wave has periods of 10 to 30 days and a vertical wavelength of 10 km, in agreement with many observational results. The upper stratospheric Kelvin waves (periods of 5 to 7 days and a vertical wavelength of 20 km) are as observed a few years ago by Hirota (1979). The mesospheric Kelvin waves have periods of 3 to 4 days and a vertical wavelength of about 40 km. These correspond closely to the wave discovered very recently by Salby et al. (1984). All these Kelvin waves transport eastward momentum upward.

SKYHI gravity waves of zonal wavenumbers 1-15 and periods ~0.5 to 2 days long are prevalent in the equatorial mesosphere. Their eastward- and westward-moving components transport eastward and westward momentum upward and contribute to the mesospheric zonal momentum balance as much as or even more than do Kelvin waves.

C. Generation and Dispersion of Equatorial Disturbances

A series of calculations has been undertaken to understand the mechanism producing the middle-atmosphere tropical disturbances observed by satellite and in SKYHI (sec. II.B). In particular, transient responses to localized, impulsive tropical latent heat releases are being investigated by an initial-value approach, which includes the effects of wave absorption and refraction.

The results show the presence of a "spectrum" of equatorially trapped, vertically propagating Kelvin and gravity waves centered about a vertical wavelength twice the depth of the imposed heating. Selective absorption of the slower, shorter vertical wavelength components of the wave spectrum appears to be responsible for the predominance of higher frequency disturbances at upper levels in the SKYHI simulations and in observations (Hirota, 1979; Salby et al., 1984).

The second result corresponds to a spectrum of normal modes with an equivalent barotropic character. These waves are vertically trapped, but they disperse energy toward higher latitudes. Accordingly, they may prove to be important in the dynamics of the middle-latitude troposphere as well.

D. Seasonal Cycle Medium-Resolution Experiment

The medium-resolution SKYHI general circulation model described in sec. II.A has been run for a couple of years with an annual cycle of solar radiation. The analysis includes a comparison of the simulation against observations (Mahlman and Umscheid, 1984). Successful simulations include the cold equatorial tropopause, the middle-latitude warm belts of the winter lower stratosphere, clear separation between the subtropical and polar night jet streams, reversed meridional temperature gradients in the winter mesosphere (and closed-off polar night jet), stratospheric summer easterlies of the proper magnitude and depth, a strong sudden warming in the model lower mesosphere, and a pronounced equatorial semi-annual oscillation.

The model's sudden warming event exhibits many features of observed warmings that do not penetrate downward into the middle stratosphere. In the lower mesosphere, the polar cap warms by more than 43° in 15 days. The higher temperatures increase the polar cap diabatic cooling rates to more than $15^\circ\text{C day}^{-1}$. Accompanying the warming is a deceleration of the mesospheric jet by more than 80 m s^{-1} . This sudden warming was initiated by a large increase in the vertical component of Eliassen-Palm flux emanating from the troposphere (Andrews and McIntyre, 1976). That flux leads to flux divergences exceeding $-40\text{ m s}^{-1}\text{ day}^{-1}$ just above the stratopause. Such a level of model forcing is sufficient to induce the large deceleration (and its associated warming). The process appears to have been facilitated by an onset of easterly winds in the Northern Hemisphere subtropics of the upper stratosphere.

E. Evaluation of Satellite Sampling of the Stratosphere

A major source of data on the structure, chemistry, and dynamics of the stratosphere comes from nadir-viewing, polar-orbiting satellites. To determine the types and magnitudes of errors to be expected in satellite sampling of the middle atmosphere, the SKYHI seasonal cycle experiment (sec. II.D) is

employed as a sample data set in which all variables are "perfectly" known. This model data set is sampled in a way similar to that in which polar-orbiting satellites sample the actual atmosphere.

Although the research is in a comparatively early stage, it has been determined that sampling can provide fairly accurate temperature spatial averages (the basic variable). However, quantities that require derivatives of the temperature field become significantly worse as the order of differentiation is increased. Thus, errors in quantities such as wind speed are noticeable, but acceptable, but quantities such as vorticity become unacceptably distorted. It is useful to know that in virtually all instances, the sampling errors are considerably larger in lower latitudes.

III. Physical Processes in the Middle Atmosphere

A. Radiative Transfer

For nearly a decade, GFDL has been developing a detailed and accurate radiative transfer model for use with SKYHI (e.g., Fels and Schwarzkopf, 1981). In the past two years, several physical processes have been added: improved CO₂ transmission functions; the (H₂O)_n continuum; and the effects of breakdown of local thermodynamical equilibrium (important above 75 km).

To better understand the effect of radiative damping on the dynamics of disturbances, a comprehensive calculation of scale-dependent radiative damping on waves in the mesosphere was undertaken, extending previous work (Fels, 1982) to shorter wavelengths and greater altitudes. The effects of the breakdown of local thermodynamic equilibrium were intentionally included. The results are complicated in detail, but yield damping times of about 1.5 days for disturbances with vertical wavelength of 6 km in the mesosphere. Simple scaling laws were derived, allowing easy extension of the results to other CO₂ mixing ratios. A doubling of the present CO₂ loading in the mesosphere will typically lead to an increase of 40% in damping rates.

B. Ozone Photochemistry

For the past several years, GFDL has collaborated with the Aeronomy Laboratory in an effort to combine a detailed ozone photochemistry model in a self-consistent way with the radiation and dynamics in the GFDL SKYHI model (sec. II.A). The photochemical code has now been developed so that either diurnal or diurnally averaged chemistry can be calculated. This allows far more economical 3-D model calculations, while maintaining self-consistency with the strongly diurnal character of stratospheric photochemistry.

C. Seasonal March of Radiative-Photochemical Temperature

The radiation transfer and photochemistry models have been combined to investigate behavior of the middle atmosphere. The model has been applied to problems that require a completely self-consistently determined ozone and temperature.

To determine the joint radiative-photochemical equilibrium of the middle atmosphere, the combined model has been run for 2 years at each of 20 latitudes. The solar insolation and surface temperature are specified as a function of season.

The results show generally good agreement with the comparable radiation-only results obtained earlier by using specified ozone distribution. This agreement suggests that joint radiative-chemical-dynamical calculations may now be planned with some confidence. Such calculations will allow a determination of the degree to which dynamics and transport are involved in maintaining the observed structure of ozone and temperature in the stratosphere.

IV. References

- Andrews, D. G., J. D. Mahlman, and R. W. Sinclair, 1983. Eliassen-Palm diagnostics of wave, mean-flow interaction in the GFDL "SKYHI" general circulation model. J. Atmos. Sci., 40, 2768-2784.
- Andrews, D. G., and M. E. McIntyre, 1976. Planetary waves in horizontal and vertical shear: The generalized Eliassen-Palm relation and the mean zonal acceleration. J. Atmos. Sci., 33, 2031-2048.
- Danielsen, E. F., 1981. An objective method for determining the generalized transport tensor for two-dimensional Eulerian models. J. Atmos. Sci., 38, 1319-1339.
- Fels, S. B., 1982. A parameterization of scale-dependent radiative damping rates in the middle atmosphere. J. Atmos. Sci., 39, 1141-1152.
- Fels, S. B., M. D. Schwarzkopf, 1981. An efficient, accurate algorithm for calculating CO₂ 15 μ m band cooling rates. J. Geophys. Res., 86, 1205-1232.
- Fels, S. B., J. D. Mahlman, M. D. Schwarzkopf, and R. W. Sinclair, 1980. Stratospheric sensitivity to perturbations in ozone and carbon dioxide: Radiative and dynamical response. J. Atmos. Sci., 37, 2265-2297.
- Frederick, J. E., and J. E. Mentall, 1982. Solar irradiance in the stratosphere: Implications for the Herzberg continuum absorption of O₂. Geophys. Res. Lett., 9, 461-464.
- Hirota, I., 1979. Kelvin waves in the equatorial middle atmosphere observed by the Nimbus 5 SCR. J. Atmos. Sci., 36, 217-222.
- Kley, D., J. W. Drummond, M. McFarland, and S. C. Liu, 1981. Tropospheric profiles of NO_x. J. Geophys. Res., 86, 3153-3161.
- Levy II, H., J. D. Mahlman, and W. J. Moxim, 1980. A stratospheric source of reactive nitrogen in the unpolluted troposphere. Geophys. Res. Lett., 7, 441-444.

- Levy II, H., J. D. Mahlman, and W. J. Moxim, 1982: Tropospheric N₂O variability, J. Geophys. Res., 87, 3061-3080.
- Levy II, H., J. D. Mahlman, S. C. Liu, and W. J. Moxim, 1984. Tropospheric ozone: The role of transport. J. Geophys. Res. (to be submitted).
- Liu, S. C., D. Kley, M. McFarland, J. D. Mahlman, and H. Levy II, 1980. On the origin of tropospheric ozone. J. Geophys. Res., 85, 7546-7552.
- Mahlman, J. D., 1975. Some fundamental limitations of simplified transport models as implied by results from a three-dimensional general-circulation/tracer model. Proc. Fourth Conf. on CIAP (T. M. Hard and A. J. Broderick, eds.), DOT-TSC-OST-75-38 (NTIS AD-A068982) 132-146.
- Mahlman, J. D., and W. J. Moxim, 1978. Tracer simulation using a global general circulation model: Results from a midlatitude instantaneous source experiment. J. Atmos. Sci., 35, 1340-1374.
- Mahlman, J. D., and R. W. Sinclair, 1980. Recent results from the GFDL troposphere-stratosphere-mesosphere general circulation model. Proc. Intl. Union Geodesy Geophys. (IUGG) Symposium 18, Twenty-Seventh IUGG General Assembly, Dec. 1979, Canberra, Australia. NCAR, Boulder, Colo., pp. 11-18.
- Mahlman, J. D., and L. J. Umscheid, 1984. Dynamics of the middle atmosphere: Successes and problems of the GFDL "SKYHI" general circulation model. Proc. U.S.-Japan Seminar on Middle Atmosphere Dynamics. Terra Scientific Publishing Co., Tokyo (in press).
- Mahlman, J. D., H. Levy II, and W. J. Moxim, 1980. Three-dimensional tracer structure as simulated in two ozone precursor experiments. J. Atmos. Sci., 37, 655-685.
- Mahlman, J. D., H. Levy II, and W. J. Moxim, 1984. Three-dimensional simulations of stratospheric N₂O: Predictions for other trace constituents. J. Geophys. Res. (to be submitted).
- Manabe, S. and J. D. Mahlman, 1976. Simulation of seasonal and inter-hemispheric variations in the stratospheric circulation. J. Atmos. Sci., 33, 2185-2217.
- Manabe, S., D. G. Hahn, and J. L. Holloway, Jr., 1974. The seasonal variation of the tropical circulation as simulated by a global model of the atmosphere. J. Atmos. Sci., 31, 43-83.
- Matsuno, T., 1980. Lagrangian motion of air parcels in the stratosphere in the presence of planetary waves. Pure Appl. Geophys., 118, 189-216.
- Plumb, R. A., 1979: Eddy fluxes of conserved quantities by small-amplitude waves. J. Atmos. Sci., 36, 1699-1704.
- Salby, M. L., D. L. Hartmann, P. L. Bailey, and J. C. Gille, 1984. Evidence for equatorial Kelvin modes in NIMBUS-7 LIMS. J. Atmos. Sci., 41 (in press).

NATIONAL ENVIRONMENTAL SATELLITE, DATA, AND INFORMATION SERVICE Boulder, Colorado

I. TIROS Operational Vertical Sounder Total Ozone

Total ozone amounts continue to be derived from radiance measurements obtained with the TIROS Operational Vertical Sounder (TOVS) on NOAA operational satellites. The satellites have provided ozone data for these periods:

TIROS-N: May 1979 - January 1981 (demise)
NOAA 6: November 1979 - June 1983 (demise)
NOAA 7: August 1981 - Present
NOAA 8: August 1983 - Present

The data set of globally averaged total ozone amounts covers the period May 1979 - March 1983. Analysis of this time series for trends has just begun.

During routine evaluation of TOVS radiances, it was noted that processing of the channel sensitive to the 9.6- μm ozone radiance introduced an error. Adjustments for limb darkening (i.e., the effect of increased atmospheric absorption when the earth is observed at angles away from the nadir) were incorrect. A method of properly correcting for limb darkening has been developed and is being evaluated for implementation by the operational processing system. In the meantime, radiances measured in the nadir view only have been assembled, and total ozone amounts have been determined from these. These data are archived and available from the NESDIS Satellite Data Services Division. The analyses discussed below are based on the corrected values.

Evaluation of the data set for the period May 1979 to November 1982 is currently available. Total ozone amounts derived from TOVS data are compared with those from Dobson and solar backscatter ultraviolet (SBUV) observations. Comparison with a global, independent set of Dobson determinations on a monthly basis yields correlation coefficients above 0.7 and generally between 0.8 and 0.95. Standard deviations of the differences between TOVS and Dobson determinations vary between 5% and 8% for the same data set. Comparisons of a set of monthly global average total ozone with similar determinations from SBUV measurements show a bias of about 8.7% (TOVS being higher). This is consistent with independent comparisons of SBUV and Dobson determinations done on a sounding-by-sounding basis (Fleig et al., 1982) which showed an SBUV-Dobson bias of 8.3% (SBUV being higher). As TOVS-derived ozone amounts are based on Dobson measurements through the regression retrieval algorithm, this result is expected. Figure 7 shows, for each instrument, the monthly average total ozone amounts for the 0°-60°N zone (the correction for the SBUV-Dobson bias has been incorporated).

With the continuation of the globally averaged satellite data set into 1983, the trend analysis will be extended and compared with trend analyses of data from other sources, particularly the Dobson network.

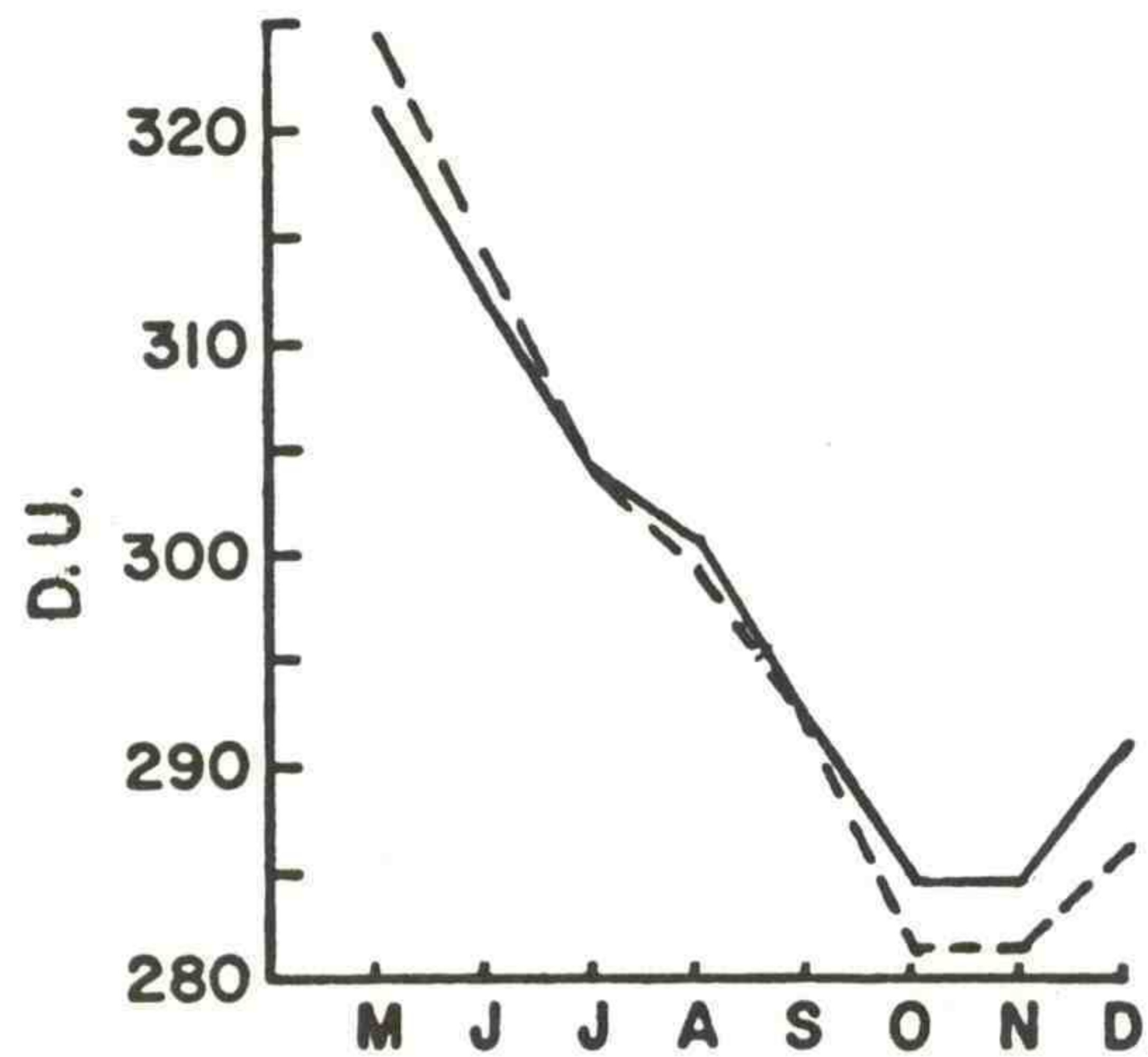


Figure 7. Total ozone determined by TOVS and SBUV for May-December 1979. Values are monthly averages over the zone 0° - 60° N. Solid curve is TOVS; dashed curve is SBUV corrected by a -8.7 bias (SBUV minus Dobson).

II. Development and Implementation of Operational Solar Backscatter Ultraviolet Instruments

The first instrument for operational use has been delivered by the contractor and is being installed on the NOAA-F spacecraft, which is due to be launched about November 1984. SBUV sensors will be flown on only the mid-afternoon satellites (i.e., 2:20 p.m. local time equator crossing). These satellites will also carry the Stratospheric Sounding Unit (SSU) capable of independently deriving upper-stratospheric ozone profiles.

Development of the software system for operational retrieval has begun. The system is based on the NASA Nimbus-7 SBUV retrieval algorithm, which will be modified to operate on NOAA computer facilities and to accept TIROS ancillary data needed in the retrieval algorithm. At present, the operational plan calls for satellite quick-look data products to be available 2 months after launch of the NOAA-F spacecraft.

III. Reference

Fleig, A. J., K. F. Klenk, P. K. Bhartia, D. Gordon, and W. H. Schneider, 1982. User's Guide for the SBUV Instrument First-Year Data Set, NASA Reference Publication 1095, 72 pp.

NATIONAL WEATHER SERVICE
Climate Analysis Center
Camp Springs, Maryland

During 1982-1983, efforts of the Climate Analysis Center, Analysis and Information Branch (AIB), have been concentrated on two main areas: (1) operational stratospheric monitoring of temperature, pressure heights, and ozone and (2) analysis of available data for trends.

I. Operational Stratospheric Monitoring

Daily (1200 GMT) global meteorological analyses of height and temperature at 70, 50, 30, 10, 5, 2, 1, and 0.4 mb (20-55 km) continue to be constructed. During the last 2 years we have modified the analysis procedure to include satellite data in the lower stratosphere and also have implemented a rocket-sonde-analysis comparison program to provide for long-term calibration (Gelman et al., 1983).

In addition to the archive of the analyses themselves, we have established an archive of several derived parameters. These include the zonal average values of wind, temperature, kinetic energy, and eddy transports of sensible heat and momentum. Daily and monthly values are being determined for all levels being analyzed (e.g., Geller et al., 1983).

Daily (1200 GMT) global analyses from the TIROS operational Vertical Sounder (TOVS) continue to be constructed. The results for the period May 1979 to November 1982, integrated over the data domain 60°N-60°S, indicate a marked decrease of about 3% during this period. This trend is under evaluation.

Planning was begun for the data flow and verification techniques to be implemented with the launch of the SBUV-2 instrument on NOAA-F in November 1984. This instrument is an operational version of the Nimbus-7 SBUV and will provide the basic ozone data set required for the early detection of change.

II. Examination of Ozone Data for Trends

Monthly average global synoptic analyses of total ozone and ozone mixing ratio at 30, 10, 5, 2, and 1 mb for the period April 1970 to December 1976 from Nimbus-4 BUUV data have been archived at the National Space Science Data Center. An examination of the temporal variation found no significant trend in total ozone in the Northern Hemisphere during this period (Miller et al., 1982).

Daily and monthly average global synoptic analyses of total ozone and ozone mixing ratio at 30, 10, 5, 2, 1, and 0.4 mb for the period November 1978 to October 1980 from Nimbus-7 SBUV data have been archived at the National Space Science Data Center. Analyses for the third and fourth years are in preparation.

LYR

MB

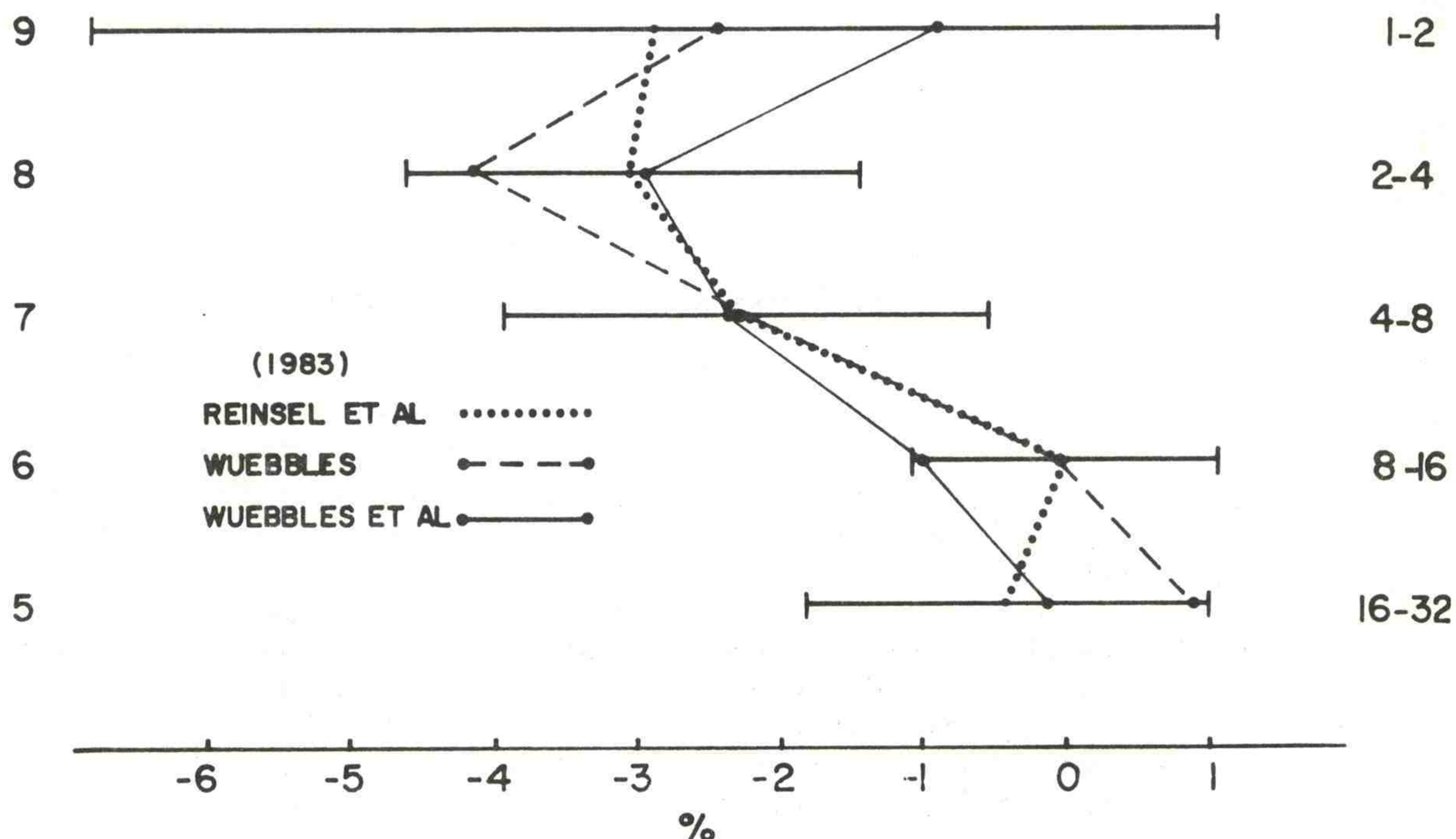


Figure 8. Ozone decadal trend, 1970-1980.

As part of the overall effort to determine not only the observed stratospheric changes but a delineation of the causes of the changes, a program was initiated to use the ozone and meteorological analyses to compute ozone transports and ozone-temperature associations (Miller et al., 1983; Nagatani and Miller, 1984). These first results are very encouraging in that they show general agreement with numerical model calculations. This program will be continued.

To evaluate global trends of ozone at stratospheric levels, connection between BUUV data ('70-'76) and SBUUV data ('78-present) must be made through the ground-based Umkehr network. In cooperation with Professors George Tiao (University of Chicago) and Gregory Reinsel (University of Wisconsin), John Frederick (NASA), John DeLuisi (NOAA), and Carl Mateer (AES, Canada), we have examined these data as the first step in achieving a total, consistent data set. Utilizing a statistical technique that includes effects for stratospheric aerosol impact on the Umkehr data, trends (1970-1980) were determined and compared with numerical model calculations of Wuebbles et al. (1983) and Wuebbles (1983). The results, published by Reinsel et al. (1984), are depicted in Figure 8. There is good agreement between observation and theory. This is the first such documented observational indication of a possible anthropogenic impact on the ozone layer. Considerable effort remains to compare these results with the global satellite data.

Currently, the Solar Backscatter Ultraviolet data analysis technique is limited at the lower level by our ability to consider single versus multiple scattering in the retrieval algorithm. Consequently, a statistical regression technique has been developed to derive ozone profile information in the lower stratosphere and upper troposphere. The ozone amount in the lower stratosphere - upper troposphere is deduced from the difference between the measured total ozone and that measured above 30 mb. The vertical variation within the lower stratosphere - upper troposphere region is determined by regression against an historical set of ozone balloon profiles. A report is in preparation.

III. References

- Gelman, M. E., A. J. Miller, R. M. Nagatani, and H. D. Bowman II, 1983. Mean zonal wind and temperature structure during the PMP-1 winter periods. Adv. Space Res., 2, 159-162.
- Geller, M. A., Mao-Fou Wu, and M. E. Gelman, 1983. Troposphere-stratosphere (surface - 55 km) monthly winter general circulation statistics for the Northern Hemisphere - four year averages. J. Atmos. Sci., 40, 1334-1352.
- Heath, D. F., A. J. Fleig, A. J. Miller, T. G. Rogers, R. M. Nagatani, H. D. Bowman II, V. G. Kaueeshwar, K. F. Klenk, P. K. Bhartia, and K. D. Lee, 1982. Ozone Climatology Series, Volume 1, Atlas of Total Ozone: April 1970 - December 1976. NASA Reference Publication 1098, 163 pp.
- Miller, A. J., R. M. Nagatani, T. G. Rogers, A. J. Fleig, and D. F. Heath, 1982. Total ozone variations 1970 - 1974 using background ultraviolet (BUV) and ground-based observations. J. Appl. Meteor., 21, 621-630.
- Miller, A. J., R. M. Nagatani, and M. E. Gelman, 1983. Meteorological influences on ozone distribution during the stratospheric warming of January-February 1979 - Part II. Paper presented at 4th Conference on the Meteorology of the Upper Atmosphere, Boston, Mass., March 22-25, 1983, American Meteorological Society.
- Nagatani, R. M., and A. J. Miller, 1984. Stratospheric ozone changes during the first year of SBUV observations. J. Geophys. Res., 89, 5191-5198.
- Reinsel, G. C., G. C. Tiao, J. J. DeLuisi, C. L. Mateer, A. J. Miller, and J. E. Frederick, 1984. Analysis of upper stratospheric Umkehr ozone profile data for trends and effects of stratospheric aerosols. J. Geophys. Res., 89, 4833-4840.
- Wuebbles, D. J., F. M. Luther, and J. E. Penner, 1983. Effect of coupled anthropogenic perturbations on stratospheric ozone. J. Geophys. Res., 88, 1444-1456.
- Wuebbles, D. J., 1983. A theoretical analysis of the past variations in global atmospheric composition and temperature structure. Lawrence Livermore Laboratory Report UCRL-53423, 161 pp.