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

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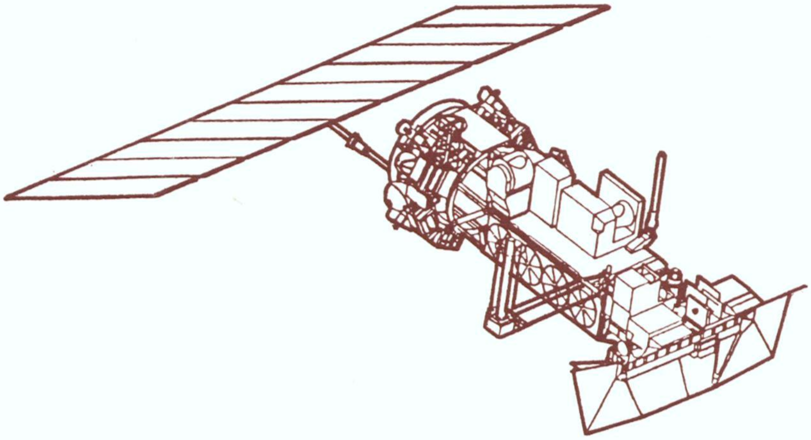
METEOROLOGICAL SERVICES AND SUPPORTING RESEARCH

National Plan for Stratospheric Monitoring, 1988 - 1997

FCM-P17-1989



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NATIONAL PLAN FOR STRATOSPHERIC MONITORING

1988-1997

FCM-P17-1988

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FEDERAL COORDINATOR FOR
METEOROLOGICAL SERVICES
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U.S. DEPARTMENT OF COMMERCE/National Oceanic and Atmospheric Administration

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FOREWORD

In 1976, the Federal Committee for Meteorological Services and Supporting Research (FCMSSR) charged the Federal Coordinator to take the leadership role in developing a national program concerning coordination of stratospheric monitoring. In 1977, Congress enacted Public Law 95-95, Amendments to the Clean Air Act of 1977, Section 126, a program for Ozone Protection. In response to Congress and FCMSSR, the Federal Coordinator published, in February 1982, the National Plan for Stratospheric Ozone Monitoring and Early Detection of Change, 1981-1986.

In 1988, the need for monitoring the stratosphere is more pressing than ever. The possibility that the ozone layer is being depleted as a result of chloroflourocarbons released into the atmosphere, plus the indications that the concentration of the "greenhouse gases" is increasing, require that a long-term national monitoring program be continued. These changes and possible remedial actions are now not only scientific issues but also public policy issues.

The National Plan for Stratospheric Monitoring, 1988-1997 is a 10-year plan that includes the development of next generation instruments for monitoring. It outlines a strategy to monitor the stratosphere. Because of budgetary uncertainties in the Federal agencies, the plan does not include a section on agency budget resources over the 10-year period.

The efforts of the Working Group Co-chairmen, Alvin J. Miller, National Oceanic and Atmospheric Administration, (NOAA) and Robert T. Watson, National Aeronautics and Space Administration (NASA), in the preparation of this Plan are acknowledged. Special recognition is also due to those individuals who drafted the Plan -- Walter G. Planet of NOAA; D. Heath, E. Hilsenrath, R. B. Hood, R. D. Hudson, J. A. Kaye, J. E. Mentall, and A. M. Thompson and of the Goddard Space Flight Center, NASA; and to A. J. Miller who coordinated the participation of the various contributors and integrated their efforts into this document.

R. L. Carnahan

Robert L. Carnahan
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EXECUTIVE SUMMARY

The initial National Plan for Stratospheric Ozone Monitoring and Early Detection of Change 1981-86 developed a program of transition from a reliance on a ground-based, geographically-biased network operated by cooperating nations to a combined satellite and ground-based monitoring program that provides global coverage of ozone and temperature.

As we enter the next phase of the program amid the significant public concerns of possible anthropogenic influence and the possible need for remedial action, we recognize that issues of stratospheric change are not centered solely on ozone. Large changes are expected in the stratosphere due to increasing concentrations of greenhouse gases. The complex interactions of chemistry, radiation, and dynamics require that meteorological parameters and many species be monitored. It is only through careful, coordinated measurement programs interfaced with research that stratospheric change can be documented and understood. This Plan recognizes these more general requirements by the change in title from Stratospheric Ozone Monitoring and Early Detection of Change to Stratospheric Monitoring. Furthermore, the original 5-year time period has been expanded to a decade so that we can consider the development of next generation instruments and their proper incorporation into a well defined stratospheric monitoring system.

During the past several years, we have come to realize that "monitoring" cannot be construed as a simple engineering problem whereby a station is established, observations made, and a trend computed. The complexities of the stratosphere, and the relatively small change per decade being sought, force us to consider monitoring as a total combination of theory, laboratory measurements, field measurements, and interpretation. Research and measurement programs cannot be artificially separated in the design and implementation of a monitoring system.

Three common themes are evident in the Plan. Because of their universal nature we consider these themes to be fundamental requirements of the monitoring system:

(1) The monitoring system cannot rely on data from a single instrument. Individual instruments have systematic errors than can lead to erroneous trend detection. Comparison of data from different instruments could yield knowledge of these systematic errors. This is true even for instruments of the same design. A fundamental requirement is sufficient operational overlap of all instruments to define the biases, drifts, and error characteristics of the measurements.

(2) Monitoring requires both a high quality, low spatial resolution ground-based system, and a high spatial resolution satellite system. Both systems must be global in extent. The ground-based system requires vigilant calibration and quality checks. The two systems back up one another and provide a strong cross check. The maintenance of these two mutually supporting systems is a fundamental requirement.

(3) Changes in an atmospheric parameter can result from natural and manmade perturbations. If detected changes are to be interpreted for regulatory purposes, then it is essential that the cause of the change be understood. It is, therefore, essential that the fundamental research programs that many agencies carry out be complementary to monitoring requirements.

The overall timeframe of 1988-1997 seems to naturally subdivide into three general periods; near- (present-early 1990s), mid- (early 1990s) and far-term (mid-1990s). In the near-term we foresee the development of the Network for Detection of Stratospheric Change (NDSC) sponsored by NASA, NOAA, the WMO, and the Chemical Manufacturers Association (CMA). This is to be a high-technology ground-based program designed to supplement the current ground based program and provide, from at least six sites, information on many species and parameters. This Network will serve as a direct monitor of many stratospheric parameters, to validate/calibrate the available satellite systems and to provide information on possible causes of ozone change. In the mid-term, the NASA Upper Atmosphere Research Satellite (UARS) is planned to be launched in late 1991 and will make measurements of many of the parameters of interest in this Plan. UARS is a unique instrument of opportunity that will be included within the monitoring program for as long as this satellite lasts. Finally, in the far-term, consideration is given to the next generation NOAA operational satellite systems and the Earth Observing System.

As indicated above, within the several agencies there are substantial ongoing and planned programs that can be assimilated into the overall monitoring program. In the following we will outline those areas where the requirements and the programs/plans match and indicate, also, where major gaps exist.

OZONE

(1) Today's monitoring program depends entirely on the joint measurement programs of the operational satellite system (SBUV/2) and the ground-based systems. These must be maintained with high quality control and emphasis on long-term stability. These efforts are synergistic in that the ground-based program, collectively, validates the satellite and the satellite serves as a transfer standard among the different ground stations.

(2) The current plan for satellite ozone monitoring includes comparison of the operational SBUV/2 with a Shuttle-borne SBUV (SSBUV) which will be employed as a reference standard. This instrument will fly on approximately 5-day missions at intervals of about 8 months and should provide an important calibration for the SBUV/2 while in orbit.

(3) In the case of ozone vertical profiles, a major difficulty exists in that the ground-based Umkehr observations are susceptible to interference from long-lived stratospheric aerosols and the balloonsonde information has substantial noise at the higher altitudes. Methods of "correction" for aerosols are being examined as are other techniques of ozone profile determination such as LIDAR (NDSC). It is imperative that these new systems be developed and deployed as soon as possible.

(4) The current NOAA operational satellite instrument, the SBUV/2, is planned to extend till about 1995 when the Polar Platform is planned to be launched. A more inclusive monitoring system, the Global Ozone Monitoring Radiometer (GOMR) is planned to be implemented at that time. There must be no gaps in the satellite record and sufficient overlap between SBUV/2 instruments as well as SBUV/2 and GOMR must take place to allow a smooth transition from one system to the other. As the instrument designated to follow the SBUV/2, the GOMR is expected to fly on any extension of the current operational satellite series.

METEOROLOGY (Temperature and Winds)

(1) The stratospheric monitoring program for temperature is in major difficulty. The requirements defined in the Chapter are not met by the present or planned instruments. Moreover, degradation of our capabilities is likely during the next decade.

(2) The current NOAA operational satellite temperature retrievals in the middle-upper stratosphere can contain biases between instruments with values reaching 8 degrees Celsius. The current launch program of the meteorological rocket sounding program is insufficient to provide a timely assessment of satellite performance. Although other ground-based methods are being developed, such as the LIDAR as part of the NDSC, these are several years from implementation. A basic subset of rawinsonde and rocketsonde stations must be designated as part of a stratospheric monitoring network to provide the measurements necessary for satellite validation/calibration. At such time as the LIDAR systems have been thoroughly tested, compared and deployed, the rocketsondes could be reduced in number.

(3) Rawinsondes provide the ground-based lower stratospheric monitoring system. A set of priority stations that maintain a high quality set of rawinsonde observations should be designated. Methods of standardization must be developed to assure a spatially and temporally consistent data set.

(4) Satellite temperature information is currently derived from the TIROS Operational Vertical Sounder (TOVS) aboard the NOAA polar orbiter satellite series. TOVS provides information throughout the entire stratosphere to about 43 km. Temperature information at these altitudes (and above) is ESSENTIAL for a stratosphere monitoring program. As currently planned, the Advanced Microwave Sounding Unit (AMSU), which is the next generation operational sounder, will not obtain temperatures above approximately 37 km. Modifications to the AMSU system should be implemented to obtain 45 km temperature information. While we note that the NASA UARS mission is scheduled to be launched in this time-frame, the actual launch date and longevity are uncertain. In the event of failure we run the major risk of having no satellite measurements and an extremely limited ground-based network.

(5) As noted under the Ozone section, the GOMR instrument is planned to be implemented in the 1995 time-frame. This instrument would measure temperature as well as ozone in the area of interest, but the data record must be placed in total context of the major gaps that may exist up to that time (item 4). Stratospheric temperature sensors to be aboard the Eos polar platforms must be carefully scrutinized. Design considerations to properly address the needs of the monitoring program must be studied and there must be continuity between the NOAA polar orbiting satellites and the EOS system.

(6) Wind measurements are necessary to understand constituent, heat and momentum budgets in the stratosphere and to understand the photochemistry of ozone. Our current capabilities of deriving wind estimates from satellite temperature data are inadequate. Efforts to develop satellite based direct wind instruments should be supported.

SOLAR ULTRAVIOLET SPECTRAL IRRADIANCE

(1) The NOAA operational SBUV/2 satellite instrument measures the solar irradiance on a daily basis from 160-400 nanometers (nm). This methodology requires deployment of a diffuser plate. That the changes in time of the characteristics of the diffuser plate are not well known for the SBUV on Nimbus-7 is the cause for the uncertainty in depiction of both the solar irradiance changes and trends in ozone values. NOAA, consequently. incorporated an on-board calibration mechanism as part of its basic design. This calibration mechanism failed on the first flight, but has since been redesigned and should work effectively for the follow-on instruments.

(2) Currently, there are no plans within NOAA to monitor the solar ultraviolet irradiance beyond the SBUV/2 lifetime. GOMR measures in the infrared portion of the spectrum.

(3) The UARS mission will provide measurements of the solar irradiance from two instruments, the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) and the Solar Stellar Irradiance Comparison Experiment (SOLSTICE). These data should be utilized as a unique data set of opportunity for the lifetime of the experiments.

(4) As the variation of the solar irradiance over the 11-year sunspot cycle can influence greatly our interpretation of ozone and temperature changes, it is IMPERATIVE that this parameter be monitored on a continuing basis following the SBUV/2 and UARS. Candidates include the shuttle version of the SBUV (SSBUV) being developed by NASA and the two solar monitors to be incorporated on UARS. These, as well as other instruments, should be evaluated for inclusion on the Earth Observing System.

SOURCE GASES

(1) Relative to ozone and trace species in the stratosphere, the monitoring of source gases in the troposphere is in good shape. A practical criterion for longer-lived source gases -- carbon dioxide, chloroflourocarbons, nitrous oxide, methane ($C0_2$, CFCs, N_20, CH_4) -- is to continue accurate and precise measurements sufficient to detect small and unexpected changes. This can be accomplished by the current ground-based network with appropriate improvements in standardization, intercalibration, frequency of observation and geographical coverage.

(2) An urgent need exists for monitoring several shorter-lived source gases that affect tropospheric and stratospheric chemistry: carbon monoxide (CO), tropospheric ozone, nitrogen oxide and nonmethane hydrocarbons. The natural spatial and temporal variability of these species requires a combination of ground-based and satellite measurement for global coverage, but the latter is not yet available for routine tropospheric sensing.

For the next decade, priority is given to:

(a) further development and deployment of CO and $N0_2$ detectors for satellite remote sensing; and

(b) development of a good climatology of tropospheric ozone, CO, NO_x and nonmethane hydrocarbons. This can be accomplished with current measurement techniques at a welldispersed network of ground sites and better exploitation of existing data sets from a variety of field experiments and monitoring networks.

(3) Monitoring activities and definition of climatologies for source gases are linked closely with basic research on the biogeochemical cycles of tropospheric odd nitrogen, carbon, and sulfur. Specific monitoring recommendations will meet the goals of trend detection only if tasks are coordinated with experimental research on source gas budgets and transformation processes. Monitoring must also be coordinated with modeling that interprets trends mechanistically.

OTHER TRACE CONSTITUENTS

Although there are far fewer long-term measurements of concentrations of other trace constituents in the stratosphere, some information about their trends has recently become available. For example, increases in the amounts of stratospheric hydrogen chloride (HCl) and hydrogen fluoride (HF) have been demonstrated by both ground and aircraft based measurements. Both ground- and satellite-based data have also been used to place limits on the maximum possible changes in the amounts of odd nitrogen species, primarily $N0_2$, due to variation in the solar cycle or in stratospheric transport processes. It is noted that much of this work is being accomplished in a research mode, e.g., unequal intervals and a variety of locations, but taken together, a substantial data base exists that must be examined and melded into the overall monitoring program. For improved determination of trace constituent trends over the 1988-1997 timeframe, the following must be done:

(1) Ground-based and aircraft-based measurements of the vertical profiles and/or column amounts of those species currently under study are essential and should be continued, including, but not limited to, HCl, HF, ClO, H_20, OH, NO, $N0_2$ and $HN0_3$. Measurement frequency and geographical coverage should be expanded wherever possible. Also, in the case of the total column measurements, substantial care must be exercised to account for concentration variations in the troposphere and mesosphere, which are not well understood, as they contribute to the total column.

(2) Existing data from several satellite systems over the past decade, (e.g. LIMS, SAGE, SAGE II, SAMS, SME, SBUV) should be examined with great care for overall trend evaluation. Similarly, this data base should be expanded by taking repeated, if short term, measurements from future space shuttle missions such as the planned ATMOS flights.

(3) The UARS mission, in addition to ozone, temperature and solar irradiance, is expected to measure 11 other chemical species with instruments that have the possibility of extended lifetimes. These data should be incorporated into the overall monitoring program as a unique data set of opportunity. The UARS instruments, as well as others, should be evaluated for possible inclusion on the Earth Observing System.

(4) Both from the viewpoint of fundamental monitoring as well as satellite validation/calibration (NOAA operational and the NASA UARS mission), the NDSC should be implemented as soon as possible.

(5) Finally, we must ensure that the basic spectroscopic and chemical kinetic parameters are sufficiently determined such that the constituent measurements have minimal uncertainty.

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CHAPTER 1. INTRODUCTION

For several decades scientists have sought to understand the complex interplay between the chemical, radiative and dynamical processes that govern the structure of the earth's atmosphere. During the last decade or so there has been particular interest in studying the processes which control atmospheric ozone. It has been predicted that man-made pollutants might cause harmful effects to the environment by modifying the ozone distribution and contributing significantly to climate change (i.e., the greenhouse effect).

Changes in the total column content of atmospheric ozone would modify the amount of biologically harmful ultraviolet radiation penetrating to the earth's surface with potential adverse effects on human health (skin cancer and cataracts) and on the aquatic and terrestrial ecosystems. Changes in the vertical distribution of atmospheric ozone, along with changes in atmospheric concentrations of other infrared active gases, could contribute to climate changes on regional and global scales by modifying the atmospheric temperature structure possibly leading to altered rainfall patterns- sea level rise and loss of soil moisture.

The ozone issue has, thus, evolved to a state that requires consideration of many chemical and meteorological parameters. The man-made and natural chemicals of interest include the nitrogen oxides from subsonic and supersonic aircraft; nitrous oxide from agricultural and combustion practices; chlorofluorocarbons used as aerosol propellants, foam blowing agents and refrigerants; brominated compounds used as fire retardants; carbon monoxide and carbon dioxide from combustion processes and methane from a variety of sources. It is now clear that these same gases are also important in the climate issue.

Scientifically, there are three prominent issues in stratospheric monitoring today: (1) The possible global decrease, since 1982, of ozone densities at high altitudes and total ozone as derived from the Nimbus-7 Solar Backscattered Ultraviolet Ozone Sensor (SBUV) and other data; (2) The rapid decrease in total ozone over Antarctica during Southern Hemisphere spring and (3) Differences between the measured ozone densities near 50 km and those calculated from models.

(1) A recent international scientific study (Ozone Trends Panel, 1988) has concluded that, after allowing for the effects of natural geophysical variability, total column ozone at latitudes between 30 and 64 degrees N shows measurable decreases from 1969 to 1986 ranging from 1.7 to 3.0 percent. The decreases were most pronounced from December to March, ranging from 2.3 to 6.2 percent. Model calculations are broadly consistent with these observations, but predict smaller decreases at mid and high latitudes in the winter. The Panel concluded that these observed changes may be due wholly, or in part, to the increased atmospheric abundance of trace gases, such as the chlorofluorocarbons (CFCs). The Panel also concluded that the SBUV and TOMS total ozone data sets should not be used, by themselves, to determine ozone trends due to the inability to obtain an unambiguous model of the instrument degradation. Global changes in total ozone can be obtained by normalizing the SBUV data to the Dobson network.

The same caveat applies to the SBUV ozone profile measurements. For their study of the trends in the ozone profiles the Panel used the data obtained by SAGE (I and II), SME, and the Dobson network using the Umkehr technique. The Panel concludes that ozone has decreased since 1979, with the peak decrease occurring near 40 km altitude. Umkehr showed a mean decrease of 9 percent, while SAGE showed a mean decrease of 3 percent, however, these values are consistent within their respective errors.

(2) The decrease in the minimum of the total column ozone at the South Pole in the Antarctic spring has been dramatic, from a value of 300 Dobson Units in 1979, to a value of 150 Dobson Units in 1986. The value obtained in 1987 was the lowest since measurements began 30 years ago. The Panel concluded that the weight of evidence indicated that the prime cause of the depletion was chemical, involving reactions of chlorine compounds derived from man-made species. However, it is the unique meteorology during winter and spring over Antarctica that sets up the special conditions of an isolated air mass (polar vortex) with the cold temperatures required for the heterogeneous chemistry to proceed. Changes in the meteorology could lead to modifications in the ozone values themselves as well as the photochemistry.

(3) As noted by the World Meteorological Organization (WMO), there is an inconsistency between measured and modeled concentrations of ozone above 35 km. Model results are typically 30 to 50 percent lower than the measured concentrations. This discrepancy is particularly troubling given that it occurs where ozone should be photochemically controlled, and it is thought that transport effects can be ignored. Furthermore, there appears to be a discrepancy between the ozone and temperature measurements. Using measured ozone and temperature, radiative calculations of globally (horizontally averaged), annually averaged heating rates show an imbalance in the vicinity of 50 km (Kiehl and Solomon, 1986; Rosenfield et al., 1987; Callis et al., 1987). More recent results (Rosenfield, 1988, personal communication) suggest that this imbalance may be smaller than previously reported; however, a significant imbalance remains.

Therefore, there exists a consistent bias between modeled and observed ozone. The radiative calculations further suggest an imbalance between ozone and temperature observations. This suggests that problems exist in the ozone or temperature measurements, our understanding of ozone photochemistry, or the radiative calculations. This general disagreement in the upper stratosphere is an issue of fundamental importance in understanding processes governing ozone.

It should be clear from the above that there are several aspects of the issue that need to be considered, i.e., understanding those processes that control the present atmospheric distribution of ozone, and those processes that need to be understood in order to be able to predict the atmospheric distribution of ozone in the future. If changes are observed in the distribution of ozone, we must be able to understand how periodic and episodic natural phenomena such as solar activity and volcanic eruptions cause ozone to vary in space and time in order to isolate the impact of the changing concentrations of gases. Thus, to really understand the processes which control atmospheric ozone and to predict perturbations, we must recognize that these are interacting systems and plans must be formed accordingly.

Domestically, in response to these concerns, Congress has required, under Public Law 95-95, Amendments to the Clean Air Act of 1977 Section 126, that eight Federal agencies undertake continuing studies of the cumulative effect of all substances, practices, processes and activities that may affect the stratosphere, especially the ozone in the stratosphere, including specifically halocarbons, other sources of chlorine, bromine compounds and emissions of aircraft propulsion systems. These studies shall also include such physical, chemical, atmospheric, biomedical or other research and monitoring as may be necessary to ascertain (a) any direct or indirect effects upon the public health and welfare of changes in the stratosphere, especially ozone in the stratosphere, and (b) the probable causes of changes in the stratosphere, especially the ozone in the stratosphere.

In response to these requirements the Federal Committee for Meteorological Services and Supporting Research charged the Federal Coordinator with the responsibility to develop and coordinate a national program for stratospheric ozone monitoring. This effort culminated in the National Plan for Stratospheric Ozone Monitoring and Early Detection of Change 1981-1986 (FCM-P17-1982).

This initial Plan called for a transition from reliance on a ground-based, geographically-based ozone observing network operated by cooperating nations to a combined satellite and ground-based monitoring program that would provide global coverage of the vertical distribution of stratospheric ozone, as well as total column ozone.

The Plan discussed the strategy, instrumentation and monitoring products to be prepared during this transition period. While it focused attention on the planning period of 1981-1986, it recognized that global atmospheric monitoring will be required to continue over several decades.

Internationally, the steps taken toward global cooperation during the last several years have been impressive. Governments have recognized that traditional national approaches to problem solving -- domestic legislation, rulemaking and enforcement -- are inadequate to deal with a problem of global dimension. A major step in international cooperation was the conclusion of the Vienna Convention for the Protection of the Ozone Layer, signed in March 1985, under the auspices of the United Nations Environmental Program (UNEP). The United States ratified the Convention in August 1986. By November 1987, fourteen of twenty ratifications needed for the Convention to enter into force had been deposited.

On September 16, 1987, the United Nations adopted the "Montreal Protocol on Substances That Deplete the Ozone Layer." This adoption was preceded by several months of intense international and domestic debate on relevant scientific, technical, legal, and diplomatic points.

The Protocol calls for (a) an early freeze on the usage of key chlorinated compounds, (b) a phased reduction in their usage leading to an eventual 50 percent decrease from 1986 levels, (c) an evaluation in 1990 of whether more or less reduction is deemed appropriate, and (d) a similar, but delayed, schedule for the brominated compounds. An international scientific assessment is planned for 1989 so that this guidance would be available as one of the inputs to the 1990 policy review.

The U.S. also plays a leading role in the World Climate Research Program (WCRP), a long-term activity undertaken by the WMO and the International Council of Scientific Unions (ICSU).

As indicated above, within the 5-year period encompassed by the original National Plan, considerable new knowledge and experience has been gained leading us to the recognition that a major update of the Plan is required and that this should extend to the 10-year period 1988-1997.

Amongst the elements discussed are:

(a) The extent of successful implementation of the monitoring program for the several parameters defined in the original National Plan, 1981-1986.

(b) Consideration of additional parameters that must be monitored to provide adequate knowledge as to cause and effect of stratospheric change.

(c) Consideration of monitoring systems, both satellite and ground-based, available now and potentially to achieve the necessary measurements.

(d) Acceleration of international cooperation and coordination, including possible sharing of resources and exchange of data.

It is clear, moreover, that it is impossible to monitor all elements everywhere and that we must select the particular parameters that will provide maximum information on the cause of the observed changes. Fortunately, a broad research program currently exists to understand the physics and chemistry of the Earth's upper atmosphere and its susceptibility to change due to natural and anthropogenic effects. This program, under the combined auspices of the Federal Government and the Chemical Manufacturers Association (CMA) supports a wide range of investigations including field measurements, laboratory kinetics and spectroscopy, modeling and data analysis. The major results and understanding obtained from this effort are summarized in a recent assessment report (WMO, 1986).

The purpose of this National Plan, then, is to build on the above concepts, an operational satellite measurement program, an effective ground-based measurement program and a coordinated research program. In this vein, the following chapters focus on the 5 major categories:

o OZONE
o METEOROLOGY
o SOLAR ULTRAVIOLET SPECTRAL IRRADIANCE
o SOURCE GASES
o OTHER TRACE CONSTITUENTS

that will provide the key answers as to cause and effect of global stratospheric change.

CHAPTER 2. OZONE

2.1. Introduction

The detection of a global ozone trend involves searching for small changes over a decade or more amidst large natural variations that occur over many time and spatial scales. Model calculations are valuable in this search by helping to define ozone variations over these scales and by predicting the amount of depletion due to anthropogenic by-products reaching the stratosphere. These models predict a complex change in both the vertical and horizontal distribution of ozone, as well as over time. Seasonal changes are predicted, but are less pronounced than latitudinal changes. In the upper stratosphere, ozone decreases are predicted at all latitudes for all seasons. In the lower stratosphere, small increases are predicted below 25 km in mid to low latitudes. The predicted net global change is of the order of one to two percent decrease per decade (WMO, 1986).

In addition, long-term changes in ozone are naturally induced by phenomena such as the solar cycle (eleven years) or volcanic eruptions (WMO, 1986). Furthermore, it is now understood that changes in the distribution of ozone will lead to changes in the temperature and wind structure in the stratosphere, which in turn can lead to climatic effects at the Earth's surface. Therefore, the verification of the existence (or absence) of an ozone trend separate from the natural variations is an absolutely essential goal of this National Plan.

Clearly there is a need to monitor global variations of ozone for the next several decades. From this monitoring program, a thorough understanding of the seasonal, interannual, latitudinal, and particularly altitude variations must be derived. In addition to providing a basic source of knowledge, the nature of these changes over the long term will provide an indicator of the processes causing these changes. Determining the cause of a trend in ozone is of equal importance as detecting it. This determination can be achieved through a complementary program of observations which include the solar irradiance, stratospheric temperature and winds, and other gases that play a role in ozone chemistry. The requirements for these observations appear in the following chapters.

In October 1986, the National Aeronautics and Space Administration (NASA), in collaboration with the National Oceanic and Atmospheric Administration (NOAA), the Federal Aviation Administration (FAA), the World Meteorological Organization (WMO), and the United Nations Environmental Program (UNEP), formed an Ozone Trends Panel involving over one hundred scientists to study and evaluate existing data from satellite and ground observations as to the existence of the global decrease in ozone which appears in satellite data taken since 1979. This report critically assesses our present knowledge of whether the composition and structure of the stratosphere has changed over the last few decades with particular attention to changes in ozone over the last decade. The results of that Panel will not be reviewed in this Chapter, however this Plan relies heavily on the lessons learned from that re-evaluation of existing data. The following are a few of the key findings relevant to ozone monitoring.

(1) An analysis of the Dobson ground-based observing system, taking into account natural geophysical variability, shows a measurable decrease from 1969 to 1986 in the annual average of total column ozone at mid latitudes in the northern hemisphere. The decreases are more pronounced in the winter months. Outside of this geographical region, the Dobson coverage is

inadequate to determine an ozone trend. Model calculations are broadly consistent with these observed changes except that the observed winter decrease is larger than predicted by models.

(2) The reported satellite data cannot be used to reliably derive ozone trends, because of the uncertainty in the satellite instrument sensitivity over the course of 7 years. This is primarily due to degradation of an optical component on the Solar Backscattered Ultraviolet (SBUV) instrument, the rate of which can not be uniquely determined. The large decrease originally reported using the archived SBUV data cannot be supported.

(3) Because of the uncertainty in the satellite sensitivity over time, the satellite data were normalized to Dobson observations. These normalized observations show a decrease of 2.5 percent between 53 degrees north and south in total ozone between 1978 and 1985. This period is coincident with the decrease in solar activity associated with the solar cycle. Model calculations predict a lesser amount of change from solar cycle variations.

(4) SAGE satellite data and ground-based Umkehr data taken since 1979 show a small decrease in ozone concentrations near 40 km of about 3 percent and 9 percent, respectively. These values agree within their observational errors. Model calculations predict a decrease of about 5 percent to 12 percent in this altitude region due to the combined actions of solar cycle variations and anthropogenic byproducts.

This chapter addresses how ozone monitoring should be accomplished. The measurement requirements are stated first. For the most part these requirements are driven by the model predictions and our existing knowledge about ozone from observations. This is followed by a discussion on the advantages and problems with the existing observational systems. Particular attention will be given to the conclusions of the Ozone Trends Panel, which has performed a comprehensive assessment of existing satellite and ground-based ozone observations. Improvements to these systems are then discussed, followed by recommendations on how the observation program should be conducted into the next century. Some of the recommendations are underway or planned, while others are new considerations based on the need to understand the geophysical processes which can cause changes in the stratosphere.

The major conclusion of this chapter is that a coordinated program of ground-based and satellite systems is required. The satellites clearly have the advantage of near global coverage, whereas the ground systems have the potential for high accuracy and precision. Space Shuttle flights will also be conducted on regular basis to perform calibration checks of the satellite instruments once they are in orbit. These systems ultimately will be used for cross checks and as independent data bases for verification of results derived from any single system.

Since the publication of the first National Plan for Ozone Monitoring and Early Detection of Change, 1981-1986, a number of observational advances have been achieved. Spatial and short term variations of ozone on global scale have been characterized to the first order by the SBUV on Nimbus-7. The precision and accuracy of the SBUV satellite technique have been investigated and the weakness and strength of this system revealed. The SBUV/2 instrument, an advanced version of the SBUV incorporating an inflight calibration check, will be operational on the NOAA polar orbiting satellites through about 1995. The measurements started with NOAA-9 in 1984. The ground-based systems have also been improved, and a major effort to intercalibrate and automate seven ground-based Dobson stations is nearly complete. A better understanding of the performance of the balloon ozonesonde has been achieved. Finally, a new technology employing laser soundings (LIDAR) for ground-based measurements is now under development. This new system will be part of the proposed Network for Detection of Stratospheric Change (NDSC). These systems show great promise for accurate and precise observations over the long term. Figure 2.1 provides a general overview on how the ozone monitoring program is presently conceived. The elements of this system are discussed here and in other chapters of this Plan.

Even with these initiatives and refinements, a number of assessments have revealed many shortcomings of these system. The Ozone Trends Panel, through the various working groups, concluded that with regard to past satellite observations, the major obstacle in deriving an ozone trend is our inability to characterize the instrument response precisely enough over the course of time. Therefore, several steps must be taken to ensure that high precision and accuracy of the measurements be maintained over the long term. This must be a long-term commitment by the researchers and the agencies that support these efforts. The steps necessary to meet this commitment are discussed in the sections that follow.

2.2. Measurement Requirements

The observed and theoretically predicted magnitude of the temporal and spatial variations in ozone associated with various geophysical phenomena provides a reference against which the required accuracy and precision of measurement systems must be established. In this way, the anticipated variation and the scientific uses of the data define the measurement requirements. Therefore, after known natural variations, such as seasonal cycles are accounted for, the minimum requirement to detect a trend is to achieve an uncertainty in the observed trend to a value less, at the statistical 95 percent confidence limit, than the trend predicted by anthropogenic by-products. Several factors contribute to the uncertainty in our ability to detect this trend. These include the precision of the measurements, the duration of the monitoring period, our ability to understand and account for natural variations, and, very importantly, our ability to account for long-term instrument drifts and biases that may come about as a result of using a series of instruments or different observational systems. The combined uncertainties in these factors should be less than the expected ozone trend at the 95 percent confidence (2 standard deviations) interval.

2.2.1. Upper Stratosphere

Current photochemical model calculations predict a maximum rate of decrease in ozone of about 0.4 percent per year near 40 km, arising mainly from the catalytic reaction of fluorocarbon by-products in the stratosphere (WMO, 1986). Detection of a trend in the upper stratosphere involves a capability to define both the magnitude of the altitude and latitude dependence of the ozone change over time. For example, to separate a solar cycle variation from a fluorocarbon related trend, differences in the altitude dependence as well as temporal variations need to be examined. Predicted ozone changes due to solar cycle variations differ depending on the characteristics of the solar ultraviolet changes. Clearly then, long-term observations of the solar ultraviolet spectral irradiance in conjunction with ozone is necessary. Solar irradiance monitoring requirements are discussed in Chapter 4 of this Plan.

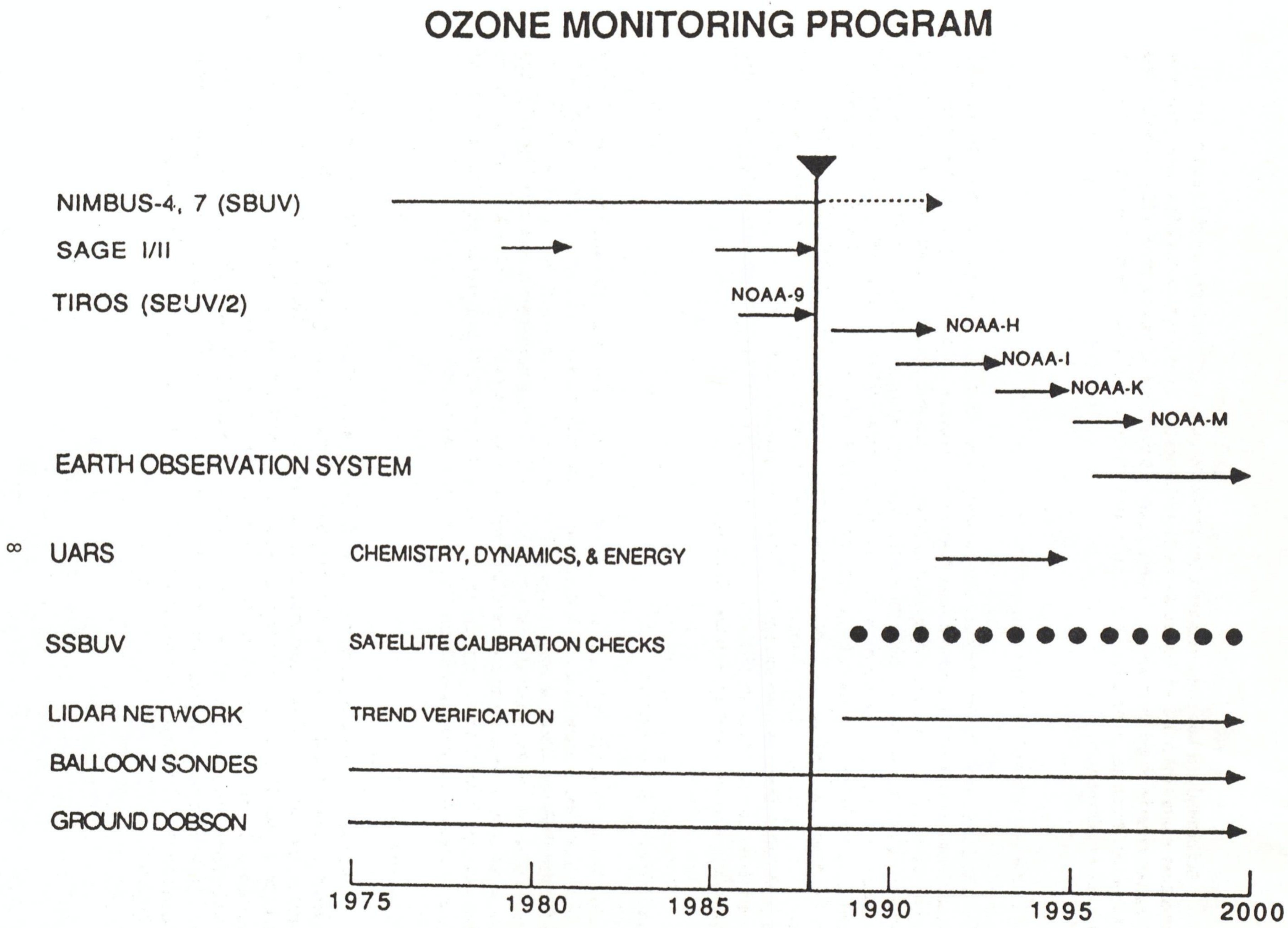


Figure 2.1
Ozone Monitoring Program

Accordingly, a minimum requirement for trend detection at 40 km would be the ability to detect an ozone decrease of 4 percent in 10 years where the predicted depletion is a maximum using the criteria established above. Note that the photochemical models predict that at 50 km and 30 km the decrease in ozone will be only about one-fourth the decrease at 40 km, or about 1 percent in 10 years.

2.2.2. Lower Stratosphere

The bulk of the total column ozone resides in the lower stratosphere, and potential climatic effects associated with infrared radiative transfer are related to ozone in the troposphere and the region immediately above the tropopause. Model predictions of trends in lower stratospheric ozone have varied greatly as the understanding of the relevant chemical processes has evolved. Furthermore, transport processes have a significant impact on lower stratospheric ozone and can lead to perturbations that have latitudinal variations. A goal of trend-related ozone measurements in the lower stratosphere is to provide the capability to distinguish between the various model scenarios of predicted ozone changes. These have varied from 1 to 2 percent decrease per decade in past calculations, to zero change or a slight increase using currently accepted chemistry. If a trend in the lower stratosphere as large as 0.1 percent per year exists, the data are required to have sufficient precision to detect it unambiguously.

2.2.3. Total Column Amount

The same reasoning applies to total column ozone, which to a substantial degree reflects the lower stratospheric abundance. Thus, the minimum requirement on a measurement system here is the capability to detect an ozone change of 0.1 percent per year in the lower stratosphere as well as in the total column amount. However, it must be emphasized that a major finding of recent years is that two-dimensional models predict large seasonal and latitudinal variations in fluorocarbon-induced ozone reductions; that is, a greater reduction in winter than in summer and greater reductions in polar latitudes than in tropical latitudes.

2.2.4. Troposphere

In the troposphere there may well be hemispheric differences in ozone trends, and the scientific requirement is to have the capability to differentiate between these. Because a 0.1 percent per year trend in stratospheric ozone has approximately the same impact on the total column as would a 1 percent per year trend in tropospheric ozone, the requirement for trend detection is not as stringent in the troposphere as in the stratosphere. Knowledge of the tropospheric ozone trends in northern and southern hemispheres to within 0.2 percent per year should be sufficient. A more detailed discussion on the importance of the role of tropospheric ozone on the climate and atmospheric gases, and recommendations for monitoring appears in Chapter 5.

2.3. Measurement Systems

2.3.1. Total Column Amount

(1) Ground-based Systems

The most widely used ground-based instrument for monitoring total ozone continues to be the Dobson ozone spectrophotometer. This instrument is a quartz-prism double-monochromator, which measures the differential attenuation of sunlight in adjacent spectral bands in the UV Huggins bands of ozone (about 320 nm). Empirical relationships between measurements on direct sunlight and zenith skylight have been derived, and allow an estimation of total ozone on partly cloudy and cloudy days but with less accuracy. As of 1986, the number of routinely reporting Dobson stations was about 20 in Europe, 11 in North America, 12 in Asia (Japan, China, northern India, South Korea), 7 in the north polar zone (including 2 Soviet stations), 11 in the tropics, 6 in the south temperate zone (all but 2 in Australia), and 4 in the south polar zone, 2 of which are operated by the British Antarctic Survey Stations.

A filter photometer system, the M-83, is used for total ozone measurements in the Soviet Union. This system is less accurate than the Dobson system, mostly because of the use of broadband filters and the assumption of constant ozone absorption coefficients. The M-83 system was improved appreciably in 1973, and since then has been integrated with the Dobson system to provide estimates of total-ozone variations in eastern Europe and Siberia. There are 16 M-83 stations which report routinely to the "Ozone Data for the World" published by the Canadian Atmospheric Environment Service.

Dobson spectrophotometers are no longer being produced. A new grating ozone spectrometer has been developed in Canada and is available commercially. This instrument, called the Brewer, has been installed as the primary instrument in the Canadian ground network for ozone monitoring. The Brewer instrument provides direct-sun total ozone observations of precision comparable to the Dobson, and in addition provides information on the total sulfur dioxide content. The long-term stability of the Brewer system is under investigation.

(2) Satellite Systems

The Backscatter Ultraviolet (BUV) instrument on Nimbus 4 was the start of a series of similar type satellite instruments yielding a record of total ozone data dating back to April 1970. Other instruments such as the Infrared Interferometer Spectrometer (IRIS) on Nimbus-3 and Nimbus-4, the Multifilter Radiometer (MFR) instrument on earlier military polar orbiting satellites, and the TIROS Operational Vertical Sounder (TOVS) instrument on the NOAA satellites have used the 9.6 micrometer channel for inferring ozone. The longest record is that of the SBUV and TOMS (Total Ozone Mapping Spectrometer) instruments. The current operational satellite instrument for total ozone measurements is the SBUV/2 (an improved version of the SBUV) which is planned to be in orbit through the lifetime of the present series of NOAA polar orbiting satellites (ca 1996) as shown in Figure 2.1. The National Plan 1981-86 had stated the requirement to fly SBUV/2 instruments on each of the morning and afternoon NOAA operational satellites;

however, insufficient data acquisition capabilities restricted the SBUV/2 instrument to be carried only on the afternoon satellites. As a result, a requirement has been established on the present single satellite system that when a replacement satellite is launched, the satellites should overlap for a period of sufficient sample size to cross calibrate the satellite systems. A shuttle SBUV (SSBUV) is also planned for conducting calibration checks of the operational SBUV/2. The SSBUV will be brought back to the ground for recalibration and reflown at predetermined intervals. These requirements will be discussed further in Section 2.5.

Total ozone amounts are also obtained from atmospheric radiances measured by the TOVS which is also flown on Tiros-N satellites. In this case, total ozone is determined from a linear regression procedure where total ozone amounts derived from a set of Dobson spectrophotometer measurements are used to establish a set of coefficients for the infrared radiances that are measured in three of the TOVS infrared spectral channels. The regression coefficients are generated from a set of approximately simultaneous satellite and Dobson observations. In order to have an independent check on the accuracy of the determinations, only a portion of the Dobson measurements are used in deriving the coefficients, while another subset is used as an independent check.

The Global Ozone Monitoring Radiometer (GOMR) being planned for post TIROS-N operational monitoring is conceived of being composed of two components: a GOMR Nadir (downward looking) Sounder (GNS) for determining total ozone and a GOMR Limb (horizon looking) Sounder (GLS) for determining vertical distribution of ozone, temperature and other trace gases at altitudes above the tropopause. The GNS is based on the Total Ozone Mapping Spectrometer (TOMS) system, the GLS on the Limb Infrared Monitor of the Stratosphere (LIMS) system, both of which have flown on Nimbus research satellite. The TOMS has the advantage of observing total ozone at high (50 km) spatial resolution and scans horizontally. The LIMS provides ozone profiles at 3 km resolution as well as profiles of other atmospheric species. These instruments, particularly the TOMS, will be discussed further in later sections.

2.3.2. Vertical Ozone Distribution

(1) Ground-based Systems

Estimates of the vertical ozone distributions have been made with the Dobson instrument using the Umkehr method which involves observing the overhead sky as the sun sets. The altitude resolution of this observation is about 7 km. In the past, Umkehr observations have been taken while the solar zenith angle moves between 60 and 90 degrees. Recently, the "short Umkehr" method has been tested and shown to be reliable when measurements are made over solar zenith angles of 80 to 89. The latter measurements contain as much information about the ozone profile as do the earlier conventional methods, and require only about one-third the observing time. As of 1986, the number of routinely reporting Umkehr stations was 4 in Europe, 3 in North America, 4 in Japan, 2 in India, 2 in the north polar zone, 3 in the tropics, and 4 in the south temperate zone (all in Australia or New Zealand).

Since the last National Plan was released an automated set of stations was made operational for Umkehr observations. Improved measurements with the automated systems are made much more frequently than previously. Automated stations now routinely reporting are Poker Flat, Alaska; Boulder, Colorado; Haute Province, France; Mauna Loa, Hawaii; Perth, Australia; and Huancayo, Peru. Lauder, New Zealand will become operational soon.

The vertical ozone distribution with approximately 1 km altitude resolution can be accomplished with in situ instruments. Two electrochemical instruments, electrochemical concentration ("ECC") and Brewer-Mast sondes, are in use today. Both sondes are based on the reaction of ozone with an aqueous solution of potassium iodide, but the sondes differ in the design of the electrochemical cell. The two must also be adjusted by coincident independent total ozone observations, and require air-pump efficiency corrections. Intercomparisons between balloon sondes show agreement within about 6 percent after corrections are applied. As of 1986, the number of routinely reporting balloon ozonesondes was 5 in Europe, 4 in North America, 3 in Japan (though very intermittent), and one in the north polar zone (Resolute) and one in the south polar zone (Syowa). Beginning in the southern spring of 1986, ozonesonde flights were also made at Amundsen-Scott and McMurdo in connection with the Antarctic "ozone hole" phenomenon. These will be continued, and there undoubtedly will be ozonesonde observations at other Antarctic sites as well until the problem of the "ozone hole" is resolved.

The ROCOZ-A (Rocket Ozone Sonde which employs solar UV absorption) has been improved and has demonstrated an absolute accuracy of about 6 percent and precision of 3 percent between 20 and 50 km. It has been used in comparison programs with ozone observations from several satellites as part of a validation program. Rocket soundings are conducted mainly from Wallops Island, Virginia, with some soundings from Natal, Brazil. At the present time this program is being phased out. However, the ROCOZ-A measurement would be very useful for validating the LIDAR ozone measurements before they become operational.

(2) Satellite Systems

(a) SBUV and SBUV/2

Solar Backscattered Ultraviolet (SBUV) type instruments have flown on spacecraft since 1970. This instrument measures both ozone profiles and total column amount. The first generation type instrument (BUV) was flown on Nimbus-4 and provided data until 1979. The next generation instrument (SBUV), which included a wider wavelength operating range and an improved noise reduction scheme for improved geographical coverage, was launched on Nimbus-7 in 1978. In early 1988 the instrument became noisy and the data are no longer processed. The first SBUV/2 was launched on NOAA-9 in 1984 and continues to operate. An on-board radiometric check, which was a refinement to this instrument, failed to function correctly. The follow-on units will correct this problem and also incorporate a new detector that will improve the measurement accuracy.

The SBUV instrument views in the nadir and has an 11.5 degree field of view. This results in a spatial resolution of 200 km. The instrument contains an ultraviolet spectrometer and views the backscattered ultraviolet radiation in 12 discrete wavelength channels spanning 250 to 340 nm. The instrument also measures the solar irradiance in these same channels. The ratio of the backscattered radiances to the solar irradiance is used to derive the vertical ozone distribution from about 30 to 1.0 mb. The solar irradiance observation is made via a reflective diffuser plate to bring sunlight into the spectrometer. Its reflectance properties are not cancelled out when taking the ratio. Therefore, the reflectance of the diffuser must be carefully measured in orbit. The system to measure the reflectance failed on the NOAA-9 instrument as discussed above. An indirect technique using flight data is under development to determine reflectance for this instrument.

Ozone observations are only available during the daylight. The altitude resolution is about one scale height (7 km). The present algorithm has undergone several refinements over the last several years and its characteristics are well understood. The most recent improvement incorporated the latest laboratory measured ozone absorption coefficients. An extensive validation program for the Nimbus SBUV has been in existence for over 10 years and continues with NOAA-9. This program consists of comparing the satellite data with nearly all available ground observation data, which has helped to check the performance of the instrument and the algorithm. Equally important, however, it has pointed out the crucial need for maintaining a validation effort to run concurrent with the satellite observations.

(b) LIMS

The Limb Infrared Monitor of the Stratosphere (LIMS) also had its predecessor on the Nimbus-4 satellite. That instrument was known as the Limb Radiance Infrared Radiometer (LRIR) and was capable of measuring only ozone and temperature. The LIMS is an advanced version of that instrument and is capable of measuring several atmospheric species, including temperature, by scanning the Earth's infrared emission in the limb at six wavelength channels between 6.2 and 15 micrometers. The instrument operated satisfactorily on Nimbus-7; however, like its predecessor, its lifetime was about seven months because of the limited supply of cryogen required to cool the detector. The LIMS instrument has demonstrated the ability to measure nitric acid, water vapor, nitrogen dioxide, ozone and temperature in the stratosphere. Data are taken during both day and night. The discussion in this section will focus on the ozone measurements only.

The LIMS ozone channel is centered at 9.6 micrometers where the 5 percent power points cover the range 925 to 1136 cm^{-1}. The radiometer consists of a scan mirror for altitude scanning, entrance optics, optical filter elements for each of the six channels, and detector assembly, which is cooled to about 63 degrees Kelvin in two stages. At the tangent height most of the radiation comes from a region 300 km wide along the instrument line of sight. Ozone profiles are derived from the measured radiances where the atmospheric temperature is first determined after which the ozone distribution is derived using an iterative technique where the measurements are compared to precalculated radiances. The altitude resolution is about 3 km, thus providing sufficient resolution to study atmospheric dynamic processes. As with SBUV, considerable effort was employed to validate the LIMS data by comparing them with available ground-based observations.

(c) SAGE and SME

The Stratospheric Aerosol and Gas Experiment (SAGE) and the Solar Mesospheric Explorer (SME) satellite also measure ozone. Two SAGE instruments were flown (see Figure 2.1). These systems are basically research experiments with limited global coverage when compared to SBUV and LIMS. The distinct advantage of SAGE is that it employs solar occultation measurements which have inherently high accuracy. This comes about because a direct absorption technique is used for deriving ozone profiles and the instrument is "calibrated" each time it scans and views the unocculted sun. However, accurate location of the direction of the instrument field of view is crucial for accurate altitude determination. Occultation measurements are and can be extremely important in providing cross checks for the operational instruments since they employ a different technique. The SAGE-II instrument measures nitrogen oxide, water vapor, and aerosols in addition to ozone by measuring the absorption of solar radiation (the visible Chappuis absorption bands are used for ozone) during sunrise and sunset.

The SME measured ozone with two instruments, one which measured UV scattered absorption in the limb, and one which measured oxygen infrared airglow, from which ozone can be derived. These instruments had limited coverage and ozone data were restricted to altitudes above 50 km.

(3) Performance of Satellite Instruments

(a) Errors

The errors of any measurement system can be separated into two components; precision and accuracy. Simply stated, precision deals with the repeatability of the measurement when the same parameter is measured over and over assuming it is invariant. The accuracy deals with how close the measurement is to the true value. For most cases precision (or imprecision) of a measurement is random. Therefore this error can usually be reduced by conducting more observations. Uncertainty in accuracy is usually systematic. This systematic error may be irrelevant to long-term observations if it can be proven to remain constant over time. It is best to eliminate as much as possible unchanging absolute errors thus improving accuracy in a global observation system. This is particularly important for verifying satellite data when comparing with different techniques. It is essential to remove changing systematic errors, however. The following is a summary of errors for a single observation in the presently employed satellite observations.

(b) Intercomparisons

Intercomparison of one observation system against another provides a quantitative means for assessing accuracy when the two techniques are based on different physical principles. Intercomparisons cannot, however, determine absolute accuracy directly since neither system may be measuring the true amount. Nevertheless, intercomparisons can provide insight into how the differing systems perform if proper care is taken. This includes allowing for sufficient intercomparison data to increase precision and accounting for space and time separations in the comparisons. Traditionally the ground-based data were considered more accurate than remote measurements since the instruments can be checked regularly. In reality this is not the case as has been shown in many instances. Ground-based systems can have inconsistent calibrations and station-to-station biases. Nevertheless these intercomparisons are very constructive in pointing out problems and paving the way for major improvements in the satellite observations. The following summarizes some results:

Comparisons of SBUV with ozonesondes and Umkehr show systematic differences of less than 10 percent but which are functions of height and latitude. It should be noted that Umkehr observations are very sensitive to aerosols (such as those resulting from the El Chichon volcanic eruption in 1982). At the present time the trends detected by SBUV cannot be unequivocally verified or disputed using Umkehr data.

A comprehensive comparison of LIMS ozone profiles with correlative measurements has been conducted. Differences were less than 10 percent from 50 to 7 mb for mid latitude balloonsondes and 16 percent from 50 to 0.3 mb for rocketsondes. For the most part these differences are within the stated errors of the measurements. Similar comparisons have been conducted with SAGE data and here again differences were of the order of the stated errors in the measurement.

In as much as the actual coincidences of satellite data from the SBUV, LIMS, and SAGE I instruments are relatively few, the approach has been to compare monthly zonal averages. Comparisons between SBUV and LIMS at the equator and near 45 degrees north show overall good agreement in profile shape with the largest disparity of about 15 percent between 10 and 30 mb (30.24 km). At pressures to 2 mb (43 km) the differences are about 3 percent then increasing to 7 percent to about 0.4 mb (56 km). From the equator to 40 degrees north, SAGE I, SBUV, and LIMS agree within 4 percent near 32 km with SAGE I larger than either. In the southern hemisphere the values are even closer. At altitudes greater than 40 km and latitudes between 40 degrees north and 60 degrees south LIMS, SAGE I, and SBUV agree to about 4 percent. These differences are consistent with the reported systematic errors presented above.

Over the course of time the SBUV and SAGE data show close correlation in the observations of seasonal and shorter term variations. Over a longer term when both the SAGE I and II are compared to SBUV, the following differences are observed. In the altitude range 34 to 48 km SAGE I is lower than SBUV by about 4 percent. When comparing SAGE II, flown about 3 years later, the differences are higher than SBUV by about 10 percent at these levels. The implication is that SBUV sensitivity decreased significantly relative to SAGE. Comparison of SAGE I with II implies a decrease of 3 percent near 40 km over an interval of about 6 years. A more detailed discussion of these results appear in the report of the Ozone Trends Panel.

On the basis of limited samples, it is difficult to ascribe specific limits of uncertainty in the absolute value of measured ozone. It has been proposed (WMO, 1986) that the following (1 standard deviation) limits as representing, at the present time, the absolute capability of measuring ozone from satellites as:

o 15 percent: 30 to 10 mb

o 6 percent: 10 to 0.5 mb

For future observations, absolute accuracy should be improved by a factor of two.

2.4. Problem Areas

2.4.1. Total Column Amount

(1) Ground Systems

There are still gaps in the Dobson total-ozone network in the south temperate zone. As of

1986, Dobson data in this region were available only from Australia, New Zealand, and Buenos Aires, Argentina. This distribution cannot give representative estimates of total-ozone variations in this zone and may not even be suitable for satellite calibration. At the minimum, a Dobson station should be established in southern Africa. It would also be desirable to have stations established in the South Atlantic, eastern South Pacific, and southern Indian Ocean. Because of the great importance of the Antarctic "ozone hole" phenomenon, total-ozone data for the British stations of Halley Bay and Argentine Island should be included in "Ozone Data for the World".

Some Dobson stations continue to suffer from poor quality control. Problems with Dobson data arise from degraded instrument calibration, inconsistent observational procedures, poor control of data processing, and on occasions there is sporadic reporting of data to the archives. These problems have been long recognized and significant progress has been made in many stations, particularly the stations recently automated by NOAA. Since the Dobson network is to provide an essential component to the ozone monitoring system, continued improvement is needed.

(2) Satellite Systems

Satellite systems which employ non-spatial scanning instruments for total ozone measurements have limited geographical coverage because their observations are confined to near the orbital track. A polar orbiting satellite has each orbit separated by about 27 longitude, with a slow precession rate that spans a full geographical coverage over a period of approximately two weeks. A NOAA satellite with an afternoon orbit has coverage in the winter hemisphere to latitudes near 50, while the Nimbus-7 satellite has a noon orbit and coverage near 60 in the winter hemisphere. This limitation results from instruments which rely on backscattered sunlight, such as SBUV and TOMS, for measuring ozone. The TOMS type instrument eliminates the longitudinal problem by spatial scanning, but the polar night problem will still remain. The single satellite system might also produce some temporal gaps if the afternoon satellite or the SBUV/2 fails before its replacement is sent up. As a backup, the TOVS system can be used to fill the gap until the replacement satellite is put into orbit.

The TOVS system has been collecting data since the first instrument on TIROS-N in November 1978. As the TOVS will be on each succeeding satellite of the NOAA TIROS-N series of satellites, total ozone determinations will be available from the same type system until the mid-1990s. The use of the data in the overall monitoring plan is now planned as a supplementary source of information. The overall accuracy of the derived ozone data products is under evaluation at this time and a thorough understanding of TOVS and SBUV/SBUV2 relations must be achieved. There are limitations on the accuracy and coverage of the TOVS instrument arising from the use of a regression procedure, presence of clouds, and the inherent insensitivity of nadir-viewing infrared systems to an atmosphere with small vertical temperature gradients as appears often in winter high latitudes.

2.4.2. Vertical Ozone Distribution

(1) Ground Systems

Problems with the ozonesonde observations have been previously documented (WMO, 1986).

The sensors in both the ECC and Brewer-Mast sondes are based on the reactions of ozone with the iodide ion to form molecular iodine. Unfortunately, this reaction is not specific to ozone. Sulfur dioxide causes a negative interference, while nitrogen dioxide gives a slight positive interference. Contamination by nitrogen dioxide should be unimportant, at least at rural sites, but sonde data from the boundary layer in polluted areas may be contaminated by sulfur dioxide. One advantage of the Brewer-Mast system is that the impact of sulfur dioxide on total ozone can be estimated more easily. Several intercomparisons involving the Brewer and ECC sondes demonstrated poor agreement in the troposphere. These differences, still unresolved, were of the order of 10 percent where the ECC sonde measurements are higher than the Brewer sonde measurements.

Another problem with ozonesonde observations, as presently processed, involves the practice of multiplying individual soundings by a correction factor to ensure that the integrated ozone column is equal to the Dobson measurement of the ozone column. This procedure involves an estimate of the ozone amount above the altitude reached by the sonde, usually about 30 km. There is no real justification for this scaling procedure, since it has not been thoroughly demonstrated that the response of the sondes is linear with respect to ozone over the entire altitude range. The scaling procedure introduces errors due to uncertainty in the ozone amount above 30 km and errors associated with the Dobson technique.

Because atmospheric photochemical models indicate that any anthropogenic influences on ozone should be a maximum near 40 km, it would be very desirable to have accurate ozonesonde data to this height. At present, most ozonesondes only attain a height of about 30 km, and the data are uncertain even above 24 km because of problems with the pump efficiency at these heights. Attempts have been made, mainly at Hilo, Hawaii, to use modified ECC sondes to obtain useful ozone data to at least a height of 40 km. The usefulness of the data so obtained is now under investigation (Komhyr, personal communication).

In situ ultraviolet photometers flown on balloons have recently demonstrated high accuracy (3 percent) and fine altitude resolution (better than 1 km) to 42 km. However, these instruments are relatively large and expensive and, therefore must fly on retrievable balloon payloads which can be flown from only a very limited number of sites (WMO, 1986). These instruments could be used for satellite data verification or, more importantly, to verify the performance of improved ozonesondes and the Lidar ozone sounders now under development.

In the case of Umkehr observations, the automation of seven Dobson Umkehr stations has substantially improved the capabilities of this system. The most serious problem remaining is that of the influence of stratospheric volcanic aerosols on these observations. The observations can be corrected, however, with LIDAR data of aerosol distribution. Therefore, LIDARS should be established at all seven sites. All atmospheric models indicate that anthropogenic influences on ozone should be most apparent near the 40 km level, the same altitude where the influence of volcanic aerosols on Umkehr measurements is most noticeable. Accordingly, this is an extremely important problem to resolve.

As of 1986, there was no ozonesonde station in operation in the south temperate zone, Aspendale having ceased operation in 1982. It is an intolerable state of affairs to have no ozonesonde data in the entire south temperate zone, especially when there is so much interest in ozone variations in the adjacent south polar zone. There is also no ozonesonde station in the tropics providing sufficient data for trend detection. Natal was supposed to have fulfilled this role, but the data have been far too intermittent for this purpose. The question as to the quality of ozone sonde data over the long term for trend detection remains unanswered.

(2) Satellite Systems

Satellite observations have near global coverage with important exceptions. A polar orbiting instrument that only views along the satellite ground track displaced by 27 degrees longitude at the equator, is sufficient for monitoring at altitudes higher than 10 mb (30 km). At lower levels, however, higher spatial resolution is required because of greater atmospheric variability. Latitude resolution is of the order of one degree which is sufficient. For the SBUV/2, the winter poles are not observed. Although this area contributes a small fraction to the mean global amount, it very important. Therefore, spatial coverage and resolution of SBUV/2 observations provide the minimum need for monitoring to detect global trends. However the need for better coverage has been clearly demonstrated with the discovery of the ozone "hole" in the Antarctic. Photochemical models now predict a latitudinal and seasonal dependence in ozone trends with larger changes at high latitude winters, therefore SBUV/2 observations alone will provide an incomplete picture of global ozone variations. Ideally a spatial scanning instrument with the resolution comparable to TOMS or TOVS (50 km) should be flown to investigate detailed features now being discovered by these instruments. However, these instruments only have the capability to measure total column amounts and it would be further advantageous to measure ozone profiles with similar horizontal resolution with an altitude resolution of 3 km. These data would enable the observation of gravity waves as well as the evolution of planetary wave activity into the upper stratosphere where ozone depletion due to CFC by-products is a maximum. An altitude resolution of 2.3 km would also be sufficient for calculating budgets and would then be comparable to the required resolution of temperature observations discussed in Chapter 3.

The LIMS type systems provide greater coverage because of night-time capability whereas SBUV/2 observations are limited to daytime only. The altitude resolution and range of the SBUV and LIMS differ also. The resolution of the SBUV is typical of nadir viewing instruments which is about one scale height or about 7 km. The LIMS is about 3 km. The altitude range of SBUV is about 20 to 55 km while the LIMS is about 15 to 60 km. At the present time, technology limits the lifetime of the LIMS type instrument to seven months. The LIMS instrument detector must be cooled by a cryogen in order to achieve the required sensitivity. The GOMR Limb Sounder, which has a non-cryogen cooled detector system, is currently under study.

The accuracy and precision of the SBUV/2 are sufficient for global ozone trend detection; however, its long term stability has yet to be demonstrated. This question will be discussed in more detail below. The accuracy depends on a combination of factors including the algorithm, how the algorithm deals with interfering atmospheric effects, and the radiometric calibration. Potential interferents to SBUV/2 ozone observations are aerosols above 25 km. The most likely sources for aerosols are volcanic eruptions. To date it seems that this has not been a problem although the SME seems to observe aerosols at these levels. The precision of SBUV is high as shown in Table 2.1, where the largest source of random error is the retrieval error. The critical element for accurate long term ozone observations is the reflectance of the solar irradiance diffuser.

Table 2.1 Performance of Satellite Instruments (WMO, 1986)

	Precision (percent, 1 stand. dev.)					Accuracy (percent, 1 stand. dev.)				
	Pressure (mb)					Pressure (mb)				
	0.4	1.0	3.0	10.0	30.0	0.4	1.0	3.0	10.0	30.0
SBUV	10	3	2.5	5	5	13	7	5	5	6
LIMS	2	2	1.5	2	1.5	26	15	16	23	35
SAGE-II*	40	13	12.0	9	10.0	7	6	6	6	7
SME (UV)	10	6	-	-	-	18	17	-	-	-

* Update for SAGE-II. This is one km resolution. Random errors can be reduced by $1/\sqrt{n}$ where n kilometers are averaged.

As shown in Table 2.1, the LIMS has large absolute errors where the largest component to this error is the uncertainty in the retrieved temperature which is used in the ozone retrieval. The ozone spectral parameters also contribute significantly to the absolute error. Radiometric calibration errors are not significant for IR instruments. For the most part precision in the LIMS instrument is determined by the radiometric random error. The precision of LIMS is comparable to SBUV.

The performance of SAGE is roughly comparable to SBUV and LIMS, but does not have the coverage capability as the SBUV and LIMS. In addition, observations are made only at sunrise or sunset which are times of the day when the ozone distribution in the upper stratosphere is in transition. This could provide a small ambiguity in comparing with other observations taken at different times of the day. As discussed earlier the SAGE measurements have a unique capability in a long term measurements program since they are nearly self calibrating each time a scan is performed. Therefore long term undetected drifts in the SAGE instrument should not occur. Error sources include radiometric imprecision, digitizer truncation, and scan pointing errors. There is an uncertainty in reference altitude of about 0.25 km which contributes to uncertainties in profile repeatability.

The most important requirements for monitoring ozone are the understanding of the long term stability of the instrument sensitivity while in orbit and maintaining continuity of instruments from one satellite to the next over the long term. For SBUV/2 instruments, a great deal of experience has been gained with this problem on Nimbus and NOAA satellites where changes in sensitivity have occurred. As discussed above, the solar irradiance diffuser is the most critical factor in the SBUV accuracy and any unaccounted for changes in the diffuser will be reflected as errors in the derived ozone values. These changes have been of the order of several percent per year for SBUV but significantly less for SBUV/2. NASA and NOAA maintain an effort to stabilize instrument drifts (on both Nimbus and NOAA satellites) by means of modeling the degradation and correcting the data, however, this has not been successful to date with the Nimbus-7 SBUV. This correction could be subsequently verified by comparisons with accurate ground-based data when available. The uncertainty in the accuracy of this correction will remain the limiting factor in how accurately an ozone trend can be determined.

2.5. Strategy for Monitoring Ozone

2.5.1. Validation of Data

Validation is one of the most critical components in the analysis and reporting of remotely sensed data. Validation of satellite data by comparison with ground-based systems has reached a fairly mature level but seems to be limited by the accuracy of the ground systems. In fact, there have been a number of instances where ground-based measurements have been shown to be in error after being compared to satellite data. It is now believed because of the high accuracy, precision, and long-term stability required for monitoring, that ground truth systems, as they presently exist, may not be accurate enough for validation. In addition, in order to achieve this high accuracy, new procedures for validation by data comparison will have to be developed and tested.

Experience with SBUV observations indicates that validation of satellite data is a two step process. The first step involves accurate calibration of the instrument prior to flight and the maintenance of that calibration while in orbit. The second step involves the verification of the algorithm that converts the observations to ozone values. One without the other is not adequate, nor can they be combined. The first must be done on a regular basis and involves periodic checking, correcting, and establishing continuity between instruments on succeeding satellites. The need to verify the algorithm may only be required initially if it can be shown that atmospheric radiative characteristics do not change.

(1) Instrument Performance Verification

Given that the present monitoring system consists of a series of SBUV/2 instruments, performance verification can and should be accomplished in the following way:

(a) Utilize an on-board calibration check. This system will measure the reflectance of the diffuser plate over the course of time. This has been implemented for the SBUV/2; however, it has not been successful to date because the onboard lamp was unstable. This system was redesigned with the expectation that the reflectance of the diffuser plate will be monitored to 1 percent.

(b) In order to eliminate possible errors due to instrument biases from one flight to the next, overlaps between data sets must be planned. This overlap should be about one year. However, there is insufficient experience in the area and the overlap period could be longer or shorter.

(c) Utilize the Space Shuttle reference calibration instrument (SSBUV). This instrument is nearly identical to the SBUV/2 satellite instrument. The Shuttle instrument will provide a transfer of absolute radiometric scales to the monitoring instrument as well as provide continuity from one instrument to the next. The SSBUV must be flown every 8 months.

(d) Because of the high stability demonstrated by the SAGE occultation type measurement an instrument of this type should be considered as part of the ozone monitoring program.

(e) Perform intercomparisons with ground-based observations. Every effort must be made to improve and establish the precision and accuracy of the ground-based network. This network will include the conventional ozone measuring systems and the developing LIDAR techniques. Further recommendations for the ground-based system will follow.

(f) Develop and implement analytical procedures for validating and comparing data sets. Although there has been several years of experience in this area, refined techniques are needed to meet the stated requirements.

(2) Satellite Algorithm Verification

Algorithm verification may need only be done initially. The validity of the algorithm depends on the soundness and completeness of the atmospheric model on which it is based. Since the atmosphere or our understanding of the atmosphere may change over the course of time verification may be an ongoing process and should include:

(a) Continuous monitoring of atmospheric parameters which would affect the retrievals. Aerosols, for example, would affect retrievals from SBUV and LIMS and the ground-based Umkehr. Stratospheric aerosols can be readily detected by ground LIDAR.

(b) The algorithm should be verified through the use of independent ground-based ozone observation. It is highly desirable that these observations be based on a minimum of five different latitude zones through all four seasons. At the present time there are seven ozone stations which are carefully intercalibrated. These stations employ the Umkehr technique which uses a similar principle as SBUV and cannot be considered totally independent. This technique is also sensitive to aerosols.

(c) These independent ground-based systems should be maintained for the duration of the monitoring period in case there is a change in atmospheric conditions which may invalidate the operational algorithm.

(3) Ground-based System Improvements

The conventional ground-based observing system which includes the Dobson, Brewer, Umkehr, and balloon ozonesonde stations can continue to play an important role in the validation of satellite data for the lifetime of the monitoring program. It is absolutely essential that the accuracy and precision of these systems be maintained at the highest level and that the data be subjected to strict quality controls. It is recognized that the establishment of seven automated Dobson Umkehr stations is a step in this direction. The following additional steps are recommended to achieve this level of high quality:

(a) Continue research to understanding performance of these systems with the objective of improving accuracy and precision. An assessment of the performance of the ground-based system should be done on a regular basis to determine its ability to perform satellite validation.

(b) A special set of 20 Dobson stations should be set up around the Earth as uniformly as possible which will be calibrated every three years against the World Ozone Standard Dobson in Boulder, Colorado. This set should include the seven automated stations and four NOAA/GMCC stations. Additional stations are needed in the south temperate zone.

(c) Since all data can be useful for comparing with satellites, the remainder of the Dobson network must be maintained with a goal to upgrade the system to be comparable to the special set. If high quality of these data cannot be demonstrated, then comparing with satellite data cannot be justified.

(d) Since aerosols can interfere with Umkehr observations, LIDAR soundings should be taken with the Umkehr observations.

(e) The linearity of the balloon ozonesonde response to 30 km, and higher if possible, must be determined to achieve high accuracy in the troposphere and middle stratosphere. This in part, includes an accurate, 5 percent or better, determination of the pump efficiency over the entire altitude range.

(f) The difference between the Brewer-Mast and "ECC" ozonesondes in the troposphere must be resolved.

(g) Extensive comparisons should be conducted between the ozonesondes and the LIDAR ozone sounders.

(h) Ozonesonde stations should be established in the Southern Hemisphere particularly in the south temperate zone.

2.5.2. Additional Requirements for Development

The verification and the determination of the magnitude of an ozone trend is a crucial objective for environmental monitoring. In addition to an operational long-term measurements program, there is a vital need for an ongoing research and long term program for development. A research program, along with the monitoring effort, is essential to develop an understanding of the mechanisms which cause changes in the stratosphere and of the geophysical and biological implication of these changes. Present measurement capabilities are not good enough to gain these understandings. New technologies are coming into use, but they must be tested to gain confidence. This will take several years. In addition, new capabilities must be developed in order to improve the spatial and altitude resolutions and accuracy of our measurements. The following are specific recommendations for development of systems which will substantially improve our understanding of ozone variations.

(1) An independent verification of a trend observed by satellite systems is desirable. The ground-based LIDAR is a good candidate for this requirement. However, it should be noted that this instrument for ozone measurements is just becoming operational and a history of experience does not yet exist.

(2) Establish the planned NDSC Network which includes the LIDAR as planned by NASA, NOAA, CMA, WMO. The goal of this Network is to provide observations to detect changes in the stratosphere and the means to understand them. This Network will provide latitudinal, seasonal, monthly, daily and diurnal observations of key atmospheric parameters. This system will also provide ground truth for the operational ozone observing system and the Upper Atmospheric Research Satellite.

(3) Because the present monitoring system consists of the SBUV/2, which does not spatially scan, coverage is limited to nadir observations only. It is highly desirable to include a scanning instrument such as the TOMS to the ozone monitoring program to investigate the development of

the Antarctic ozone "hole" and perturbing events such as volcanoes. At the present time launch of a TOMS is being planned and must be strongly supported.

(4) The TOMS observations are also limited to daylight, however the TOVS has a nighttime capability but its accuracy is poor at high latitudes in winter. A more extensive study should be initiated to better characterize this instrument to determine its suitability for climatological studies in the polar night.

(5) Beyond the time of the current system, the GOMR advanced ozone monitoring system is planned for the post-ATN period on the Polar Platform. The planned infrared vertical sounder based on LIMS is a radical departure from the present system for obtaining ozone profiles. Although we have no experience with this system for long term monitoring, it will provide data not available from the SBUV/2. It is, therefore, essential that to ensure no biases are introduced as a result of an instrument change, an extensive overlap be planned between the last SBUV/2 instrument and the GOMR system. This overlap must allow for observation of a known interannual change by both systems, such as the quasi-biennial oscillation. This two year interval will provide assurance that a smooth transition occurs between the two systems.

(6) At the present time, there is no instrument with the ability to measure ozone profiles with high spatial resolution and has global coverage. An instrument with this capability is necessary for computing ozone budgets and tracking gravity waves which are important dynamic features in the stratosphere. This instrument should have a spatial resolution of 50 to 100 km and an altitude resolution of about 3 km. The next opportunity to fly this instrument is on the Earth Observing System (Eos) in the middle 1990s. This development must be strongly supported.

(7) Perform on-orbit calibrations utilizing a Space Station based satellite service system. These systems are only in the planning stages; however, on-orbit calibrations should be considered in a future long term Earth observing system.

CHAPTER 3. METEOROLOGY

3.1. Introduction

Measurements of meteorological quantities are of fundamental importance to stratospheric monitoring. Only through careful monitoring of temperature and wind fields, and concomitant modeling efforts, will it be possible to isolate natural stratospheric changes from changes caused by ozone depletion and greenhouse gas increase. In the past, meteorological measurement strategies for the stratosphere have focused on temperature because of the temperature dependence of ozone photochemistry and the well known dynamically driven ozone temperature relationship in the lower stratosphere. This plan states the need to also measure winds directly.

Two levels of measurement exist. The first simply allows the detection and the quantification of change. The second allows understanding the cause of any observed changes. The data density required for understanding is much higher than that required for detection. The existing and proposed data gathering systems do not meet the necessary requirements outlined in this chapter for understanding stratospheric changes. The requirements for detection of change can only marginally be met.

This plan, therefore, proposes two strategies. First, a strategy is proposed to assure the best possible data set given the known available measurement systems. Second, a strategy is outlined that highlights what should be done to form an adequate stratospheric monitoring system.

In the past, the bulk of the data has not been collected with long-term monitoring in mind. It has been collected for the operational needs of the weather service and military. As will be detailed in the rest of this chapter, the stratospheric temperature measurement system is at a critical point. Unless quick action is taken, the quality of stratospheric temperature data for the purpose of determining trends will deteriorate rapidly during the next decade. The plan outlined in this chapter should prohibit this deterioration and lead to a high quality monitoring network.

3.1.1. Temperature

Chapter 14 of WMO (1986) highlights the difficulties of determining stratospheric temperature trends from existing data sets. Data from each of the stratospheric measurement systems (radiosonde, rocketsonde, and satellites) are used to calculate trends. Because of lack of global coverage and discontinuities related to instrumentation changes, the trend calculations reported in WMO (1986) are inconsistent with one another and therefore inconclusive.

Improvement in the ability to detect trends because of regular global coverage by satellites has not been realized. The operational satellite systems were not primarily designed as temperature monitoring systems, and therefore, it has not been a high priority to assure that satellite instruments are consistent with one another. The same type of instrument flown on succeeding satellites produces measurements which are significantly different from each other. Therefore the satellite data set is not a continuous, consistent data set.

Another difficulty inherent in satellite derived temperature data is the effect of different inversion algorithms. Algorithm effects are frequently as large as calculated temperature trends. One possibility of avoiding the algorithm effects is to look directly at the satellite radiances prior to the inversion to temperature profiles (e.g. Nash and Forrester, 1986). To assure the reliability of this method, the same detection channels must appear on a series of instruments, and these instruments must be calibrated against each other.

Given the difficulties previously documented with temperature trend detections studies, a special working group of the Ozone Trends Panel (1988) was formed. This group did not simply review the available data, but reanalyzed the data taken since 1970. The following highlights the major findings of this group:

(1) Above 30 mb, trends could not be determined from the data prior to 1979 because the satellite data are not adequately calibrated and the rocketsonde data have insufficient spatial coverage.

(2) Since 1970 there are no significant temperature trends below 30 mb "except perhaps in the equatorial and Antarctic regions".

(3) "The stratospheric radiosonde and satellite temperature data sets intercompare reasonably well over the period 1979-1986 although points of disagreement exist".

(4) The 1982-1983 data have been significantly perturbed by the El Chichon aerosol cloud. Arithmetic differences between the 1979 and 1980 average and the 1985 and 1986 average suggest a temperature change of -1.75 degrees Kelvin (°K) to 1.5°K at 0.5 mb and -1.0° Kelvin to 0.5°K between 5 mb and 1 mb.

(5) The satellite data (SSU) do not detect the quasibiennial oscillation (QBO) that is well documented in the rocketsonde and radiosonde data.

The QBO comprises a major part of the natural temperature variability. The failure of the satellite to detect this signal must be understood and connected.

The trend analyses by the Ozone Trends Panel once again emphasize the difficulties of producing a consistent temperature data set. It is imperative that steps be taken to assure the collection of a global data set that is consistently accurate in both space and time domains.

3.1.2. Winds

To document changes in the climatological state of the stratosphere temperature measurements alone may be sufficient. To understand meteorological and ozone changes in the stratosphere, it is necessary to also have information about the wind. As discussed below, our ability to estimate winds from temperature data is insufficient. Therefore. direct wind measurements of the stratosphere are needed.

Direct wind measurements consist of radiosondes in the lower stratosphere (below 10 mb) and rocketsondes in the upper stratosphere (above 10 mb). Global geostrophic estimates of the wind field are derived from geopotential height fields inferred from satellite temperature data and a reference level height analysis.

Wind data are necessary for understanding ozone measurements at all altitudes in the stratosphere. Figure 3.1 shows the ozone response to temperature perturbations calculated with and without consideration of the winds. The largest errors in these calculations arise from using geostrophic winds to calculate the transport. The extension of these calculations to other seasons and lower altitudes is limited by the quality of the wind measurements (Douglass et al., 1985; Douglass and Rood, 1986). Accurate determination of ozone (and other constituent) budgets throughout the entire stratosphere is of fundamental importance in understanding the stratosphere. The inability to determine relative roles of dynamics and chemistry in the Antarctic ozone depletion illustrates the need for accurate wind data to supplement temperature data.

Recent studies indicate that the geostrophic estimates of stratospheric winds may have errors greater than 25 percent in middle latitudes in winter (e.g., Elson, 1986; Boville, 1987). Derived quantities (e.g., eddy fluxes, potential vorticity) may have errors in excess of 100 percent. Winds from a stratospheric data assimilation provide much more accurate determinations of constituent budgets than geostrophic analyses (Rood, et al., 1988). However, differences between observed and calculated constituent budgets are still large.

Wind measurements are a basic quantity for determining and understanding the climatology of the stratosphere. It is only through wind measurements that the mixing processes which determine heat and constituent budgets will be understood. The quality of temperature derived wind data is insufficient, and our understanding of stratospheric processes is incomplete because of a lack of good wind measurements.

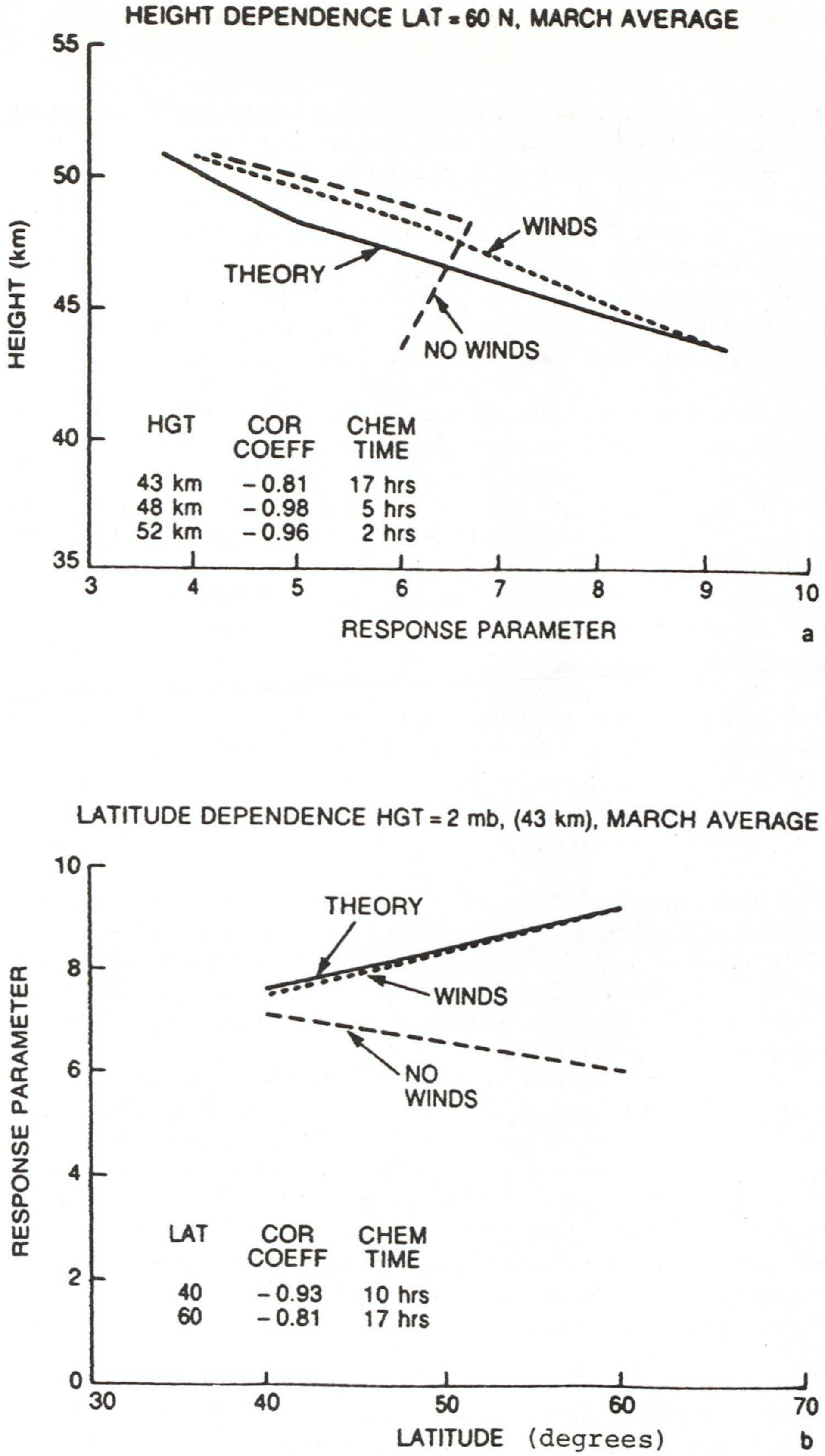
The limited spatial and temporal extent of ground-based wind data restricts its usefulness in global budget studies. It is essential, however, that the current wind measurement system be maintained. Wind measurement instruments will be aboard the UARS satellite and are proposed to be on the Eos platform. These instruments are unproven but should provide a feasibility study for direct stratospheric wind measurements from space. Research for the development of satellite based wind instruments should receive high priority.

3.2. Measurement Requirements

3.2.1. Domain

In order to understand the processes important in determining the constituent budgets in the stratosphere, data must be taken throughout the troposphere, stratosphere, and mesosphere (1000 mb to 0.1 mb). Dynamical and chemical processes which occur in the mesosphere may have a profound influence on stratospheric ozone (for example, Solomon et al., 1982; Solomon and Garcia, 1983).

The stratopause region (1 mb to 50 km) is of fundamental importance for understanding processes relevant to ozone, and high quality data are required at this height. This region should be characterized by photochemical domination of the ozone distribution. Chemistry models, however, consistently underestimate ozone at the stratopause. Radiation calculations using



HGT	COR COEFF	CHEM TIME
43 km	−0.81	17 hrs
48 km	−0.98	5 hrs
52 km	−0.96	2 hrs

LAT	COR COEFF	CHEM TIME
40	−0.93	10 hrs
60	−0.81	17 hrs

Figure 3.1

Ozone response to temperature perturbations, with and without considerations of the winds.

observed ozone and temperature data indicate an imbalance in the radiation budget. This general inconsistency between ozone, temperature, and radiation fields suggests either a misunderstanding of the physical processes involved, problems with the data, or both.

At 40 km ozone reduction from chlorine compounds is expected to be largest. Above 40 km loss processes from different catalytic cycles are expected to become more important. These cycles will have a different temperature dependence from the chlorine cycle. Therefore, accurate temperature and wind measurements are crucial in the upper stratosphere and lower mesosphere to understand ozone photochemistry.

Aside from processes directly related to ozone, changes in the radiation budget due to greenhouse gases should have a stronger signal at the stratopause (and upper stratosphere) than in the troposphere (Ramanathan et al., 1987). Therefore, the upper stratosphere serves as a sensitive measure of the greenhouse effect. It is also necessary to disentangle ozone changes caused chemically by chlorine or other pollutants from ozone changes caused by response to radiatively or dynamically driven temperature changes.

3.2.2. Vertical Resolution

Analysis of the LIMS data suggest that the vertical resolution of the LIMS instrument is necessary to understand stratospheric constituent budgets (for instance, Douglass and Rood, 1986). Therefore a stratospheric monitoring system should resolve data on standard pressure surfaces defined in mb by:

$$P(n) = 1000 * 10^{-n/6}, \quad n = 0, 1, \ldots$$

This is the same as the UARS "standard atmosphere" and corresponds to a resolution of approximately 2.7 km.

3.2.3. Horizontal Resolution

The previous National Plan calls for horizontal resolution on the order of 1000 km (longitudinally at 45° latitude) and 2.5° latitude in the lower stratosphere (below 10 mb). It called for 2000 km and 5° latitude above 10 mb. Current temperature measurements should have this resolution. However, constituent budget studies suggest that sub-planetary wave scales (zonal wave number > 3) have large errors (e.g. Douglass et al., 1985). These errors are largely related to wind errors. If this degree of resolution were attained for both temperature and wind data it would be adequate for most monitoring purposes. Accurate information about synoptic scales is necessary for understanding ozone variability in the lower stratosphere.

3.2.4. Time Resolution

Daily global coverage is necessary for both temperature and wind data to understand stratospheric processes and stratospheric changes. Recent model analyses suggest that 12-hour data coverage provides a significantly better constituent budget calculation.

3.2.5. Measurement Precision and Accuracy

In order to determine trends on a decadal time scale and to identify the cause of the trend, the following requirements for individual observations must be met:

Temperature:	1° Kelvin
Winds:	5 meter per second (each horizontal component)
Geopotential:	150 meters

Measurements should be as accurate as possible. However, precise measurements with instruments that have accurately quantified biases can be used for monitoring purpose.

3.2.6. Very Small Scale Processes

It has become evident that processes of much smaller scale than represented by the previous resolution requirements are important in determining the temperature and constituent distributions in the stratosphere. Gravity wave processes in the mesosphere, for instance, are instrumental in determining the global meridional circulation. Therefore, it is necessary to study the temperature, wind, and constituent fields at a much higher resolution than cited above. MST (Mesosphere, Stratosphere, Troposphere) radars provide essential information on small scale processes and must remain operational. Further studies must be done to define the monitoring needs of small scale processes.

3.3. Measurement Systems

3.3.1. Radiosonde (Rawinsonde)

The radiosonde network is concentrated over land areas and contains a variety of instruments. Currently, worldwide, there are approximately 35 instruments provided by 17 manufacturers (WMO, 1982). Corrections are applied to some and adjustments to others to bring the data from the individual systems to a unified data base. McInturff and Finger, (1968), for instance, argue that adjustments on the order of 5.7° K may be necessary to assure a consistent data set. These adjustments are instrument dependent and are only valid as long as the instruments are invariant.

The past few years have seen a proliferation of radiosonde types in the U.S. Previously one instrument was in general use, but the military has procured different instruments and NWS will be flying more than one instrument type. The variance of instruments worldwide and the need for instrument dependent corrections and adjustments suggest the need for instrument standardizations or the development of a standard comparison instrument.

Radiosondes provide significant land coverage. Ocean coverage is sparse, and there are large regions of the Southern Hemisphere that are virtually void of regular data. The density and the quality of the data decrease rapidly with height. Thomas and Finger (1974) report that only 45 percent of the sondes that reach 100 mb reach 70 mb and less than 15 percent reach 10 mb. Due to cold temperatures, radiosondes ascend into the stratosphere less frequently in the tropics and high latitudes. The best coverage is at middle latitudes in the Northern Hemisphere. This level of performance has probably declined since 1974 due to requirement changes and the use of smaller balloons.

Error estimates for U.S. radiosondes and rawinsondes are given in Meteorological Data Error Estimates (published by the Secretariat, Range Commander's Council, White Sands Missile Range, New Mexico 88002). The errors in the temperature measurement generally are a linear function of height from the surface to 30 km. The errors at the surface are usually a few tenths of a degree with the errors at 30 km somewhat larger than a degree. The wind speed error estimates vary from instrument to instrument, but are generally on the order of 1 to 4 meters per second.

Nash and Schmidlin (1987) showed general consistency with time of data from the same instruments. There is a bias between instruments with the spread of measurements being 0.6° K at 100 mb. This spread increases rapidly with height and may be as high as 3° K at 10 mb. These results suggest that the errors in the stratosphere may be larger than reported above (see Figure 3.2).

Automatic Radiosonde Tracking (ART) stands to produce a better overall data product. Data from the ART system, however, indicate serious changes in geopotential heights between the old and new systems. These discrepancies must be explained and corrected.

The most fundamental problem of the radiosonde data is the limitation of data collection to populated land masses. These limitations are important in the discrepancies reported in radiosonde trend studies in Chapter 14 of WMO (1986). Other problems exist because of the biases between the instruments. Radiosondes have been primarily a device to provide operational information for synoptic weather charts. Recent difficulties in attempts to determine stratospheric trends have motivated research to better characterize the properties of radiosonde errors, corrections, and adjustments. Such research must continue if the past and current data are to be put on a consistent basis.

The radiosondes provide the longest time series of stratospheric temperature and wind data that is useful for trend detection. Therefore, the radiosonde data is the primary data base for trend detection. It is necessary to maintain a high quality effort to obtain stratospheric wind and temperature data from radiosondes. Problems with measurements of pressure are revealed by comparing Figure 3.2b to Figure 3.2a. The radiosonde height and pressure data provide the information necessary for building geopotential height fields from satellite fields. The quality of rocketsonde and satellite data relies on careful, accurate operation of the radiosonde network.

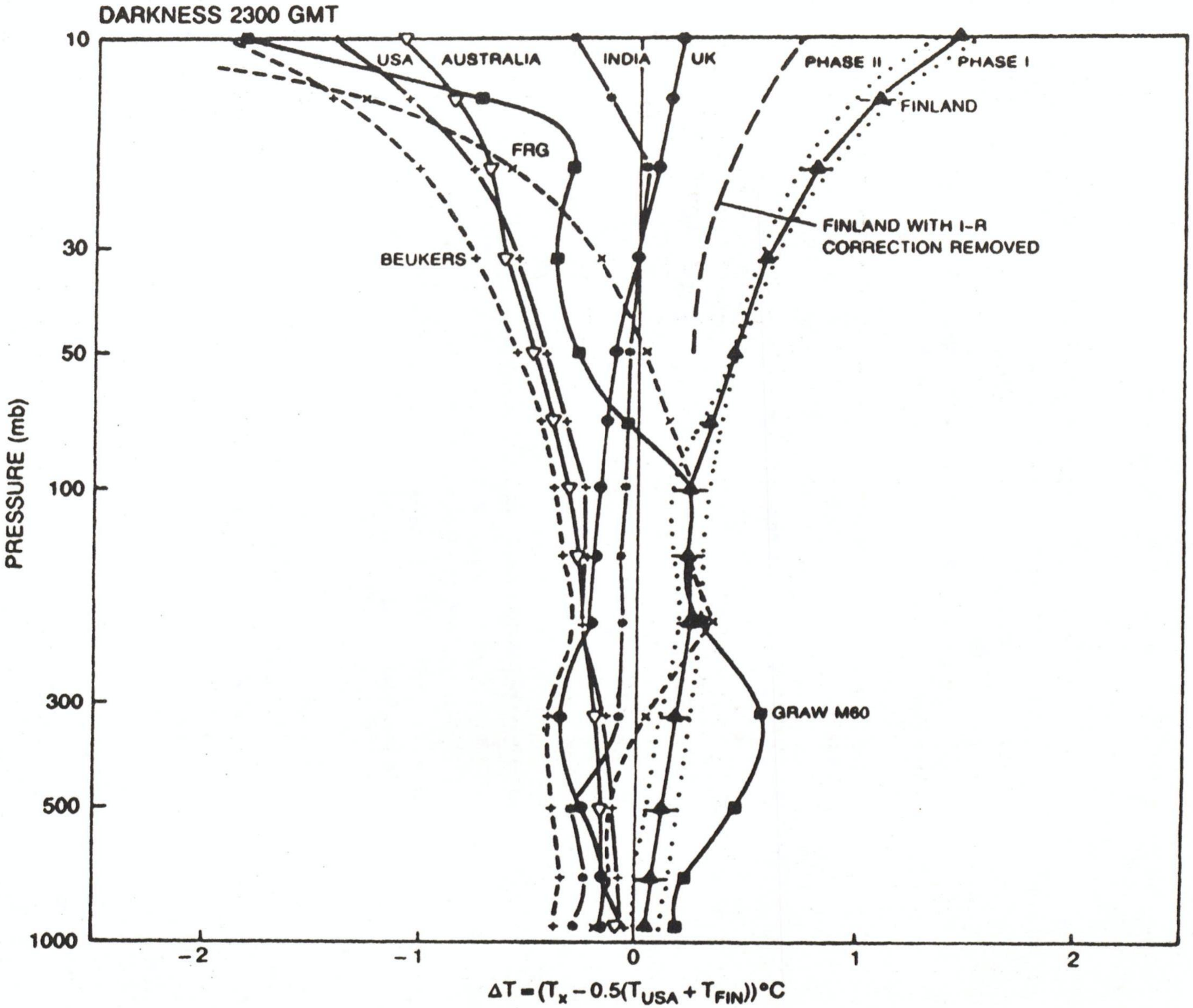


Figure 3.2a
Difference of Rawinsonde Temperatures
by Instrument Type, from Average of
U.S.A. and Finnish Instruments

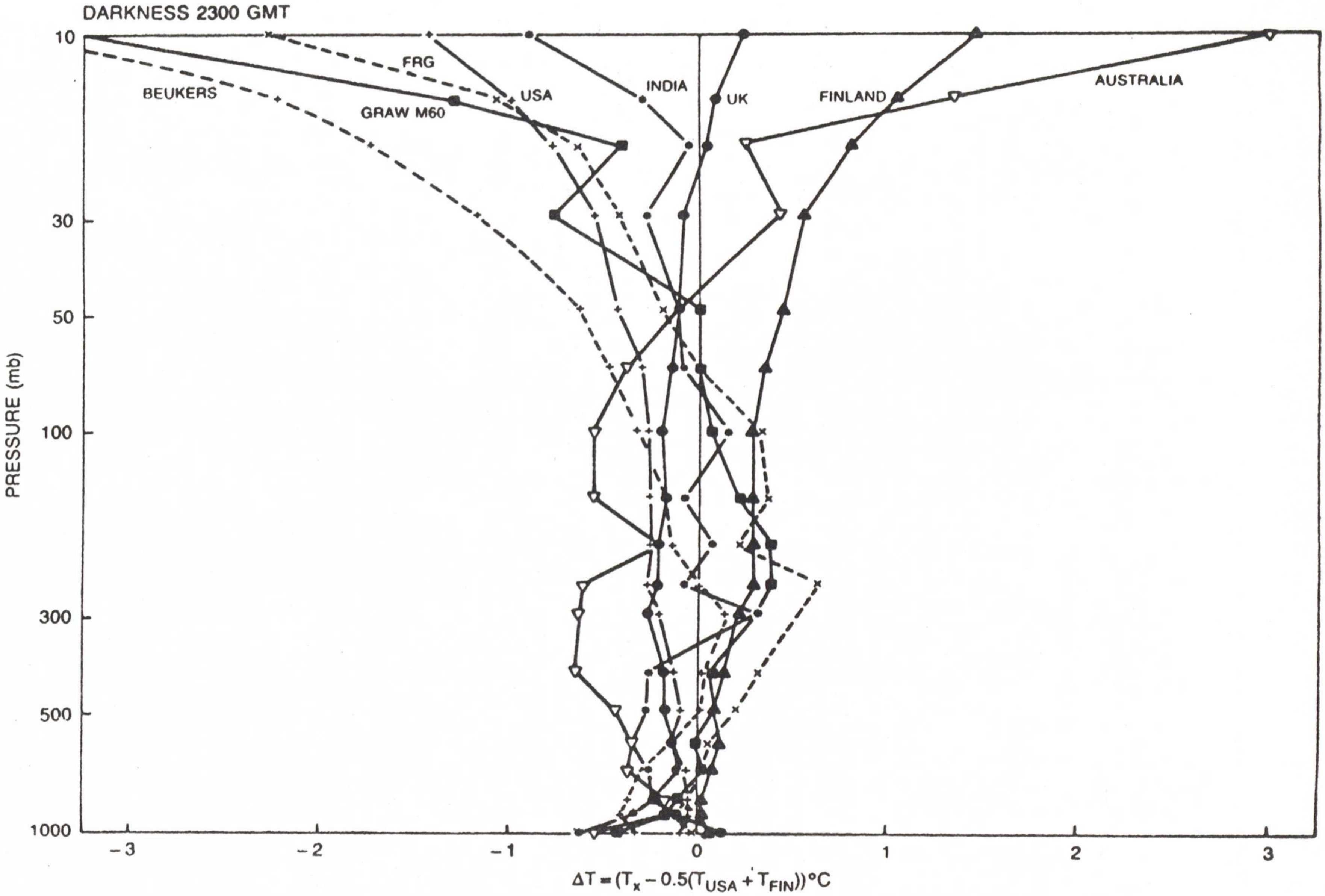

DARKNESS 2300 GMT
PRESSURE (mb)
10
30
50
100
300
500
1000
−3
−2
−1
0
1
2
3
ΔT = (T$_x$ − 0.5(T$_{USA}$ + T$_{FIN}$))°C
FRG
BEUKERS
USA
GRAW M60
INDIA
UK
FINLAND
AUSTRALIA

Figure 3.2b

3.3.2. Rocketsonde

The rocketsonde network routinely provides temperature and wind data in the height range from 25 to 60 km at a small number of stations (See Table 3.1). Soundings are taken approximately once a week. Since 1977 the number of stations in the US has decreased dramatically and the number of observations has dropped from 2000 to less than 500 annually.

Currently, instruments from the U.S. and USSR are in predominant use. Historically many instruments have been used. Comparisons indicate that the different instruments generally agree below 50 km (Finger et al., 1975; Schmidlin et al., 1980). Above 50 km the Russian instrument significantly disagrees with the other instruments. The error estimate of U. S. rocketsonde varies from 0.5° K at 25 km to 3.8° K at 65 km (Schmidlin, 1981). The quality of the rocketsonde data declines above 55 km and the high altitude data must be used cautiously. The lower levels of the rocketsonde flights overlap the upper levels of the radiosonde allowing a direct comparison of the two methods. The two methods generally agree to within 1° K.

The rocketsondes offer a direct measurement of upper stratospheric wind by tracking of the falling payload. The 2 km layer mean wind measurement errors are estimated at 3 meters per second.

The rocketsonde measures temperature as a function of height. The temperature is linked to the standard pressure levels through a supporting radiosonde flight and the hydrostatic equation. Therefore the pressure and temperature are not independent measurements.

The rocketsonde network provides the only operational ground-based system for monitoring upper stratospheric and mesospheric temperatures and winds. The rocketsondes provide the best wind data in the tropical upper stratosphere. The lack of global coverage of the rocketsonde network limits its use to only rudimentary estimates of stratospheric trends.

In Chapter 14 of WMO (1986) changes in rocketsonde instrumentation are cited as the possible cause of a measured stratospheric temperature decline in the early 1970s. Recent reevaluation of this data suggests that the temperature decline may be real. As with the radiosondes, it is necessary to more carefully scrutinize the rocketsonde measurements and error characteristics. Such research should be a priority item of a monitoring plan.

It is critical to maintain and improve the rocketsonde network. The rocketsonde measurements provide the longest upper stratospheric data set. The rocketsonde data are most important in the calibration of satellite temperature data. The satellite data are not of sufficient quality to stand as an independent data set. The loss of the rocketsonde network would severely impact the quality of stratospheric temperature fields that are used not only for monitoring, but for generating an analysis essential for aerospace aircraft operation. The rocketsonde data will prove useful in the future for verifying wind measurements from the UARS satellite.

Table 3.1 Operational Rocketsonde Station (from North to South)

Station	Longitude/Latitude (in degrees)	Type of Instrument
Heiss Island	58E, 80N	USSR
Primrose Lake*	11OW, 55N	US
Volgograd	44E, 48N	USSR
Ryori	141E, 39N	Japanese
Wallops Island	75W, 38N	US
Point Mugu	119W, 34N	US
White Sands**	106W, 32N	US
Cape Canaveral	81W, 28N	US
Barking Sands	160W, 22N	US
Antigua	62W, 17N	US
Kwajalein	168E, 9N	US
Thumba	77E, 8N	USSR
Ascension Island	14W, 9S	US
Molodeznaja	46E, 68S	USSR

Note: The USSR maintains 20 ships with rocketsonde capability. On the order of 5 are generally operational. Several facilities exist with the capability of routine observations. Several facilities take occasional measurements for operational requirements.

* Primrose Lake may be closed in the near future.
** White Sands only takes soundings as needed, not on a routine basis.

3.3.3. LIDAR

Recent developments in LIDAR technology indicate that LIDAR systems can provide an accurate ground-based temperature measurement system for the stratosphere and mesosphere (see Chanin and Hauchecorne, 1987). LIDAR temperature measurements are based on Rayleigh scattering and, therefore, are more accurate above the aerosol layers (25km). Below this level Mie scattering is also important. The Nd-YAG lidar is the closest to being operational and can produce temperature measurements in 1 km layers with an accuracy better than 1° K. LIDAR measurements require clear skies and practicality leads to nighttime measurements. Remsberg (1986) offers a comparison of LIDAR and LIMS temperature.

The LIDAR system must still be considered a research instrument. However, initial results with this system are promising, and LIDAR may, ultimately, be a viable replacement for rocketsonde temperatures. Extensive comparisons with rocketsondes in an operational environment must be performed to characterize the differences between the two methods. LIDAR systems should allow for a more systematic accurate monitoring of upper stratospheric temperature. Wind data are much more difficult to obtain. LIDAR systems require operators with a high level of technical expertise, and station locations are limited to areas with predominantly clear skies (and preferably high altitudes).

3.3.4. Satellite Systems

The current operational global temperature measurement system is the TIROS N Operational Vertical Sounder (TOVS). This sounder consists of the High Resolution Infrared Sounder (HIRS), the Microwave Sounding Unit (MSU), and the Stratospheric Sounding Unit (SSU). The first TOVS was launched in October 1978, and the TOVS instrument will be the operational sounder until the early 1990s. The TOVS system was not originally conceived as a long- term monitoring system. The general level of accuracy that might be expected from the TOVS instrument is given below (from Quiroz and Gelman, 1972):

Pressure	Error Estimate
10 mb	2° K
1 mb	4° K
0.4 mb	6° K

The TOVS instrument is to be replaced by the Advanced Microwave Sounding Unit (AMSU) and the High Resolution Infrared Sounder (HIRS/2) in the early 1990s. These instruments will also be on the proposed Earth Observing System (Eos) polar platform in the mid 1990s. The AMSU would provide the core of the stratospheric data set. The AMSU provides much better vertical resolution in the stratosphere than the TOVS (SSU), but its top channel peaks at about 40 km, which is too low for stratospheric monitoring (Figure 3.3).

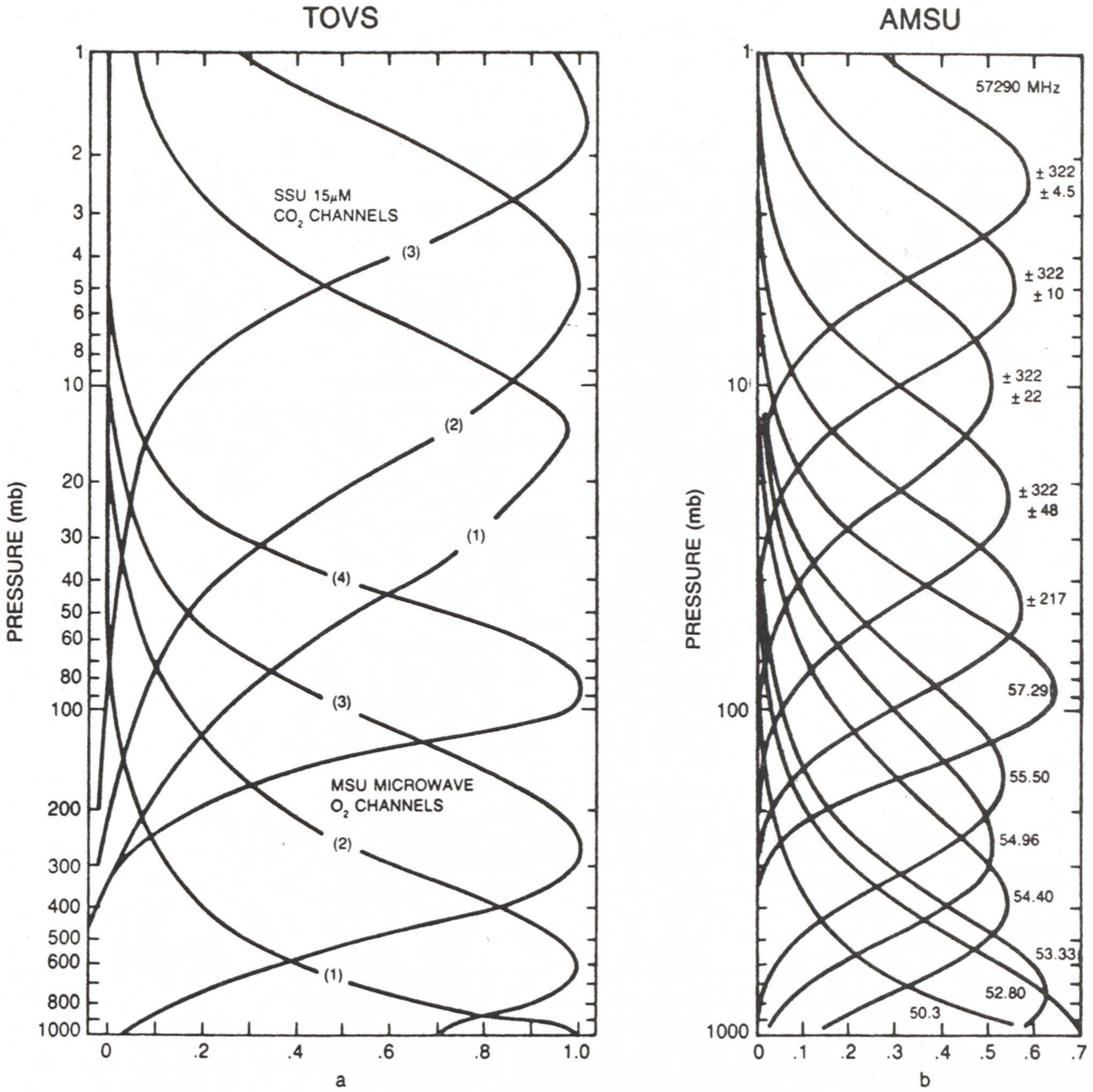


Figure 3.3

Weighting functions for the TIROS N Operational Vertical Sounder (TOVS) and the Advance Microwave Sounding Unit (AMSU)

Plans are to fly GOMR (Global Ozone Monitoring Radiometer) on the Eos Polar Platform. This instrument should provide temperature data of sufficient vertical resolution throughout the stratosphere and mesosphere. The characteristics of this instrument will presumably be similar to LIMS. Because this is not a scanning temperature instrument, the horizontal resolution is limited.

The Upper Atmosphere Research Satellite (UARS) satellite is scheduled to be launched in the early 1990s. The two primary temperature measurements will be made by the limb scanning infrared instruments CLAES (Cryogenic Limb Array Etalon Spectrometer, 18 month lifetime) and ISAMS (Improved Stratospheric and Mesospheric Sounder, mechanical refrigeration). These instruments will provide redundant data for comparison with the operational NOAA system flying at the same time. Together the UARS instruments provide coverage throughout the stratosphere and mesosphere. The UARS project should also provide information for improved designs of future monitoring instruments.

The wind measurement instrument, HRDI (High Resolution Doppler Imager), on UARS is of particular interest. HRDI will measure stratospheric and mesospheric winds with a data void expected in the stratopause region. The success of HRDI will prove the capability of direct wind measurements. Therefore, strategies for developing wind monitoring systems should arise from UARS. Winds from HRDI should provide the first global evaluation of measured stratospheric winds with wind fields derived from satellite temperature and height fields.

The most obvious advantage of the satellite system is daily global coverage with the same instrument. The most obvious disadvantage is the use of complex algorithms to invert the radiance data to temperature profiles. These algorithms have a significant impact on the calculated temperature field. Analysis of consistent radiance data might provide the most accurate use of satellite data.

The greatest failing of satellite systems to date has been the inconsistency of instruments and a lack of planned and rigorous comparison between instruments on different satellites. Therefore step function discontinuities between the data sets are common features that confound attempts to extract temperature trends. These problems are discussed in Chapter 14 of WMO (1986).

3.4. Strategy for Monitoring Meteorology

Both ground-based and space-based measurement systems have been described. Neither ground or space-based systems are capable of standing alone. The monitoring system must consist of a variety of instrument systems complementing each other.

Alone, the ground-based system does not provide enough horizontal or altitude coverage to adequately provide a monitoring system. Errors arise because measurements are primarily limited to land masses and because a variety of nonstandardized instruments are in use. The satellite instruments can provide global coverage with a single instrument, but the long-term behavior of a particular instrument, differences between instruments, and properties of ever changing inversion algorithms, assure that satellite data is not of sufficient quality to independently define a monitoring system.

Even if satellite data could be made of sufficient quality to provide an independent monitoring capability of the stratosphere, another independent data set is needed as verification. The ideal monitoring system would have multiple, totally independent measurements of the same variable.

Furthermore, the ground-based measurements provide a much longer data base than the satellite measurements. Longevity is fundamental to defining natural variability. Therefore it is crucial to maintain ground-based measurements that are consistent with the past as a primary part of any monitoring scenario.

Two levels of performance can be defined for a monitoring network. The first level is the simple detection that a change has taken place. The second level is understanding the causes of the change. The requirements of this plan have been aimed at the second level; not just detection, but understanding.

The proposed temperature and wind instruments for the next decade will not satisfy the requirements of this plan, and do not provide an adequate monitoring system. Global satellite wind measurements have yet to be made, and all of the instruments are currently in the research stage. UARS will fly wind measurement instruments, and by the mid-1990s global monitoring of winds may be possible. Further research into direct wind measurements and the use of stratospheric data assimilation to generate improved winds from temperature observation is needed.

The temperature measurement system stands at a critical point. There is a proliferation of radiosonde types both nationally and internationally could lead to more biases in the data record. The very existence of the rocketsonde network is in question. The LIDAR is not operational to the point of replacing rocketsonde temperature measurements. The current configuration of the AMSU to be launched in 1991 obtains no temperature information above 40 km (a loss of information compared to TOVS). The proposed GOMR system on the proposed Eos platform should provide sufficient vertical resolution, but the horizontal resolution will not be adequate for budget calculations. UARS will provide valuable temperature information, but UARS is not intended as a monitoring device.

If the temperature system is allowed to degrade, then not only our ability to understand but our ability to detect changes is compromised. Two strategies are outlined below. The first is aimed at the existing and planned ground-based and satellite-based instrumentation. This strategy directs itself at obtaining the best data set that can be derived from the current system. This strategy should not only maintain, but improve, the ability to detect stratospheric change. It will supply basic information for understanding change. The second strategy provides an outline of what needs to be done to assure the implementation of a monitoring system that greatly improves the capability of understanding of the cause of any trends.

Fundamental to any rational monitoring plan is research to help define requirements and direction. For meteorological monitoring requirements several basic needs exist. These include: definition of instrument errors, corrections, and adjustments under a complete range of geophysical conditions; the effects of inversion and data reduction algorithms; the effects of assimilation techniques on data sets; and the effects of corrections, adjustments, and statistical technique on trend detection calculations. Further research in these and other areas must be carried out if a proper monitoring network is implemented.

3.4.1. Strategy I, Existing Measurement Systems

The greatest hindrance to temperature trend detection is the inability to assimilate existing data sets into one consistent, long-term data set. In order to assure a consistent data set, overlap is required for all systems. When new instrumentation is implemented, the old and new instruments should be used in an operational sense simultaneously for sufficient time to determine if either the statistics of the two systems vary, or bias exists.

The minimum overlap of two systems should be one year. This tests the performance of the instruments for all conditions of a seasonal cycle. Removal of the annual cycle from the data reveals that a quasibiennial oscillation is prominent in most stratospheric data sets. Therefore a 3-year overlap not only evaluates the performance of new instruments over an important scale of variability, but begins to test drift characteristics.

For satellite systems each successive operational satellite should overlap for at least one year. When a totally new operational system is implemented, not only should there be overlap, but a backup capability with the old operational system should be available in case the new operational system proves flawed.

In order to assure improvement of the current system of wind and temperature measurements, and to assure consistency the following specific recommendations are made:

(1) Radiosondes (and all instruments) should be standardized. This could be achieved by designation of a standard instrument. However, rather than designate a standard instrument, it is better to define standards and test procedures that all radiosondes must meet. Standardization would assure that different radiosondes could be used consistently. Standardization is a call for accuracy and not just precision. An international effort is required.

(2) Operational procedures should be modified to assure that radiosondes reach stratospheric levels more consistently. Field operators need to be aware of the value of stratospheric data. International cooperation is required to assure a global data set.

(3) A subset of the global radiosonde network should be identified as priority stations (homogeneously distributed in latitude and longitude, 40 to 100 stations). These stations should have uniform operation procedures and should be the subject of frequent intercomparisons and calibration with the standards defined in item 1. An international effort is required.

(4) The rocketsonde network should be maintained at sufficient levels to generate meaningful stratospheric temperature and wind statistics. Measurements from tropical, midlatitude, and polar regions of northern and southern hemispheres are needed. The rocketsondes should be located at a subset of the high priority radiosonde stations defined in item (3). Coordination with the proposed NDSC is desirable. The capability of reducing the cost of rocketsondes should be investigated.

(5) LIDAR technology must be developed to an operational state to provide upper stratospheric temperature fields. LIDAR instruments should be placed at rocketsonde stations and the two methods compared. Only when the characteristics of the differences between the two systems are understood can LIDAR temperature measurements be considered a viable replacement for rocketsonde temperature measurements.

(6) The ground-based data must be complemented by satellite data to provide global coverage throughout the stratosphere and mesosphere. Currently only satellite temperature measurements are possible, but UARS should provide a feasibility study of satellite wind measurements.

(7) There must be an overlap of the NOAA satellites to assure that succeeding TOVS and AMSU and HIRS/2 instruments are operating properly and that a consistent time series is formed.

(8) If possible, AMSU should be modified to obtain temperature measurements at 1 mb and above.

(9) There must be at least one year overlap between Eos and the last NOAA satellite.

(10) Campaigns and shuttle experiments must be designed and executed to monitor and understand small scale processes in the stratosphere and mesosphere. Incoherent scatter radars, known as MST (Mesosphere, Stratosphere, Troposphere) radars, must continue to operate to help understand atmospheric mixing processes and to help detect change in small scale processes.

3.4.2. Strategy II, A Dedicated Monitoring System

Strategy I outlines how existing and planned operational systems can be used to increase our ability to detect stratospheric change. This section will outline a dedicated monitoring system to complement the operational instruments. The priority ground stations defined in Strategy I are an essential part of this system.

It is the expressed goal of this document to be able to detect stratospheric change, primarily ozone change, on a decadal time scale. It is also the expressed goal of this document to understand the cause of any measured change, be it natural or anthropogenic.

The measurement systems in current use and designated for implementation were not planned for monitoring purposes. Therefore coordination of the individual components of the system and consistency of the data sets was not a priority. The recent efforts to determine trends reveal the prodigious task of coordinating this system after the fact.

Strategy I, described above, addresses the problem of coordinating the various components of the system during the data gathering process. However, even with coordination, and careful, conscientious implementation, there remain inadequacies that cannot be addressed by the current and proposed instrumentation.

The major failing is insufficient horizontal and vertical resolution. A point of specific weakness is detailed information of temperature and wind fields between the altitudes of 40 and 55 km.

A logical plan would be a dedicated monitoring system. A system directed at the specific needs of stratospheric monitoring. The NDSC and the ground-based system described in Strategy I, numbers 1 through 5, are essential parts of a dedicated system.

Design of a dedicated satellite system requires further research. Of fundamental value is research to characterize the information content and errors that are realized with various satellite sampling scenarios. Accurate instruments, with expected lifetimes of several years, should be designed, and more than one instrument should be in space at any one time. Such a system might be envisioned to have several small satellites in simultaneous operation.

Such a dedicated system is the ideal way to acquire the information necessary for monitoring meteorological parameters of the stratosphere. A study to define such a system should be initiated. Improvements in the current and planned systems should proceed as outlined in Strategy I.

CHAPTER 4. SOLAR ULTRAVIOLET SPECTRAL IRRADIANCE

4.1. Introduction

The need for long-term monitoring of changes in the ultraviolet (UV) solar spectral irradiance in the 175 to 320 nanometer (nm) region is of primary importance because of its role in driving the photochemistry of the middle atmosphere and its influence on dynamical processes through heating. The birth and decay of active regions on the sun result in a variation of the solar irradiance. These active regions persist for several solar rotations resulting in a 27-day modulation of the solar flux as the number of active regions facing the Earth changes. Measurements from the Solar Backscattered Ultraviolet Experiment (SBUV) on the Nimbus-7 satellite have established the magnitude of the 27-day modulation as approximately 6 percent (minimum to maximum) at 200 nm and nearly zero at 300 nm (Heath, et al., 1984). Changes in ozone correlated with this modulation have been detected (Chandra, 1986). During the 11-year sunspot cycle the average number of active regions on the sun increases from the quiet sun value of nearly zero to a maximum and then decreases again to the quiet sun number. The magnitude of the change in the solar irradiance over the 11-year cycle is poorly determined but based on observations by SBUV and SME is probably not much different than the 27-day modulation. If true, this would be considered a negligible change except that it is desired to detect changes in the total column ozone on the order of a few percent per decade (WMO, 1986).

Changes in the solar flux incident upon the atmosphere affect the rate of production and loss of ozone differently in different regions of the spectrum (Keating, 1981). A decrease in the solar UV irradiance in the 180 to 250 nm region results in a decrease in ozone due to: (1) a decrease in the production rate of odd oxygen from the photodissociation of oxygen (0_2), and (2) a decrease in the photolysis of nitrogen oxide (NO_x) compounds with a corresponding increase in the catalytic destruction of ozone (0_3) by nitric oxide (NO). However, a decrease in the 250 to 310 nm region results in a net increase in total 0_3 due to: (1) decreased O(lD) production leading to decreased NO and OH production and thus less 0_3 destruction, and (2) temperature decrease leading to decreased 0_3 destruct ion. With these competing processes, an overall 2 percent decrease in solar flux results in approximately a 1 percent decrease in total ozone (Keating, 1987). This change in ozone mimics the change due to an increase in the concentration of chloroflourocarbons (CFCs) in the stratosphere. Thus, without monitoring the solar ultraviolet (UV) flux, it would not be possible to differentiate between natural and anthropogenic perturbations in the atmosphere.

4.2. Measurement Requirements

It is required that ozone monitoring systems be able to measure a 4 percent change per decade at the 95 percent statistical confidence level at 40 km (WMO, 1986); the altitude at which it is predicted that ozone is more sensitive to catalytic destruction by CFCs. Recent analysis of the relationship between ozone changes in response to 27-day UV solar flux changes indicates that the ratio of the change in UV flux at 205 nm to the change in the ozone concentration at 40 kilometers (km) is 0.4 (Keating, 1987). Thus it is desirable to measure a change in solar irradiance at 205 nm of 1.5 percent per decade at the 95 percent confidence limit. It is emphasized here that it is not necessary to measure the absolute solar flux to this accuracy, only the change.

4.3. Measurement Systems

A list of existing instruments for measuring the solar spectral irradiance is contained in Table 4.1. Currently operating satellite instruments are the Solar Backscattered Ultraviolet Experiment (SBUV) on Nimbus-7, the Solar Spectrometer on SME, and SBUV/2 on NOAA-9. None of these three experiments has a means of determining if its sensitivity has changed while in orbit except via comparison with measurements obtained from rockets or using empirical models to compare observed with predicted changes in the solar flux. Measurements from rocket and balloon-borne platforms have not yet demonstrated that they are capable of an accuracy or precision better than to within 5 percent. Hence, up to the present time it has not been possible to verify either the absolute accuracy of the measurements or the stability of the instruments to within the required accuracy of the ozone monitoring program. Over time scales of several years, the existing data base cannot differentiate between solar induced and chemically induced changes in the ozone layer. Additionally, the Nimbus-7 and SME instruments have operated well past their anticipated lifetimes and may fail within the next several years. Until the beginning of the 1990s, only the SBUV/2 instrument on NOAA-9 can be depended upon to continue to take solar flux measurements. SBUV/2, an improved version of the instrument on Nimbus-7, is one of a series which will be launched on NOAA operational satellites.

Although the SBUV/2 instrument appears to be very stable, improvements in accuracy to the solar flux measurements await the launch of new generation UV instruments. Two of these instruments, one a European Solar Irradiance Experiment (ESIRE) and the other from NRL the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) were successfully flown on Spacelab I and II, respectively. Both these experiments contain in-flight calibration lamps which will improve the precision of the measurements to perhaps a few percent.

The launch of the Upper Atmosphere Research Satellite (UARS) in 1991 will provide the first opportunity to make continuous measurements of the solar UV irradiance with a precision approaching 1.5 percent per decade. UARS will contain a satellite version of the SUSIM instrument and a solar irradiance experiment from the University of Colorado (SOLSTICE). SOLSTICE will obtain an in-flight calibration by observing a sequence of hot UV stars. Continuum emission originating in the photospheres of these hot stars extends below 200 nm and should be very stable.

Periodic measurements of the solar irradiance will also be made using the Space Shuttle as an observing platform. SUSIM and the ESIRE are to be flown on the Atlas Shuttle Pallet starting in 1991. Additionally, one of the SBUV/2 instruments has been modified to fly on the shuttle as an attached payload. This experiment (SSBUV) has a set of on-board calibration lamps and is expected to make observations 1-2 times per year.

4.4. Strategy for Monitoring Ultraviolet Solar Spectral Irradiance

Starting in the 1990s a number of satellite and shuttle borne instruments will be launched which have the potential of measuring changes in the solar irradiance of a few percent per decade. However, all but one of these instruments relies on the accuracy and stability of conventional spectral irradiance sources for their calibrations while in orbit. The absolute error in standard lamps calibrated at the National Bureau of Standards (NBS) is 6 percent at 200 nm, 2.5 percent

Table 4.1 Currently Operating and Future Solar Irradiance Experiments

Experiment	Platform	Dates of Operation	Wavelength Range (nm)	Remarks
SBUV	Nimbus 7	Nov. 7, 1978 to present	160-140	Probably nearing end of operation.
SME	SME	Oct. 11, 1981 to present	120-305	Probably nearing end of operation.
SBUV/2	NOAA 9	March 12, 1985 to present	160-400	Appears to be stable.
SBUV/2	NOAA 10	Continuation of NOAA 9	160-400	Continuation of series.
SUSIM	UARS	1991 Launch	115-400	Has on-board calibration lamps.
SOLSTICE	UARS	1991 Launch	115-400	Uses UV stars for in-flight calibration.
SSBUV	Shuttle	1989 Launch	160-400	Shuttle version of SBUV/2. Has on-board calibration lamps.
SUSIM	Shuttle	1991 Launch	115-400	Successfully flown on Spacelab-2. Has on-board calibration lamps.
ESIRE	Shuttle	1991 Launch	200-358	Successfully flown on Spacelab-1. Has on-board calibration lamps.
GSFC	Rocket	1/year	150-340	Yearly observations since 1978.

at 250 nm, and decreases to 1.7 percent at 350 nm. Clearly this does not meet the requirements of this program. Prelaunch calibrations of SUSIM and SOLSTICE are obtained using the NBS electron synchrotron facility (SURF). When the utmost care is used, the uncertainty in the photon flux from this source is 0.7 percent. Calibration of satellite and shuttle borne instruments should be carried out at SURF. A program should be undertaken by NBS for improving the accuracy of conventional light sources and developing new ones.

No satellite instrument can be expected to maintain its calibration to within 1 percent over a 10-year period. Periodic measurements, preferably from the shuttle, are necessary to validate the satellite measurements. The GSFC SSBUV experiment is particularly well suited to this task since it is scheduled to be flown 1 to 2 times per year over the next decade in a very well controlled environment. Because of the extreme accuracy which is required, measurements should be made using several instruments with periodic reviews of agreements and disagreements among the observations. Data from these measurements must be made available for comparison in a timely manner so that differences between data sets can be analyzed. Special emphasis should be placed on maintaining continuity in the long-term record and phasing in new measurement techniques as they become available. When phasing in new measurement systems, the period of overlap should be sufficiently long, preferably several years, to allow comparison of both the absolute value of the solar spectral irradiance and the accuracy of the trend determined by various systems.

Because of the limited data base which exists for determining the long-term variability of the sun, a number of models have been devised which attempt to correlate parameters observable from the Earth's surface, such as the 10.7 cm radio flux, with changes in the UV spectral irradiance. Although there has been some success in this direction, the accuracy is limited. A more promising model involves the measurement of the line profile of the Mg II line at 280 nm by satellite instruments (Heath and Schlesinger, 1986). The emission at the center of this line originates above the solar surface while emission in the adjacent wings originates in the photosphere. Studies of data from SBUV on Nimbus-7 have shown that the ratio of the variation at the center of this line to that in the wings is correlated with the 27-day modulation of the UV flux at shorter wavelengths, more specifically, below the Al-I absorption edge at 220 nm. Such a ratio of fluxes at closely spaced wavelengths is quite insensitive to drifts in instrument sensitivity. Hence, it may be possible to use this line to monitor the ratio of the flux at 220 nm to the flux at 280 nm with high accuracy over time scales of decades. Measurements of this ratio need to be continued to demonstrate the accuracy of this technique over longer time scales.

In order to assess the biological effect of increased exposure to solar radiation, a network of ground-based instruments measuring the amount of UV radiation reaching the Earth's surface should be established. The "bottom line" of the ozone monitoring program is to determine if the amount of harmful UV radiation reaching the Earth's surface is changing and this would provide a direct measurement of this parameter. Such a network would also provide information as to how changes to the atmosphere, aerosol concentrations or global cloud cover for example, affect its transmission. These surface based instruments should have a spectral resolution of 5 nm within the UVB range. As these measurements will be affected by purely local atmospheric conditions as well as changes in the solar irradiance and column ozone, to interpret the data it will be necessary to monitor a wide variety of parameters. This network should be supported for long periods of time, i.e., two or more solar cycles. Correlation between these measurements and stratospheric ozone measurements is desirable.

Measuring the solar UV spectral irradiance with an accuracy of 1 percent per decade will clearly call for an improvement in the state of the art. Currently operating instruments are capable of making measurements which are accurate to within 5 to 10 percent. The next generation of instrument, expected to be launched at the beginning of the next decade, will improve this accuracy but it remains to be determined by how much. Reaching the goal set by the ozone monitoring program may require the development of more accurate and stable calibration light sources.

CHAPTER 5. SOURCE GASES

5.1. Introduction

"Source gases" refers to gases that originate in the troposphere and are transported into the stratosphere where they participate in photochemical reactions related to ozone destruction and/or contribute to modifications of climate that feed back to ozone chemistry and dynamics. These gases may be: (1) direct sources of stratospheric ozone modification; (2) participants in photochemical cycles in the stratosphere affecting ozone indirectly; (3) trace species active in climate perturbation; (4) tropospherically reactive gases and transients that affect stratospheric source strength and lifetime, (i.e., troposphere-to-stratosphere transfer rates). A given trace constituent may fall into several of these categories. For example, tropospheric ozone is a greenhouse gas and is also the source of the OH radical, a transient that determines the lifetimes of many stratospherically active gases.

Ambient levels of a number of source gases have been changing over the past decade. These changes have received considerable attention in the literature and their links to stratospheric ozone change are reviewed in Atmospheric Ozone: 1985 (Chapter 3) (WMO No. 16, 1986). Tropospheric chemistry associated with source gas perturbations is described in the same volume (Chapter 4). The reader is referred to (WMO, 1986) for an introduction to the complex nature of perturbed tropospheric chemical cycles and their connection to stratospheric ozone.

This chapter reviews the current status of source gas monitoring by: (1) identifying the most important species and explaining their role in stratospheric change; (2) describing measurement techniques and monitoring strategies in general; (3) recommending a monitoring strategy for each source gas. Many specific recommendations are based on a recent document, "Global Tropospheric Chemistry: Plans for the US Research Effort" (Chapter 3) (UCAR, 1986). For brevity, we highlight only major points of that report.

5.2. Measurement Requirements

The practical criterion for a monitoring Plan for longer-lived source gases ($C0_2$, CFCs, N_20, CH_4, etc.) is to have accurate and precise measurements sufficient to detect sudden and/or subtle changes in current trends. This is underway and recommendations build on existing techniques, strategies and programs. Areas for improved standardization, intercalibration, frequency and geographical coverage, are noted.

For source gases of shorter lifetime and more variable occurrence (CO, NO, $N0_2$, ozone, nonmethane hydrocarbons) monitoring is best achieved by combined ground and satellite-borne instruments, the latter not yet available for routine remote sensing of the troposphere. Priority is given to development of a better climatology from ground-based networks. A realistic Plan for the next decade calls for deployment of a satellite sensor for CO (and possibly $N0_2$) and definition of a good climatology for tropospheric ozone, NO_x, and CO. The latter can be accomplished partly by regular measurements at new and existing monitoring sites, but it will also rely on basic research efforts, both experimental and theoretical, that are directed towards understanding biogeochemical cycles of odd nitrogen, carbon, and sulfur. Even if an "ideal" ground and satellite monitoring strategy existed, measurements would be meaningless without appropriate interpretive modeling and a better knowledge of chemical budgets and transformation processes than we have at present. A review of biogeochemical cycles appears in the volume: "Global Tropospheric Chemistry: A Plan for Action" (NRC, 1984).

In the previous National Plan for Stratospheric Monitoring Report (NOAA, 1982) and in a 1986 NASA Workshop Report on Detection of Ozone Changes in the Stratosphere (NASA, 1986), the list of source gases is limited to four Cl-containing 0_3 perturbers: CFC-11, CFC-12, $CH3CCl_3$, and CCl_4. These are recognized as primary substances released in the lower atmosphere which, transported unchanged to the stratosphere, photolyze to reactive chlorine (Cl, ClO), destroying ozone:

$$\mathrm{Cl} + 0_3 \text{ -> } \mathrm{ClO} + 0_2$$

$$\mathrm{ClO} + 0 \text{ -> } \mathrm{Cl} + 0_2$$

$$\overline{\qquad\qquad\qquad\qquad}$$

$$0_3 + 0 \text{ -> } 20_2$$

Other gases can destroy ozone in similar cycles. Brominated halocarbons release bromine radicals in the stratosphere and destroy ozone in the same way as CFCs. NO and $N0_2$, with NO produced by reaction of electronically excited oxygen atoms (O(lD)) with N_20, (a substance emitted from a variety of natural and anthropogenic processes), also destroy ozone catalytically. Atmospheric concentrations of N_20 are increasing steadily and may be contributing to stratospheric ozone change. NO may be injected directly into the lower stratosphere in large amounts by jet aircraft.

Other gases are connected to stratospheric ozone change less directly. For example, methane (CH_4) is a major source of stratospheric water vapor and odd hydrogen; CH_4 also reacts with reactive chlorine to prevent ozone destruction. Model predictions of future ozone depletion are critically sensitive to projected levels of atmospheric methane (WMO, 1986). Methane has been increasing 1 percent per year over the past decade and appears to have more than doubled since 1800. This increase may be caused by increasing methane emissions or by an increased methane lifetime due to decreasing OH (Khalil and Rasmussen, 1985; Thompson and Cicerone, 1986).

Trace gases that affect climate are related to stratospheric 0_3 change because of the interaction of stratospheric temperature, ozone, and dynamics. Besides $C0_2$, long recognized for its critical part in climate control, radiatively important trace gases include CH_4. N_20, CFCs, tropospheric ozone and stratospheric water vapor. These species, when their effects on radiative forcing are added together, could contribute as much to temperature perturbation over the next century as $C0_2$ alone (Wang, et al., 1976; Ramanathan, et al., 1985).

Perturbations in some source gases may be connected to a complex set of photochemical changes in the troposphere. For example, increases in NO_x. nonmethane hydrocarbons (NMHC), CO, and tropospheric 0_3 and decreasing levels of OH may all affect methane levels. Ideally one wants to monitor all these species.

A list of source gases appears in Table 5.1, along with a summary of their atmospheric role and recent observations. These are arranged by "family," with halogens first, then N, C, 0, and sulfur gases following.

5.3. Measurement Systems

This section reviews the way that monitoring is approached for a given source gas. An instrument and sampling technique must be chosen and locations must be selected to meet the goals of determining the extent and magnitude of change. Ideally, one would like the high-frequency global coverage provided by satellites. Unfortunately, cloud coverage and water vapor limit the ability of current, mostly "passive," remote sensing techniques to monitor the troposphere, except for a few species (NASA, 1987). Satellite monitoring may also be prohibitively expensive. Thus, to follow trace gas trends in the troposphere, in situ methods are usually used, limited in spatial and temporal coverage. For gases with lifetimes of more than a year or so, this is adequate provided monitoring sites are well chosen. Of course, even when remote sensing is available to track shorter-lived source gases, there is always a need for ground stations and a network of vertical sounding sites for calibration of satellite-borne instruments and algorithms. This has become clear from experience in satellite monitoring of ozone (See Chapter 2).

5.3.1. Instruments and Collection Techniques

Generally speaking, instruments used to monitor trace gases are of two types: highly specialized instruments developed for one particular application (e.g. a single species in a given range of concentration at a prescribed measurement frequency); instruments that scan absorption/emission spectra or physically separate compounds to measure a number of species. Both types appear on the list of measurement methods presented in Table 5.2.

Operational and collection methods vary. Some instruments operate continuously with "instantaneous" sampling or with short integration periods to collect adequate sample size. Some methods work at the ground and can also be used on aircraft or balloons for vertical profiles. Spectrograms have been used as historic archives to recover concentrations of selected species at earlier times (Rinsland, et al., 1985). Gas chromatography is well suited to analysis of "grab samples" brought from field to lab and chromatographs can be intercalibrated with suitable standards.

In choosing a method for monitoring a particular gas. one must consider potential interferences, ease of calibration, stability of calibration standards, and instrument stability, especially for instruments that are used at remote observing sites for long periods of time with limited maintenance available. Because of cost and maintenance requirements commercially available instruments are desirable for deployment at multiple sites.

5.3.2. Monitoring Strategies - General Considerations

(1) For Long-Lived Gases

Factors to consider in devising measurement requirements for a trace gas are listed in Table 5.3. For a given species, several factors influence choice of technique and monitoring strategy.

TABLE 5.1 SOURCE GASES and SUMMARY OF TRENDS

GAS	ATMOSPHERIC SIGNIFICANCE	TREND	REFERENCES
CFCs	greenhouse gas; UV photolysis in stratosphere catalyzes ozone loss		
CFC-11 ($CFCl_3$)		increasing 6%/yr (1978-1983)	(Cunnold, et al., 1983a; WMO, 1986; Rasmussen and Khalil, 1986)
CFC-12 (CF_2Cl_2)		increasing 6%/yr (1978-1983)	(Cunnold, et al., 1983b; WMO, 1986)
CH_3CCl_3		increasing 4-8% yr (1978-1984)	(Prinn, et al., 1983b; WMO, 1986)
CCl_4		increasing 1%/yr (1978-1984)	(Simmonds, et al., 1983; WMO, 1986)
CFC-113 (CCl_2FCClF_2)		increasing 10-13%/yr	(Khalil and Rasmussen, 1986)
Halons	greenhouse gases; UV photolysis in stratosphere catalyzes ozone loss		
$CBrClF_2$ (Halon 1211) CF_3Br (Halon 1301)		increasing rapidly - monitoring in initial phase	(Khalil and Rasmussen, 1985)
		(TABLE 5.1, CONTINUED)	
N_2O	greenhouse gas;	increasing 0.2%/yr,	(Weiss, 1981; Khalil and

	source of stratospheric NO_x	1977-1980; more in Northern Hemis. than So. Hemis.	Rasmussen, 1983)
NO_x	reacts w/O_3 and ClO_3 in stratosphere from jet aircraft	combustion source reaches stratosphere (?); direct injection	
CH_4	greenhouse gas; modulates tropospheric CO, OH, ozone, source of stratospheric H_2O	doubled since 1700-1800; increasing 1-1.5%/yr since 1950	(Craig and Chou, 1982; Rasmussen and Khalil, 1981; Blake, et al., 1982; Rinsland et al., 1985; Steele, et al., 1987)
C_2H_6 (& other NMHC)	greenhouse gas; natural & anthropogenic sources	increased from 1951-1985; tracks OH	(Rinsland and Levine, 1986)
CO	modulates tropospheric OH, atmospheric lifetime	increasing (?)	(Khalil and Rasmussen, 1984; Rinsland and Levine, 1985)
CO_2	greenhouse gas	increasing since 1700's	(Keeling, 1983; Gammon et al, 1985)
Tropospheric Ozone	greenhouse gas source of OH, controls atmos. lifetime	product of photochemical smog and biomass burning; may be increasing	(Logan, 1985; GMCC, 1985; Oltmans and Komhyr, 1986)
COS,DMS (dimethyl sulfide)	source of stratospheric sulfate aerosols; affects radiation budget.		(Charlson, et al., 1987)

TABLE 5.2 TECHNIQUES FOR SOURCE GAS MEASUREMENT

A. SPECTROSCOPIC TECHNIQUES

1. ultraviolet, visible, infrared, (UV, ir)

2. in situ, total column or local

3. Method of choice for:
   $C0_2$ (non-dispersive ir)
   0_3: Dobson spectrophotometer (total ozone column; 0_3 profiles by Umkehr effect) and differential absorption via LIDAR NMHC, NO_x; numerous species can be characterized spectroscopically and quantified after the fact -- historical record

4. Advantage: suitable for automated, in situ detection archival record in the case of UV, ir plates

5. Disadvantages: identification and quantification of desired constituent subject to interferences; Dobson calibration difficult; Umkehr affected by aerosols

B. CHROMATOGRAPHIC

Gas chromatography: detection by electron capture (GC-EC), flame ionization (GC-FID), or flame photometric detection (GC-FPD)

Versatile - application for many species; commercially available instruments readily deployed in field; can be intercalibrated by reference standard

Method of choice for:

> N_20, Halocarbons, CO, CH_4 and other hydrocarbons; COS, H_2S Adaptable for in situ monitoring or laboratory analysis of grab, stored samples. Lab. analysis -- for intercalibration, species confirmation by mass spectrometry

C. REACTIVE CHEMICAL METHODS

Chemical reaction transforms species of interest to the detected species; Sometimes only practical choice for shorter-lived, more reactive species.

Ozone - electrochemical concentration cell (ECC); CO - HgO detector

Table 5.3 CONSIDERATIONS FOR A MONITORING STRATEGY

Lifetime of Species -

Long-lived (>1 yr): CO_2, N_2O, CH_4
Moderately long-lived (weeks -- months): C_2H_6, C_2H_2, CO
Moderately short-lived (hours -- weeks): HNO_3, H_2O_2, isoprene
Transient (secs - hr): NO, OH, NO_2

Nature of Sources

Few, many
Large regions (e.g. oceans, tropical jungles)/smaller regions (urban areas, volcanoes)

Temporal Characteristics

Long-term trends
Interannual variability
Seasonal behavior
Diurnal variability
Annual
Synoptic
High variance

Lifetime and physical/chemical stability of the species are chief considerations. In general, the longer-lived the gas, the sparser the coverage required for determining background values. For example, for gases with lifetime greater than 3 years there is nearly uniform global distribution, except for a small gradient between Northern and Southern Hemispheres and enhanced values near high source regions; monitoring is usually adequate at two or four sites in a semi-hemispheric mode.

Besides species lifetime, choice of a monitoring network (locations and amount of coverage) depends on source regime for the gas in question -- distance from source to site -- and the type of information sought.

This is illustrated by carbon dioxide ($C0_2$), which has been monitored for the past thirty years. Two basic strategies evolved in response to different needs: a low density network with frequent measurements, and a high density network with infrequent measurements. The low density network (NOAA/GMCC Program) was patterned after the work of C. D. Keeling and co-workers at Mauna Loa, Hawaii. It consists of four remote locations to monitor long-term trends in baseline concentration (Table 5.4). Continuous measurement at these observing stations enables detection not only of long-term global trends, but collection of data on interannual variations, annual cycles, seasonal and diurnal behavior, and response to synoptic events. These are as important for understanding $C0_2$ and the global carbon budget as the long-term increase.

The low frequency-high density strategy for measuring long-lived gases is illustrated by grab sampling at NOAA's 26-station $C0_2$ "flask network" (Figure 5.1; GMCC, 1985). This approach to monitoring was adopted to determine vertical and horizontal $C0_2$ distribution and transport patterns near regional sources, to establish source/receptor relationships and to facilitate interpretation and ultimately prediction of long-term CO behavior. Methane is also being sampled at the $C0_2$ flask network.

A second major U.S. network for tracking long-lived gases which are amenable to high frequency measurement by automated in situ techniques is the ALE (Atmospheric Lifetime Experiment) -- now GAGE (Global Aerosols and Gases Experiment). The ALE began monitoring four chlorocarbons and N_20 in 1977. (Prinn, et al., 1983; Cunnold, et al., 1983). At GAGE sites the air is nearly always marine. GMCC and GAGE sites are also used for grab sampling -- whole air is collected for laboratory analysis -- and some flasks are kept for long-term storage, forming a vital archive. A third US network is run by Rasmussen and Khalil of the Oregon Graduate Center (OGC). Flask sampling of 10-30 gases has been conducted since 1978-79. Currently operating stations are listed in Table 5.4.

(2) For Shorter-Lived Species

Monitoring gases of shorter lifetime (few days to few months) poses special problems. Temporal and spatial variability are tremendous and remote sites may be too far from sources to allow detection of long-term trends. On the other hand, closer to sources there is so much day-to-day variability that detection of trends above natural noise is almost impossible.

TABLE 5.4 Remote Baseline Stations for US-based Monitoring Programs (Continuous Sampling)

ALE - GAGE NETWORK MONITORING SITES

Adrigole, Ireland (52 N, 10 W) to 1983
Macehead, Ireland (53 N, 9 W) since 1987
Cape Meares, Oregon, US (45 N, 124 W)
Ragged Point, Barbados (13 N, 59 W)
Point Matatula, American Samoa (14 S, 171 W)
Cape Grim, Tasmania (41 S, 145 E)
Species measured: CCl_4, CF_2Cl_2, $CFCl_3$, CH_3CCl_3, N_20, CH_4
CCl_2FCClF_2 (since 1985) (consistency with use of formulas)

NOAA - GMCC SITES

Point Barrow, Alaska (71 N, 157 W)
Mauna Loa, Hawaii (20 N, 155 W)
Point Matatula, American Samoa (14 S, 171 W)
South Pole - Amundsen.Scott Station (90 S, 25 W)

Species measured: $C0_2$, CH_4, 0_3 (continuous surface, total column), CCl_4, CF_2Cl_2, $CFCl_3$, CH_3CCl_3, N_20
Condensation nuclei, aerosols (inferred from nephelometer) UV (direct beam and global downward directed flux) Stratospheric water vapor (monthly at Boulder)
Species being added: CO, $CHClF_2$(CFC-22), $C_2Cl_2F_4$(CFC-114), CH_3Br, etc.

Point Barrow, Alaska (71 N, 157 W)
Cape Meares, Oregon (now in GAGE)
Mauna Loa, Hawaii (20 N, 155 W)
Cape Kumukahi, Hawaii (19.5 N, 155 W)
Point Matatula, American Samoa (14 S, 171 W)
Cape Grim, Tasmania (41 S, 145 E)
South Pole - Amundsen - Scott Station (90 S, 25 W)

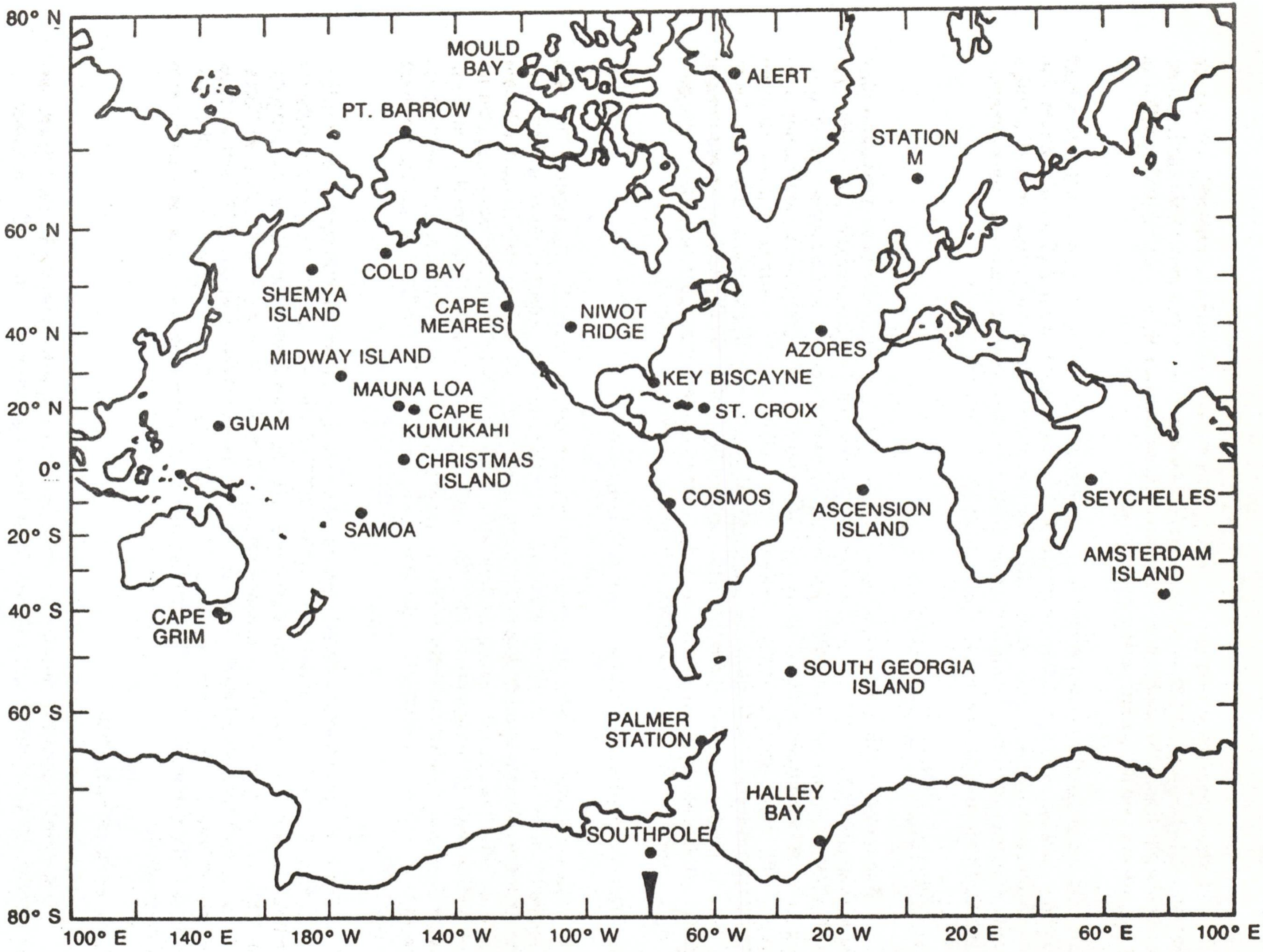


Figure 5.1 (GMCC, 1985)

Locations of NOAA's 26-station carbon dioxide "flask network"

In this category are tropospheric ozone, nonmethane hydrocarbons (NMHC) and carbon monoxide (CO) -- gases critical in controlling the abundance of tropospheric OH, which in turn determines the tropospheric lifetime (rate of troposphere-to-stratosphere transfer) of CH_3CCl_3 and other carbon compounds with reactive hydrogens.

In one sense it is a research problem to determine the number, frequency, and accuracy of soundings that are required to evaluate variability of species like ozone and CO and to determine the magnitude of any long-term trend. This Plan assumes that a suitably dense network of high frequency measurements can define a climatology for these species and indicate possible trends as in the CO study at Cape Meares, Oregon, (Khalil and Rasmussen, 1984).

5.4. Strategy for Monitoring Source Gases

This section summarizes present status of monitoring for principal source gases and makes recommendations based on: (1) current technology and instrumentation; (2) monitoring requirements and available networks; (3) potential for satellite remote sensing where appropriate. In general, recommendations build on existing strategies because these have proved adequate to measure long-term trends for most long-lived gases. Many specific recommendations echo the UCAR (1986) Report, which should be consulted for details. Other pertinent documents include: (1) a list of instruments and research aircraft (Chapter 9 of (NRC, 1984)); (2) space-borne remote sensing instrumentation (current and projected, with measurement requirements for each trace gas) (NASA, 1987). A summary of the recommendations appears in Table 5.5.

5.4.1. Chloro- and Bromo- Fluorocarbons (CFCs and BrFCs)

Measurement techniques and monitoring strategies for most chlorofluoro-carbons (CFC) and grominated fluorocarbons (trade name Halons) are sufficiently developed to detect trends. For CFC ALE/GAGE sites operate essentially continuously and GMCC flask samples are collected weekly at GMCC sites and analyzed in Boulder by NOAA. GMCC sites are being upgraded to continuous operation. Standards for CFC flask analysis at NOAA/GMCC are based currently on Oregon Graduate Center standards, giving a network of nine baseline stations for halocarbons. Independent (but cross-compared) standards are being developed at GMCC. Halons are measured at OGC sites.

Recommended additions and refinements to current halocarbon monitoring include: addition of $CC1_2FCClF_2$ (CFC-113) and $CHClF_2$ (CFC-22) and the Halons $CBrClF_2$ and CF_3Br to monitored species; addition of a mid-Northern Pacific site downwind of Eurasian sources; regular measurements along ship tracks to examine certain circulation features (UCAR, 1986; see Table 5.5). In addition to ground-based measurements vertical profiles determined by GC-MS analysis of balloon-collected samples (Fabian, et al., 1981; Lal, et al., 1985; Gallagher, et al., 1983) are needed on a regular basis. These show CFC accumulation in the troposphere and penetration into the stratosphere.

5.4.2. Carbon Dioxide ($C0_2$)

The global monitoring network that has been following atmospheric $C0_2$ for 30 years has been very successful in determining where $C0_2$ is increasing and at what rate. Recommended

TABLE 5.5 RECOMMENDATIONS FOR SOURCE GAS MONITORING*

Halocarbons

- Continue GMCC / GAGE (baseline) measurements: CFC-11, CFC-12, CH_3CCl_3, CCl_4
- Add: CFC-113 (GAGE), Halons -- $CBrClF_2$ (Halon 1211), CF_3Br (Halon 1301)
- Add sampling site in Northern Pacific downwind of European and Asian source regions
- Conduct regular measurements along ship tracks
- Regular vertical profiles from baseline stations
- Re-activation of GAGE cooperative site in Adrigole, Ireland (underway)

Carbon Dioxide (CO_2)

- Add flask sampling sites to current network in mid-latitude northern and southern low latitudes
- Expand NOAA/GMCC program for measurement of C isotopic abundances
- Fill in any calibration gaps in global networks
- Add regular vertical profiling to baseline sites to determine tropospheric abundance

Methane (CH_4) & Nitrous Oxide (N_2O)

- Upgrade measurements to continuous at baseline (GMCC) sites (**)
- Improve intercalibration and network comparisons
- Increase frequency of measurements at CO_2-flask-type sites (***) for better definition of seasonal and interannual trends
- Collect vertical profiles regularly at flask-type sites

(Table 5.5 continued)

- Make isotopic C and N measurements routine part of flask analysis from baseline and flask-type sites

Methyl Chloroform (CH_3CCl_3)

- Increase frequency of sampling at flask-type sites
- Take vertical profiles of $CHCCl_3$ at GMCC baseline sites and as many flask sites as possible

Carbonyl Sulfide (COS)

- Monitor COS at baseline (GMCC and/or GAGE) stations

Carbon Monoxide (CO)

- Continuous CO measurements needed at GMCC and/or GAGE sites especially in Northern Hemisphere
- Upgrade intercalibration and intercomparison of instruments and standards
- Regular vertical profiles are needed to determine seasonal behavior; should be simultaneous with ozone profiling
- Increase extent of flask sampling network for global mapping
- Reconfigure and deploy MAPS CO instrument for satellite operation

Tropospheric Ozone

- Resolve instrumental discrepancies to aid in identification of trends in existing data
- Make daily vertical soundings at baseline stations where continuous surface measurements are taken
- Take more regular vertical soundings at WMO ozone network sites to define tropospheric ozone climatology
- Make better analysis of current ozone data bases to look for trends

(Table 5.5 continued)

Nonmethane Hydrocarbons (NMHC)

- Incorporate ethane and propane measurements into flask-sample analysis from baseline stations
- Improve standardization and intercalibration among sampling groups for light hydrocarbons

Aerosols and Precipitation

- Exploit precipitation networks (NADP, GPCP) as monitoring sites for $HN0_3$ and organic acids
- Upgrade precipitation monitoring sites to event sampling to separate wet and dry deposition
- Analyze and coordinate existing network data for determination of seasonal patterns and detection of trends

Nitrogen Oxides (NO_x)

- Make routine NO_y measurements at more flask-type and baseline sites
- Make vertical soundings for PAN and NO_y
- Develop space-borne remote sensor for tropospheric $N0_2$

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* Most of these are compiled from Chapter 3, (UCAR, 1986)

** Baseline or high frequency-low density sites (NOAA/GMCC and ALE/GAGE prototypes) are designated TYPE I in (UCAR, 1986) Report

*** Flask-type or low frequency-high density sites (GMCC $C0_2$-flask network prototype) are designated TYPE II in (UCAR, 1986) Report improvements (Table 5.5) include: increasing measurements of isotopic abundances; maintaining a high.quality calibration laboratory; regular measurement of vertical profiles to determine tropospheric abundances.

The success of $C0_2$ monitoring illustrates the point that it is critical to have several independent, but interacting networks operating. Although this is costly, it is the only way to maximize absolute accuracy and to assure continuity, quality and impartiality in determination of trends. For example, GMCC, OGC, and GAGE networks are intercompared at Samoa. It is too costly to do this for all source gases, but for a few key constituents (e.g. CFCs, $C0_2$) with long records and globally distributed sources, the multi.network approach is warranted.

The monitoring history of $C0_2$ also raises the issue that monitoring is only one part of understanding what is happening to atmospheric $C0_2$. For a trace gas with a complex biogeochemical cycle, measurements obtained from a monitoring network go hand in hand with modeling (DOE, 1986) and with research to determine fluxes of $C0_2$ from one carbon reservoir to another (e.g. in the recent GTE/ABLE missions).

5.4.3. Nitrous Oxide (N_20) and Methane (CH_4)

The lifetime of N_20 is much greater than that of methane, but monitoring approaches for these two gases are similar. Sampling at most GMCC sites is by flask. Upgrading to continuous sampling is in progress for methane, where it is needed to study seasonal variability and possible interannual variation. There may be indications of differing Northern Hemisphere-Southern Hemisphere rates of increase, or a slowing down in the rate of CH_4 increase (GMCC, 1985). Since the magnitude and causes of methane increase are somewhat uncertain (it may be due to an increase in CH_4 sources, loss of atmospheric OH or both), it is important to monitor CH_4 behavior with as much temporal detail as possible. An additional recommendation for CH_4 and N_20 (Table 5.5) is improvement of intercalibration and network comparisons; the standards accuracy achieved in $C0_2$ monitoring should be attainable for these two gases. These gases are too critical to possible climate and ozone change to not know the magnitude of long-term increases, and interannual and seasonal variations.

The isotopic composition of N in N_20 and C in CH_4 at baseline sites is recommended. This information, along with knowledge of isotopic origin of various CH_4 and N_20 sources, is needed to determine the causes of recent CH_4 and N_20 increases. This effort must be coordinated with research into fluxes and biogeochemical cycles of the isotopes of CH_4 and N_20 (e.g. NASA/GTE/ABLE).

5.4.4. Methyl Chloroform (CH_3CCl_3)

Unlike N_20 and methane, sources of CH_3CCl_3 are all anthropogenic and sources are known from production figures. It is a useful tracer and is frequently used to test 3-D and 2-D models (Prather, et al., 1986; Crutzen and Gidel, 1983)). Since reaction with OH is the only known loss for CH_3CCl_3, and its rate is known, comparison of CH_3CCl_3 source and computed losses, (with OH) defines a globally averaged OH mean (Prinn, et al., 1987). Total OH abundance may be decreasing with time, as CH_4, CO and perhaps, nonmethane hydrocarbons, increase. Since OH is transient (and has not been measured widely in the troposphere) CH_3CCl_3 is used to deduce global OH. Thus, monitoring of methyl chloroform is vital to keeping track of global OH, which is a principal atmospheric oxidant. The GAGE network of continuous measurements should be maintained and GMCC is encouraged to include this compound. Vertical profiles of CH_3CCl_3 should also be taken at GMCC baseline stations (Table 5.5).

5.4.5. Carbonyl Sulfide (COS)

This is the longest-lived and most abundant sulfur species. COS may be a major source of sulfur to the stratosphere (hence, sulfate aerosols) during times of low volcanic activity (Crutzen, 1976). Roughly 25 percent (NRC, 1984) of COS emissions may be anthropogenic -- from biomass burning, coal-fired power plants, automobiles, etc. -- and these sources may be increasing. For these reasons it is important to monitor COS, at least at a few GMCC or GAGE sites. Unfortunately routine measurements of COS and related sulfur gases CS_2 and $(CH_3)_2S$ may not be feasible. An upcoming NASA/GTE/CITE (Chemical Instrument Testing and Evaluation) mission (McNeal, 1987) will determine whether sulfur instrumentation and standards are adequate for monitoring at remote sites.

5.4.6. Carbon Monoxide (CO)

Despite difficulties monitoring gases of a few months' lifetime, determining the long-term behavior of CO is of highest priority because it contributes to tropospheric ozone formation and helps control the abundance of tropospheric OH, hence atmospheric lifetimes of many gases. Approximately 25 to 50 percent of CO emissions on a global scale derive from combustion (Logan, et al., 1981) and these sources are probably increasing in some regions and decreasing in others (Kavanaugh, 1987). Efforts to monitor CO and to develop a CO climatology should not be separated from determinations of trends and behavior in CH_4 (a photochemical precursor to CO), NMHC (natural and anthropogenic; also precursors of CO and sometimes competitors for reaction with OH), and tropospheric ozone with which CO is often correlated (Fishman and Seiler, 1983).

Instruments for measuring CO include both in situ detectors (gas chromatographic and chemical conversion) and a passive space-borne remote sensor. Improvements in CO monitoring require modifications in instrumental technique (Table 5.5) and adoption of combined ground-based network and satellite measurement strategy.

Specific recommendations include: (1) continuous CO monitoring at several GMCC and/or GAGE baseline stations; (2) better intercalibration of standards (3) vertical profiles of CO at baseline sites to determine seasonality, which is so far based only on surface observations; whenever possible these profiles should be made simultaneously with ozone, temperature, and H_20 profiles; (4) expanded flask sampling network to increase knowledge of global distribution of this gas.

Two Space Shuttle flights (1981 and 1984) have demonstrated feasibility for remote sensing of CO by a gas correlation filter radiometer, called MAPS (Monitoring of Air Pollution by Shuttle) (Reichle, et al., 1986). Presently MAPS gives only mid-troposphere CO, but offers promise of three-level viewing, in lower, mid and the upper troposphere. Because of recent delays in NASA's Shuttle schedule and relatively high cost of deploying this instrument for short periods it is recommended that MAPS CO be reconfigured, if needed, for launch on an expendable vehicle in order to avoid further delays due to Shuttle problems. Continuous operation is needed for mapping global CO concentrations and determining the relationship between CO and tropospheric ozone on large scales. Satellite observations of CO offer the best hope for mapping CO source regions (from urban and nonurban biomass combustion), transport characteristics and latitudinal and longitudinal variations.

Since modifications for making a satellite version of MAPS will take at least 1 to 2 years only a ground-based network for CO is available for short-term monitoring. Space-borne CO measurements and in situ CO monitoring (surface and vertical soundings) will remain complementary to one another. The global coverage of satellite will be required for monitoring, but it is unlikely that a satellite instrument can achieve the vertical resolution required to interpret CO chemistry and trends.

5.4.7. Tropospheric Ozone

Chapter 2 of this report is devoted to ozone monitoring, but not with an emphasis on the troposphere as a source region. With growing concern for tropospheric ozone as a greenhouse gas and with recently published evidence (Bojkov, 1986; Oltmans and Komhyr, 1986; Angell and Korshover, 1983) for a possible background ozone increase over the last century (at least in Northern mid-latitudes) there is new urgency in monitoring tropospheric ozone.

Satellite remote sensing for tropospheric 0_3 is not feasible at present. Recommendations (Table 5.5) are aimed at continuing to develop a good basic climatology from ground-based measurements (See Chapter 2). Table 5.6 lists the major ozone sounding network. This is an international effort. GMCC baseline stations (Table 5.4) have been used to measure surface ozone since the early 1960's. The greatest needs are: (1) to resolve instrumental difficulties; existing ozone data are hard to evaluate for trends because inaccuracies occur with some instruments and discrepancies among them exist which cannot be resolved. (Surface GMCC measurements which use UV absorption are an exception to this); (2) add more marine locations and Southern Hemisphere stations to the ozonesonde network; (3) frequent vertical soundings at baseline stations coordinated with continuous ground-based recording. Regular balloon sounding is starting at the South Pole, for example, where renewed interest has been sparked by the Antarctic ozone hole (Komhyr, et al., 1987). Ground-based LIDAR methods are also promising in this regard. NOAA/RITS (Radiatively Important Trace Species) is developing a differential absorption LIDAR method to implement at several sites. Ground and in situ instrument intercomparison is part of this effort. Coordination is planned with related ozone studies (e.g., total 0_3 from the Dobson and ozonesonde networks).

Although tropospheric ozone data is not easily available from satellite remote sensing, it has been possible to learn a lot about tropospheric ozone from satellite data (e.g., TOMS, SAGE II) in certain regimes, (Fishman et al., 1985; 1986). There is no doubt that a better tropospheric ozone climatology can be developed with existing satellite data.

5.4.8. Nonmethane Hydrocarbons (NMHC)

Oxidation of nonmethane hydrocarbons (NMHC), like CH_4, in the presence of high levels of NO_x, leads to ozone formation. NMHC are emitted by a variety of natural and anthropogenic processes (biomass burning, combustion, vegetation), with each process emitting a characteristic

Table 5.6 WMO Ozonesonde Stations - 1985*

Northern Hemisphere	Latitude	Longitude	Start (MO/YR)
Resolute, Canada	75	95W	1/66
Churchill, Canada	59	94W	10/73
Prague, Czechoslovakia	59	13E	1/79
Edmonton. Canada	53	114W	10/72
Goose Bay, Canada	53	60W	6/69
Lindenberg, G.D.R.	52	14E	1/75
Legionowo, Poland	52	21E	1/79
Uccle, Belgium	51	40E	1/69
Hohenpeissenberg, F.R.G.	48	11E	11/66
Garmish/Parten., F.R.G.	47	11E	1/78
Payerne, Switzerland	47	7E	8/68
Biscarosse, France	44	1W	3/76
Sapporo, Japan	43	141E	12/68
Cagliari, Italy	39	9E	7/68
Wallops Island, U.S.A.	38	76W	5/70
Tateno. Japan	36	140E	12/68
Kagoshima, Japan	32	131E	12/68
Southern Hemisphere			
Natal, Brazil	6	35W	8/79
Aspendale/Laveton, Australia	38	145E	6/65
Syowa, Antarctica	69	39E	11/69

*Compiled from data available from the World Ozone Data Center in May 1985 from (UCAR, 1986).

mixture of hydrocarbons, e.g. terpenes and isoprenes from vegetation, saturated and nonsaturated hydrocarbons of all classes from combustion, refining or manufacturing processes. Monitoring of hydrocarbons in urban areas is part of routine air quality measurements.

At typical levels of OH and 0_3, most NMHC are oxidized within a day to various forms of oxygenated carbon: aldehydes, ketones, organic acids; organic nitrates may form. Only C_2H_2 (acetylene), C_6H_6 (benzene), ethane and propane live more than a day, and can be expected to exhibit long-term trends in background levels. Ethane and propane background concentrations are typically 0.1 to 2 ppbv. Like CO and CH_4, these gases are lost by reaction with OH; therefore an increase over time means that sources have increased or OH, on average, has declined.

A climatology of ethane and propane has not been developed because measurements of these compounds though frequent, are not systematic. Better definition of ethane and propane distributions and detection of possible trends would both by served by: (1) routine ethane and propane measure at baseline stations; weekly flask samples would be adequate to detect long-term trends. Careful standardization and calibration is vital for this effort. (2) If upward trends in ethane and propane are observed, isotopic C measurements should be performed to help pinpoint the origin of the increase.

5.4.9. Aerosols and Precipitation

A number of trace gases (chiefly nitric acid, sulfuric acid, organic acids, peroxides, aldehydes) are removed from the atmosphere in aerosols or precipitation. Appreciable amounts of these gases are also dry deposited on surfaces.

Two types of precipitation networks operate:

(1) In the Northern Hemisphere, chiefly in Western Europe and North America, precipitation is measured routinely for acidity (pH), which is assigned to sulfuric, nitric or "other" acids, the latter presumed to be lower carbon acids. Whether or not acidity is increasing at nonurban sites in the US has been the subject of controversy. The reasons for the ambiguity include methods of statistical analysis and interpretation of data; instrumental calibration and methods for determining acidity; and the uncertain role of increasing alkalinity. The range of low pH rainfall extends far beyond pollution sources and this range is probably increasing in size. In the US the National Acid Deposition Program (NADP) sponsors approximately 200 stations (Table 5.7).

(2) The Global Precipitation Chemistry Project (GPCP), a US-sponsored program run with international participation, began to operate 5 stations in remote sites around the world in 1979, in roughly semi-hemispheric coverage (Galloway, et al., 1982). It currently numbers seven stations, including one in China (Table 5.7). The purpose of GPCP is to map background precipitation: acidity, ionic and elemental composition. Spatial studies have been very fruitful; it is too early to say anything about temporal trends.

Natural variability of precipitation owing to the synoptic nature of the physical processes (deposition) is very great. Nonetheless, it is recommended that both regional and global networks for precipitation be better exploited for trend analysis. This means: (a) more frequent and careful measurement. Weekly collection is the norm at some places and it may include combined wet and

TABLE 5.7 Global Precipitation Chemistry Project (GPCP) Network*

Site	Start
Bermuda	1970
Amsterdam Island, Indian Ocean	1980
Katherine, Australia	1980
Mauna Loa, Hawaii	1983
Cape Point, South Africa	1983
Kruger Park, South Africa (discontinued 1987)	1983
Torres del Paine, Chile	1984
Lijiang, China	1987

* Does not include short-term cooperative studies at other sites or participating ship cruises

Note:
The National Acid Deposition Program (NADP) has approximately 200 stations in continental U.S. Eighteen are run by NOAA, the remainder by cooperating institutions according to NADP sampling protocol and standards.

dry deposition. Event by event wet sampling is preferable, though not always practical; (b) careful evaluation of data collected to date to determine seasonal patterns at each site so temporal trends can become clear at both near-source and remote sites. In particular, sulfuric, nitric and organic acids should be monitored because they are transformation end products of S, N and hydrocarbon source gases that are too short-lived to monitor directly. It is essential to see how source gas increases correlate with end product acid increases. This may be a relatively easy way to keep track of the transients and to assess source/receptor relationships.

Elemental composition, seasonal behavior and transport characteristics of aerosols also complement the source gas picture as chemical tracers.

5.4.10. Nitrogen Oxides (NO_x)

NO, and $N0_2$ ($NO_x = NO + N0_2$) are short-lived tropospheric source gases. Natural sources include soils, lightning and lightning initiated biomass burning which support extremely low values of NOCl at unpolluted marine locations and moderately low NO at remote continental sites. Increased emissions of NO_x are assumed to be responsible for urban smog, organic nitrates measured at nonurban locations, and acidity in precipitation. If there is an upward trend in tropospheric ozone over time, it is probably due to elevated levels of NO_x in addition to higher CO and hydrocarbon concentrations (Dignon and Hameed, 1985).

Another effect of increasing NO_x may be increases in longer-lived forms of reactive nitrogen to which NO_x converts by photochemical reactions: $HN0_3$, peroxyacetylnitrate (PAN), and organic nitrates. Although NO and $N0_2$ are too short-lived to monitor at background sites it would be appropriate to track the consequences of NO_x emissions by measuring total odd nitrogen (NO_y - $NO + N0_2 + N0_3 + N_20_3$ + PAN + organic nitrates) at a network of sites near but not in the source region. Instruments suitable for routine NO_y measurements are available (Dickerson, 1984; Fahey, et al., 1985). PAN instrumentation is being developed and intercalibrated as part of the GTE/CITE Program, but it may not be practical for regular measurements at remote sites.

There is hope that a satellite instrument can be developed for $N0_2$ (NASA, 1987), which would permit monitoring of NO_x source regions and detection of NO_x increases. Until this becomes available, monitoring $HN0_3$, organic nitrates and mid-tropospheric and upper tropospheric PAN through NO_y is probably the best surrogate for detection of NO_x trends.

5.5. Conclusions

5.5.1. Longer-Lived Gases

Recommendations for source gas monitoring may be summarized as follows:

Monitoring strategies are well developed for a number of gases ($C0_2$, some CFCs, CH_4, N_20) and recent trends are reasonably well-defined. Major needs are:

(1) Improved standardization and intercalibration among instruments and networks.

(2) Maintenance and improvement of networks to fill in a few geographical gaps, while avoiding duplication of cost and effort.

(3) Regular vertical profiles at remote (baseline) stations, at least.

(4) Identification of sources and transport patterns by measuring isotopic C and N.

5.5.2. Shorter-Lived Gases

An urgent need exists for monitoring several medium-lived source gases that affect tropospheric and stratospheric chemistry, chiefly tropospheric ozone and CO. The natural spatial and temporal variability of these gases makes monitoring difficult without the global coverage that space-borne remote sensing provides. Recommendations:

(1) Modify and deploy the space-borne tropospheric CO instrument (MAPS-CO) for satellite operation.

(2) Develop a space-borne $N0_2$ detector.

(3) Define a global climatology for tropospheric CO, ozone, NO_x, and nonmethane hydrocarbons. In the absence of global remote sensing from space, this must be done with current measurement techniques and more consistent sampling at a well-disposed network of sites. This includes regular vertical profiles of CO and ozone, preferably with H_20 vapor and temperature.

5.5.3. General Recommendations:

(1) Continued vigilance and attention to detail must be maintained in monitoring, especially for the longer-lived gases. Even though some of these trends seem "well-established", the atmosphere is complex and sudden, sometimes subtle changes may be important.

(2) It is vital to archive whole air samples for future analysis as new measurement techniques, mechanisms and important species are discovered.

(3) Although present source gas networks have many deficiencies, much archived data, e.g., from large field expeditions, smaller-scale measurement programs, precipitation networks, and current monitoring stations, remains under-analyzed and interpreted. Better exploitation of these data is required for understanding trends and developing climatologies.

(4) Specific recommendations will meet the goal of trend detection only if monitoring tasks are coordinated with experimental research on defining source gas budgets and with modeling that interprets trends mechanistically.

CHAPTER 6. OTHER TRACE CONSTITUENTS

6.1. Introduction

In order to understand whether long-term changes which might be observed in stratospheric ozone concentrations arise from changes in the chemical composition of the Earth's atmosphere, it is important to have accurate observations of those species whose concentrations are known to be related to that of ozone. For example, it is believed that increasing chlorine concentrations in the upper stratosphere should lead to large reductions in ozone in the stratosphere. Measurements of ozone decreases alone can only document the changes which occur; they do not demonstrate that increased chlorine concentrations are responsible for them.

The complexity of stratospheric chemistry requires that concentrations of a variety of chemical species be measured if one is to have sufficient data for a complete understanding of any observed ozone changes. Measurements of species containing hydrogen, nitrogen, and chlorine atoms are all vital, since constituents containing these atoms play important roles in controlling the amount of 0_3 in the stratosphere. Measurements of bromine and fluorine-containing species would also be useful. In addition, aerosols and polar stratospheric clouds may affect the propagation of radiation in the stratosphere which may in turn influence the remote sensing of ozone and other gases, and serve as a site for heterogeneous chemistry, so their concentrations and compositions must also be known.

In this section we focus on the necessity of, and instrumentation for, long-term monitoring of these species. We consider only those species which undergo appreciable formation in the stratosphere; source gases such as CH_4, N_2O, and the various chlorofluorocarbons are treated in Chapter 5 of this report. H_2O, which has appreciable tropospheric and stratospheric sources, is treated in this chapter. The molecules considered here include active free radicals (e.g., NO_2, C10) and longer-lived reservoir species (e.g., HCl, HNO_3). We do not consider atomic species (O, O(1D), H, Cl, N) whose concentrations during daytime are simply derivable from those of precursor molecules by use of photochemical equilibrium expressions (during nighttime their concentrations are exceedingly small). For each molecule, we review the rationale for monitoring, measurement requirements, and current instrumentation qualified for monitoring, with emphasis placed on ground-based and satellite-based measurement systems. Less attention will be given to aircraft and balloon-borne measurement techniques where applicable because of the difficulty of making frequent measurements with them. Emphasis will also be placed on measurement precision and stability of calibration; absolute accuracy, while valuable, is of less importance in the determination of the long-term trends which are the focus of stratospheric monitoring.

In considering strategies for monitoring, we focus on several time frames which constitute the 10-year period covered by this report. First, we consider the present and immediate future (abbreviated 0-2) which restricts locations and techniques to those currently operating. Next, we consider the 2- to 5-year period (abbreviated 2-5) during which it is hoped that the ground-based monitoring system, the Network for Detection of Stratospheric Change (NDSC) currently being planned by NASA, NOAA, the CMA, and WMO will become operational. It is expected that measurements made by the system will continue indefinitely once it is operational. We then consider the 4- to 8-year period (abbreviated 4-8) in which NASA's Upper Atmosphere Research Satellite (UARS) should be operational for most of the period. Finally, we consider the period near the end of the 10-year time frame (abbreviated 8-10) when it is hoped, NASA's Earth Observing System (Eos) satellite will be launched. Measurement systems will be grouped under the time periods they might become operational. For example, all satellite-based remote sensing methods possibly appropriate for Eos will be grouped in the last time period, even though their development must begin as soon as possible.

Species will be reviewed by family (trace element, e.g., H, N, Cl) in the following section. Those species that can be considered members of more than one family will usually be included in the family of the lower concentration element (for example, HCl and $ClON0_2$ will be considered as chlorine-containing species). An assessment of priorities for monitoring, based on both the perceived importance and quality of measurement techniques available, will be given in the Conclusions section.

For citations to the original literature, the reader is referred to the 1986 WMO Report #16 "Atmospheric Ozone 1985" (WMO, 1986), which has a very comprehensive list of references covering the period until the end of 1985. Only references not included in WMO 1986 (including more recent work) will be cited here.

6.2. Measurement Requirements and Systems

In this section, the rationale for monitoring, measurement requirements, and current instrumentation qualified for monitoring will be discussed for each of 20 constituents. Available measurements for each constituent showing measurement type (e.g., in situ, aircraft-based, etc.) are summarized in Table 6.1. A more detailed breakdown of constituents whose concentrations have been or are to be measured from space-based platforms (satellite or shuttle-borne experiments) is presented in Table 6.2. Identification of acronyms used in Table 6.2 and elsewhere throughout the text is made in the Appendix B, List of Acronyms. Expected diurnal variation of constituents is summarized in Table 6.3, along with some information on the rate of day-night transitions. These quantities are important because of their implications for measurement strategies. For instance, those species to be measured by ground-based solar absorption at occultation (sunrise, sunset) will need to be made with very good temporal resolution if their day-night transition is rapid. For those species undergoing little or no diurnal variation, temporal resolution requirements are less stringent. The subject of temporal resolution will be discussed separately for individual constituents, as needed.

6.2.1. Hydrogen-Containing Species

(1) Water (H_20)

(a) Rationale for Monitoring

The major role of water vapor in the stratosphere is as a source of the hydrogen atoms that are contained in the crucial free radicals OH and $H0_2$. These are important in controlling 0_3 concentrations in the stratosphere and for partitioning other trace constituents among the different members of their families (e.g., the catalytically active $N0_2$ vs. the inactive $HN0_3$). Water also is radiatively important, so its concentration will have an effect on the thermal structure of the atmosphere.

TABLE 6.1 Summary of Existing Measurement Techniques

	In Situ	Ground-based		Aircraft-Based	Space (Satellite/ Shuttle) Based
	Profile	Column	Profile	Column	Profile
H_20	X				X
OH	X	X			
$H0_2$	X	X	X		
H_20_2	X				
NO	X	X		X	Y
$N0_2$	X	X		X	X
$N0_3$	X	X			
N_20_5	X				Y
$HN0_3$	X	X		X	X
$HN0_4$	Z				Y
ClO	X	X	X		
HCl	X	X	X	X	Y
$ClON0_2$	X				Y
HOCl	Z				
OClO		X			
Aerosols	X	X	X		X
BrO	X				
HF	X	X		X	Y

X - information available from indicated technique(s)
Y - shuttle only
Z - exceedingly little data - single altitude or upper limit only

TABLE 6.2

Past, Present, and Planned Space-Based Constituent Measurements

	H_2O	NO	NO_2	N_2O_5	HNO_3	HNO_4	ClO	HCl	$ClONO_2$	Aerosols	HF	SO_2
SBUV Nimbus 7 10/78 to 2/87 UV scatt		x										x
LIMS Nimbus 7 10/78 to 5/79 IR thermal emission	x		x		x							
TOMS Nimbus 7 10/78 to Present UV scatt. at occult.										x		x
SAM II Nimbus 7 10/78 to Present IR solar absorp. at occult.			x			x						
SAGE AEM-2 2/79 to 11/81 IR-vis. solar emission vis. scatt.			x							x		
SME SME 10/81 to 12/86 IR thermal at occult.	x		x							x		
SAGE-II ERBS 10/84 to Present IR-vis solar absorp. occult.	x	x	x	x	x	x		x	x	x	x	
ATMOS Spacelab 3 4/30/85 to 5/6/85 IR solar absorp. at occult.	x	x	x	x	x					x		
ISAMS USARS Est. 1991 IR thermal emission	x	x	x	x	x					x		
CLAES UARS Est. 1991 IR thermal emission	x	x						x			x	
HALOE UARS Est. 1991 IR solar absorp at occult.	x						x					
MLS UARS Est. 1991 Microwave thermal emission	x		x		x					x		
GOMR-GLS EOS Est. 1995 IR thermal emission												

TABLE 6.3 Summary of Time Variability

	Day	Night	Rate of Change
H_20	none	none	none
OH	large	none	fast
$H0_2$	large	none	fast
N_20_2	none	none	none
NO	large	none	fast
$N0_2$	small/moderate	large*	fast
$N0_3$	very small	large	fast
N_20_5	moderate	large*	slow
$HN0_3$	none	none	none
$HN0_4$	none	none	none
ClO	large	none/small*	fast (sunrise) slow (sunset)
HCl	none	none	none
$ClON0_2$	small	large*	slow
HOCl	small and complicated*	none	slow
OClO	very small	large	fast (sunrise) slow (sunset)
Aerosols	none	none	none
BrO	large	none	fast (sunrise) slow (sunset)
HF	none	none	none
$S0_2$	none	none	none
Metals	none	none	none

*strong altitude dependence

However, the distribution of H_20 in the stratosphere is not simply explained. A significant fraction of the H_20 in the stratosphere is transported upward from the troposphere, primarily in the tropics, while most of the remainder is formed in the oxidation of CH_4. Dynamical processes account for most of the meridional and vertical structure of stratospheric water vapor. The existence of important meridional and vertical gradients in stratospheric H_20 as seen by the Limb Infrared Monitor of the Stratosphere (LIMS) on Nimbus-7 implies that during times of strong dynamical activity (e.g., stratospheric warming events), H_20 will have both longitudinal and temporal dependence. Increasing concentrations of CH_4 imply that upper stratospheric concentrations of H_20 may be increasing with time. The amount of H_20 entering the stratosphere depends very sensitively on the temperature of the tropical tropopause and the rate of vertical transport through it, so changes in these quantities, which might result from changes in the atmosphere's thermal state, may also affect the amount of H_20 in the stratosphere.

Because of its central role in affecting the chemistry of a variety of important trace constituents in the stratosphere and its expected variability due to dynamical processes, long-term monitoring of stratospheric H_20 is crucial to any long-term study of stratospheric composition.

(b) Monitoring Requirements

Any program for monitoring stratospheric water concentrations must have sufficient measurement frequency and precision to allow isolation of any potential secular trend in water from the observed short-term, seasonal, biennial, and long-term variability. In the absence of a detailed statistical treatment of short-term water concentration variability, it is difficult to establish a minimum precision requirement for monitoring. Such requirements are intimately connected with the sampling frequency and the anticipated correlation between measurements.

One secular trend that one would ideally be able to pick out from long-term water data would be the growth predicted due to the increase in atmospheric CH_4. Using the approximate rate of CH_4 growth (1 percent per year) and the approximation that half of the stratosphere's water comes from CH_4 oxidation, we see that a rate of increase of upper stratospheric H_20 on the order of 0.5 percent per year is quite possible. The interfering influences may be quite large. For example, of concern is a long-term nonlinear variation in lower stratospheric water concentration over Washington, D. C. observed in the frost-point hygrometer measurements over a 15-year period. If such variations occur elsewhere in the stratosphere [they are not seen in measurements made since 1980 from Boulder, Colorado (Oltmans, 1986)], it might be impossible to observe a secular CH_4-induced variation with only 10 years of measurement.

(c) Equipment Qualified for Monitoring

Historically, most of the information on stratospheric water vapor measurements has come from balloon-borne instruments, using frost-point hygrometers or detection of fluorescence of electronically excited OH produced in the Lyman alpha photodissociation of water. There is some disagreement between these two methods on the basis of data obtained during the International Intercomparison of Stratospheric Water Vapor Instrumentation of 1981 and 1983. The Lyman alpha technique has also been used in an airborne mode as part of the Stratosphere-Troposphere Exchange Program (STEP) and the Airborne Antarctic Ozone Experiment (AAOE). Several spectroscopic techniques have also been developed. These techniques were compared as part of the Balloon Intercomparison Campaigns of 1982 and 1983. Use of any of these techniques for monitoring is possible, although not ideal, as pointed out above.

Satellite-based measurements of stratospheric H_20 were made successfully with the LIMS instrument on Nimbus-7, and are currently being made by the Stratospheric Aerosol and Gas Experiment II (SAGE II) instrument on the Earth Radiation Budget Satellite (ERBS) (Larsen et al., 1986). Similar instruments of either type (LIMS measured H_20 by detection of infrared thermal emission; SAGE II measures H_20 by infrared solar absorption at occultation) could be used for monitoring purposes. A variety of techniques are available. On the UARS satellite four different instruments will measure water vapor concentrations. Infrared thermal emission will be used by the Cryogenic Limb Array Etalon Spectrometer (CLAES) and Improved Stratospheric and Mesospheric Sounder (ISAMS) instruments, infrared absorption at occultation will be used by the Halogen Occultation Experiment (HALOE) instrument, and microwave thermal emission will be used by the Microwave Limb Sounder (MLS) instrument. The MLS will cover the largest vertical range (15.85 km), while HALOE will cover the smallest. Both the CLAES and ISAMS instruments should yield information on nearly the entire vertical extent of the stratosphere and the lower mesosphere, although both may be susceptible to non-local thermodynamic equilibrium (non-LTE) effects; such effects have been shown (Kerridge and Remsberg, 1987) to have contaminated the LIMS H_20 measurements. CLAES is the only one of these instruments planned to have a finite lifetime. Any of these techniques should be suitable for monitoring if long-term stability of calibration can be assured.

Ground-based measurements of stratospheric water content may become possible in the foreseeable future. An improved version of a microwave spectrometer that has been used with great success in studying the concentrations of mesospheric H_20 is currently being developed so as to be applicable to stratospheric H_20. This improved instrument should be able to determine vertical profiles of H_20 down to 20 km with sampling times of approximately 2 hours (longer sampling times will be needed for mesospheric measurements).

Similar altitude coverage should come from both the Atmospheric Trace Molecule Spectroscopy (ATMOS) and Millimeter-wave Atmospheric Sounder (MAS) Instruments, which are shuttle-borne payloads.

Ground-based infrared measurements of the tropospheric water vapor profile have recently been demonstrated. Extension of these measurements to yield information on stratospheric H_20 would also make them suitable for monitoring. Recent advances in balloon-borne far-infrared emission observations (Abbas et al., 1987) suggest that satellite-based determination of stratospheric H_20 profiles might become possible over the time frame of this document.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue frost-point hygrometer measurements at a fixed location (probably Boulder, Colorado, for continuity with recent results) with the aim of extending previous time series. Place special interest in lower stratospheric water concentrations and determination of whether there is some non-linear cyclical variation. Add several additional sites for regular measurement.

(ii) (0-2) Attempt to understand absolute calibration difference between frost-point hygrometers and photodissociation-induced fluorescence techniques to help determine absolute amount of water in the stratosphere.

(iii) (0-2, 2-5) Continue regular satellite measurement of stratospheric water vapor by SAGE II.

(iv) (0-2, 2-5) Increase frequency of ground-based microwave measurements of upper stratospheric and mesospheric water. Attempt to make these measurements regularly at one or more locations over an extended period of time.

(v) (2-5) Continue development of ground-based microwave system(s) which will allow determination of stratospheric H_20 profiles. When development is complete, test in the field and then make operational at one or more stations. As part of testing and development, carefully compare with frost-point hygrometer measurements until behavior of instrument is well understood. The longer term goal could be a ground-based calibration system for correcting satellite sensor drift.

(vi) (4-8) Use H_20 measurement capability of UARS to determine H_20 concentrations over as long a period as possible.

(vii) (4-8) Carry out necessary laboratory experiments and model calculations for improved assessment of non-LTE effects associated with infrared thermal emission detection of stratospheric and mesospheric H_20.

(viii) (8-10) Develop and construct next generation satellite.based detection system(s) for inclusion on Eos, such as the proposed NOAA Global Ozone Monitoring Radiometer (GOMR) and/or far-infrared emission detectors.

(2) Hydroxyl (OH)

(a) Rationale for Monitoring

Hydroxyl is in many ways the central hydrogen-containing radical in the stratosphere. It can be thought of as the first one formed, (primarily in the reaction of O(lD) with H_20). It is involved in the loss of odd hydrogen in the atmosphere (by reactions with $H0_2$, $HN0_3$, and $HN0_4$). It may be converted into H and $H0_2$ by simple reactions, and also provides the hydrogen for $HN0_3$ by a simple recombination reaction with $N0_2$. It initiates the destruction of CH_4 and HCl, thus playing a crucial role in the partitioning of chlorine among its catalytically active and inactive forms. In the topmost part of the stratosphere, OH is the most abundant hydrogen-containing radical. It may vary both as a function of season and possibly of the solar cycle, and may also be affected by volcanic eruptions, so that long-term monitoring may be necessary to establish any good measure of its average concentrations. Like most stratospheric radical species, it has a strong diurnal variation, being nearly nonexistent throughout the stratosphere at night.

Because of its low concentrations (believed to be nearly always below 1 ppbv in the stratosphere, with mixing ratios increasing rapidly with altitude), its remote measurement is difficult. In addition, its concentration can be fairly accurately inferred, at least in a two-dimensional sense, from measurements of longer-lived constituents such as H_20, 0_3, $N0_2$, and $HN0_3$, especially in the upper stratosphere (the accuracy of such inference procedures is discussed by Kaye and Jackman (1986). Thus, in spite of its importance, its monitoring is probably of less interest than that of its precursors. Should improved techniques become available, however, their application could be very useful.

(b) Monitoring Requirements

The major requirement for monitoring of OH amounts is that measurements be sufficiently frequent and over a long enough time period that accurate determination of seasonal and "intermediate-term" trends can be assessed. In particular, it would be worthwhile to understand whether or not there is a solar cycle dependence in the total OH column (which is most commonly measured OH quantity), because such a dependence could easily mask longer-term secular trends, such as those produced by changes in stratospheric ozone or water. Sufficiently frequent measurements are needed to accurately characterize the seasonal variation, which must be removed prior to making any attempt to assess these intermediate and long-term variations. Because of the strong diurnal dependence of OH, it would be helpful for detection techniques to have sufficient sensitivity so that (i) measurements can be made over a short enough period of time and (ii) no major correction for this dependence need be incorporated into the individual data points. In addition, extremely high sensitivity will be needed to measure the small OH concentrations in the lower stratosphere (under 0.01 ppbv below approximately 20 mb).

(c) Equipment Qualified for Monitoring

Measurement capability for stratospheric OH is very limited; and, up to now, measurements of vertical profiles have consisted solely of in situ measurements. Total column measurements, which include tropospheric and mesospheric, as well as stratospheric OH, can be made relatively routinely from the ground. Since balloon techniques are far from optimal for long-term monitoring, especially for constituents which are not well mixed, we will focus here on ground-based column measurements.

Numerous measurements of the total column amount of OH have been made at several locations using absorption of solar ultraviolet radiation by OH, (Burnett et al., 1988), but their interpretation is not especially simple. First, there is the problem that the OH column has approximately equal contributions from stratospheric and mesospheric OH. Tropospheric OH is expected to contribute up to 10 percent of the total. Thus, variations of the total OH column do not directly provide information about the stratosphere. Second, the OH column has a strong diurnal component, with its variation being controlled mostly by the solar zenith angle. Comparison of measurements at different times must therefore be made with care. Nevertheless, if long-term monitoring of OH is to be carried out in the near future, column measurements such as these may well be the methods of choice.

A new ultraviolet technique for measurement of stratospheric OH is currently under development and has been successfully demonstrated in balloon flights (Torr, et al., 1987). Consideration is being given to its possible use in ground and space-based OH monitoring.

A ground-based lidar technique has been proposed, which should be able to give good measurements of OH in the 25.75 km range. The absolute accuracy of this technique will be limited by the quality of the state-to-state rate coefficients needed in the lidar inversion algorithm, but the results should be of sufficient precision that trend measurements could be made with confidence.

OH has been spectroscopically detected in the stratosphere by balloon-borne far-infrared techniques, and the determination of vertical profiles in this way should be possible (Abbas et al., 1984). Also, capability for making measurements in this way from space-borne platforms may be developed over the time frame covered by this document.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue ground-based measurement of total OH column. Attempt to increase measurement frequency and number of stations making measurements, including regular measurement in the Tropics and the southern hemisphere. Give special attention to assessing whether non-linear, possibly cyclical behavior measured previously is continuing and global.

(ii) (2-5, 4-8, 8-10) Develop and implement ground-based techniques that could lead to determination of vertical profile of OH, including but not limited to LIDAR and other ultraviolet methods.

(iii) (8-10) Begin development of satellite-based methods for OH monitoring, including ultraviolet and sub-millimeter far-infrared.

(3) Hydroperoxyl ($H0_2$)

(a) Rationale for Monitoring

Hydroperoxyl will be the dominant hydrogen-containing radical over much of the lower and middle stratosphere, and its accurate measurement will be important in understanding odd-hydrogen chemistry at those levels. It leads to the formation of $HN0_4$ (by recombination with $N0_2$), which is a reactant in the major lower stratospheric odd hydrogen removal reaction (with OH). In the upper stratosphere $H0_2$ reacts with OH to provide the major sink for odd hydrogen there. $H0_2$ can also react with ClO to form HOCl, a potentially important chlorine reservoir species, about which little is known. Finally, $H0_2$ plays an important role in controlling the odd oxygen balance in the upper stratosphere, as the reaction $0 + H0_2 \rightarrow OH + 0_2$ may be considered a key step in the catalytic cycle.

As with OH, the concentration of $H0_2$ (at least in two dimensions) can be inferred from that of its precursors, which might serve to make its measurement of less importance. However, there is evidence that models and inference procedures may give rise to incorrect $H0_2$ concentrations in the lower stratosphere. Observational data showed much larger amounts in this region than were predicted. The accurate measurement of $H0_2$ is clearly important, but long-term monitoring of its concentration may be less important than resolving the questions concerning its absolute abundance, which might be resolved with only a limited set of measurements.

(b) Monitoring Requirements

For monitoring of $H0_2$, the most important requirement is that reasonably accurate mixing ratios be obtainable throughout the stratosphere and preferably into the lower mesosphere. As for OH, measurements should be sufficiently frequent that seasonal effects can be removed for long-term trend studies, and sensitive enough that the diurnal dependence can be characterized and dealt with in data analysis.

(c) Equipment Qualified for Monitoring

Like OH, most of the current data about composition of stratospheric $H0_2$ has been made by in situ measurements. One reasonably successful ground-based measurement has been made based on analysis of millimeter wave emission, which provides a column amount for $H0_2$ above 35 km and some information about the vertical profile above that altitude. This technique has the disadvantage of requiring several days of signal integration, which requires correction for the diurnal variation of $H0_2$. The one profile obtained appears to be inconsistent with many of the in situ measurements of $H0_2$ made so far. Usefulness of this technique for monitoring of stratospheric $H0_2$ may increase as technological advances lead to improvements in sensitivity. Balloon-borne detection of $H0_2$ in the submillimeter wavelength range should be possible, and if implemented, could play a role in $H0_2$ monitoring.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Make additional measurements using ground-based millimeter-wave techniques. Further develop instrumentation so that shorter signal integration time is possible, simplifying consideration of diurnal effects.

(ii) (2-5) Attempt to either develop ground-based techniques capable of accurately measuring $H0_2$ concentrations in the lower stratosphere, or make periodic in situ measurements (preferably simultaneous and co-located with ground-based measurements) of lower stratospheric $H0_2$ with an aim of resolving the apparent discrepancy between in situ measurements of lower and middle stratospheric $H0_2$ and ground-based measurements of upper stratospheric $H0_2$ amounts.

(iii) (8-10) Develop methodology for space-based remote sensing of $H0_2$ using millimeter wavelength or other techniques as appropriate.

(4) Hydrogen Peroxide (H_20_2)

(a) Rationale for Monitoring

Hydrogen Peroxide is a reservoir species for odd hydrogen and is formed by the disproportionation reaction of $H0_2$ ($2H0_2 \rightarrow H_20_2 + 0_2$). It is expected to have very strong variation with latitude and height and to be present in greater amounts than OH and $H0_2$ in the lower stratosphere. However, its concentrations will typically be much smaller than those of $HN0_3$, another hydrogen-containing reservoir species, so its measurement is not crucial. H_20_2 concentration does have the advantage of being approximately related to the square of the $H0_2$ concentration, so it may reflect more strongly atmospheric variability due to dynamical processes than would OH and $H0_2$ concentrations. H_20_2 concentration can be inferred from $H0_2$ and OH values, but if $H0_2$ is itself inferred (i.e., from 0_3, H_20, $N0_2$, etc.), the quadratic dependence on $H0_2$ makes the inferred H_20_2 concentrations very sensitive to the model parameters used, thus creating large uncertainties.

The current experimental situation concerning H_20_2 is muddled (Chance and Traub, 1987). Results are not entirely consistent with each other or with photochemical models and inference procedures, so it would be prudent to better understand H_20_2 concentrations before any long-term monitoring strategy is implemented.

(b) Monitoring Requirements

H_20_2 presents a difficult challenge for monitoring. Its expected large variability suggests that very frequent measurements be made in order to average short-term variability resulting from meteorological processes. Its diurnal dependence is small, however, so short signal integration time may be less of an issue than it is for the strongly-diurnally varying radicals OH and $H0_2$. Its large seasonal dependence requires that accurate characterization be made before removing variability for assessment of trends. The low concentrations expected at high latitudes and mid latitudes in winter (peak mixing ratios on the order of 0.1 ppbv) demand high instrument sensitivity. Any useful technique should be able to determine accurate concentrations at all latitudes and seasons, at least near the expected mixing ratio peak. Since it is expected to have very strong vertical gradients above and below its mixing ratio peak (at approximately 30 km), better vertical resolution is required for useful measurements of H_20_2 than for OH and $H0_2$.

(c) Equipment Qualified for Monitoring

There are currently no ground-based measurements which have provided vertical profiles of H_20_2. Ground-based millimeter-wave techniques have been used to determine an upper limit to H_20_2, which is a factor of two larger than a model-derived profile, and thus may be much larger than the actual amount of stratospheric H_20_2 present. Improvements in millimeter-wave technology will be needed if ground-based H_20_2 monitoring is to be feasible.

A satellite-based technique using microwave thermal emission for determining the amount of H_20_2 in the 30 to 40 km altitude range has been developed for UARS (the MLS experiment). This measurement is expected to be difficult, and will require long integrations during data processing. Measurements on only a monthly basis are expected to be obtainable by the MLS instrument.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue attempts to make in situ measurements of H_20_2 vertical profiles.

(ii) (2-5) Further develop ground-based millimeter-wave techniques with the aim of increasing instrument sensitivity so that actual concentrations rather than upper limits can be determined.

(iii) (4-8) Make measurements from UARS using MLS instrument.

(iv) (8-10) Pursue development of improved satellite-borne microwave or sub-millimeter instruments possibly for Eos) which could obtain frequent distributions of H_20_2.

6.2.2. Nitrogen-Containing Species

(1) Nitric Oxide (NO)

(a) Rationale for Monitoring

Nitric Oxide is expected to be the predominant odd-nitrogen containing species in much of the stratosphere during daytime; at night it is quickly lost by reaction with 0_3 to form $N0_2$. Its interconversion with $N0_2$ can lead to loss of odd oxygen by the cycle

$$\begin{array}{l} NO + 0_3 \rightarrow N0_2 + 0_2 \\ 0 + N0_2 \rightarrow NO + 0_2 \\ \hline 0 + 0_3 \rightarrow 0_2 + 0_2 \end{array}$$

which is known to be the major odd oxygen destruction cycle in the lower and middle stratosphere. It also plays an important role in the interconversion of hydrogen, and chlorine-containing radicals, by the processes

$$H0_2 + NO \rightarrow OH + N0_2$$

and

$$ClO + NO \rightarrow Cl + N0_2$$

respectively.

Direct measurement of NO is of less importance than measurement of $N0_2$, since a nighttime measurement of $N0_2$ will provide information about the amount of both NO and $N0_2$ in daytime. During daytime the concentrations of NO and $N0_2$ are believed to be simply related by the photochemical equilibrium expression

$$\frac{[NO]}{[N0_2]} = \frac{J(N0_2 + hv \rightarrow NO + 0) + [O]k(O + N0_2 \rightarrow NO + 0_2)}{[0_3]k(NO + 0_3 \rightarrow N0_2 + 0_2) + [ClO]k(ClO + NO \rightarrow Cl + N0_2)}$$

where J and k are used respectively to represent the photolysis rate and reaction rate of the indicated processes. Measurement of daytime NO would be useful in assessing the accuracy of expressions such as that above, but this might not require long-term monitoring; a few selected measurements made simultaneously with those of NO_2 should be adequate for this purpose.

(b) Monitoring Requirements

The quality needed of the techniques used for monitoring NO depends markedly on what types of variation are to be sought. If the slow secular trend in NO expected on the basis of the increasing concentration of N_2O (approximately 0.2 percent per year) is to be isolated, high measurement frequency and instrument sensitivity are required. If other scales of variability are being searched for (e.g., possible solar cycle influence) (Callis and Natarajan, 1986), less sensitivity is required. Monitoring of NO as part of an attempt to monitor the NO/NO_2 ratio could also impose strict requirements, as the anticipated ozone changes are fairly small. We note that NO will vary both seasonally and over short-term periods in response to meteorological activity, and measurement frequency must be sufficient for these variations to be averaged.

If ground-based column measurements are being used, care must be taken to correctly treat those days with large tropospheric NO amounts (which might contribute a non-negligible fraction of the total column). These techniques require long atmospheric path lengths, corresponding to high zenith angles at which time NO concentrations are undergoing rapid diurnal variation. Consequently, high instrument sensitivity to ensure short integration times is helpful.

Satellite techniques need to have sufficient range to be able to accurately pick out low concentrations (1 ppbv) of NO in the lower stratosphere, and also need to be able to properly respond in those cases when large amounts of NO are brought down into the upper stratosphere from the mesosphere.

(c) Equipment Qualified for Monitoring

Satellite-based techniques for the determination of vertical profiles of NO have been developed for the UARS mission, and these would constitute the preferred methods for monitoring. All three infrared instruments (CLAES, ISAMS, and HALOE) on UARS will determine vertical profiles of NO; of these, ISAMS will cover the broadest altitude range (approximately 15-50 km). Some concern about the use of infrared emission techniques in determining NO concentrations in the stratosphere due to non-thermal emission processes has been expressed (Kaye and Kumer, 1987); this should be able to be dealt with, if necessary, after the relevant laboratory experiments have been carried out. The HALOE experiment, based on infrared absorption, will not be affected by such problems, but can only get information on two latitudes per day.

Ground-based and aircraft-based measurements of the total NO column can also be made, as can aircraft-based measurements of the local concentration of NO in the lower stratosphere. The column measurements, which are based on infrared absorption, require long atmospheric path lengths and so far have been restricted to times close to sunrise and sunset. There is some disagreement between the NO columns measured from aircraft by two different groups, although the differences may not be significant due to overlapping error bars. Nevertheless, some questions may still exist about absolute accuracy of aircraft-based NO column measurements. The ground-based measurements made at one location appear to be quite reasonable, however, and would be an important component of any monitoring program.

Some information about the column amount of NO in the upper stratosphere and mesosphere was determined by the Solar Backscattered Ultra Violet (SBUV) experiment on Nimbus-7 up to February 1987 when it was operated in the spectral scan mode. This technique measures fluorescence of the NO gamma bands. Capability for making similar measurements (using either spectral scan mode or an appropriate choice of programmable wavelengths in 12-wavelength mode) exists on NOAA's SBUV-2 satellite, but has not yet been used.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Make additional ground-based measurement of total NO column at high solar zenith angles. Attempt to improve technology so that measurements can be made at lower zenith angles where complications associated with rapid changes in $NO/N0_2$ ratio are fewer.

(ii) (0-2) Make continued aircraft measurements of stratospheric NO column, preferably co-located and simultaneous with selected ground-based measurements. Aircraft measurement frequency can be less than that for ground-based measurements once the relationship between the aircraft-based and ground-based columns is understood.

(iii) (0-2, 2-5) Make periodic measurements of NO using programmable wavelengths (in vicinity of gamma bands) from SBUV-2 satellite.

(iv) (4-8) Make measurements of NO from ISAMS, CLAES, and HALOE experiments on UARS.

(v) (4-8) Carry out laboratory experiments and modeling calculations necessary for accurate assessment of non-LTE effects in stratospheric NO which may influence detection by infrared thermal emission.

(vi) (8-10) Develop improved instrumentation for satellite-based remote sensing of NO for use on EOS.

(2) Nitrogen Dioxide ($N0_2$)

(a) Rationale for Monitoring

Over much of the stratosphere $N0_2$ is expected to be the dominant odd nitrogen species at night; only $HN0_3$ (and perhaps N_20_5 in polar night) will be present in comparable amounts. As mentioned above, it is involved in the major pathway removing ozone from the stratosphere. It reacts with OH, $H0_2$ and ClO to form the reservoir molecules $HN0_3$, $HN0_4$, and $ClON0_2$, respectively. The amount of $N0_2$ in the stratosphere is especially important, as the efficiency of chlorine in destroying ozone increases non-linearly, and the amount of chlorine at which the non-linearity becomes important is very dependent on $N0_2$ concentrations.

Stratospheric $N0_2$ can vary with location and time, however. Because it can be easily converted into NO, $HN0_3$, and N_20_5, its concentrations will not be simply related to the total available odd nitrogen concentration, especially since $HN0_3$ and N_20_5 are sufficiently long-lived that they may be subject to transport. There is evidence that the amount of odd nitrogen, especially $N0_2$, may be affected by downward transport of NO from the mesosphere in polar winter; this may be related to the solar cycle. The large changes originally suggested (Callis and Natarajan, 1986) based on a preliminary analysis of satellite data appear not to have occurred, based on subsequent analysis of both satellite and ground-based measurements (Ozone Trends Panel, 1988). This variability and complexity mean that measurements of $N0_2$ over long periods of time will be needed if one is to get a good idea of any long-term trends, as individual measurements, especially at high latitudes in the winter, may not reflect average global conditions.

(b) Monitoring Requirements

Similar considerations for monitoring $N0_2$ apply as for NO discussed in section 6.2.2. (1)(a) above. An important difference, however, is that column $N0_2$ measurements may be made by visible absorption techniques as well as by infrared techniques, as have been used for NO. Thus, different zenith angles for measurement may be available for $N0_2$ than for NO depending on the spectrometers employed.

(c) Equipment Qualified for Monitoring

Other than 0_3, $N0_2$ is the constituent for which the most information has been obtained from satellites. $N0_2$ data has been obtained from four different satellites -- LIMS, SAGE, SAGE II, and SME -- using several different observational techniques. Measurements corresponded to several different local times, approximately 1 and 11 p.m. for LIMS, sunrise and sunset for SAGE and SAGE II, and 3 p.m. for SME. LIMS covered nearly all latitudes and longitudes, while the SAGE and SAGE II instruments gave information on only one or two latitudes per day and SME gave information on only 4 longitudes per day (over North America).

Of these, the LIMS experiment clearly gave the most nearly complete global information, and such a technique is therefore preferable for monitoring, although one must be concerned about possible non-LTE effects (Kerridge and Remsberg, 1987) and long-term stability. Infrared emission measurements of stratospheric $N0_2$ are being planned for both the ISAMS and CLAES experiments on UARS. The CLAES instrument is expected to obtain vertical profiles to higher altitudes than ISAMS, but ISAMS should have a longer useful lifetime due to its use of refrigeration, rather than a solid cryogen, for cooling. The HALOE experiment on UARS also will obtain vertical profiles of $N0_2$, and could be quite useful for monitoring in spite of the fact that it can obtain information on only two latitudes per day, i.e., at sunrise and sunset.

There have also been numerous ground- and aircraft-based measurements of the $N0_2$ column amount. They have been very useful in determining information concerning the short-term, seasonal, and latitudinal variability of $N0_2$. It appears that the current ground-based (visible) techniques can be quite useful in long-term monitoring of $N0_2$. Instrument development currently underway may make improved regular ground-based measurement of $N0_2$ possible in the not-too-distant future.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue existing ground-based measurements of total $N0_2$ column amount from several stations over an extended period of time and implement improved instrumentation as it becomes available.

(ii) (0-2) Make a limited number of aircraft-based measurements of stratospheric $N0_2$ column for comparison with ground-based measurements.

(iii) (0-2, 2-5) Continue current SAGE-II satellite measurements of $N0_2$. Carefully analyze and compare with SAGE-I data.

(iv) (4-8) Make $N0_2$ measurements from UARS with ISAMS, CLAES, and HALOE instruments.

(v) (4-8) Improve understanding of state-resolved chemistry of $N0_2$ in order to better assess possible non-LTE effects and their effect on infrared thermal emission.

(vi) (8-10) Develop new satellite-based techniques for determination of $N0_2$ concentrations and implement on Eos (using IR system as planned for the NOAA GOMR instrument and/or other techniques).

(3) Nitrogen Trioxide ($N0_3$)

(a) Rationale for Monitoring

The major role of $N0_3$ in the stratosphere is as a precursor for N_20_5 through the reaction $N0_2 + N0_3 \rightarrow N_20_5$. Daytime concentrations of $N0_3$ are expected to be very small due to its rapid photolysis. Nighttime concentrations should also be small (below 1 ppbv) because of the reaction with $N0_2$. Monitoring of $N0_3$ is therefore of limited interest; individual measurements, preferably simultaneously with those of $N0_2$, 0_3, and N_20_5, are useful in testing understanding of stratospheric nitrogen chemistry.

(b) Monitoring Requirements

A major consideration in monitoring $N0_3$ is its instrument sensitivity; concentrations are expected to be exceedingly small during daytime (total column density below 1014 molecules cm^{-2}, peak mixing ratios of approximately 1 pptv). During nighttime, larger concentrations may occur; values up to 0.5 ppbv have been observed at midlatitudes at 40 km. Useful monitoring must be able to routinely measure concentrations at these levels with high precision. Large dynamic variability during winter is expected, so high measurement frequency during that time is needed.

(c) Equipment Qualified for Monitoring

Ground-based determination of nighttime $N0_3$ columns by visible absorption spectroscopy using lunar or stellar light sources can be carried out routinely. These measurements have provided substantial information about the amount, variability, and relationship to meteorological processes of the total $N0_3$ column at night (the daytime column is quite small because of rapid photolysis), long-term monitoring of $N0_3$ by this technique should be straightforward.

The only measurements of the vertical profile of stratospheric $N0_3$ were made using balloon-borne spectrometers. It thus appears that monitoring of this quantity is not practical with current technology.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue measurements of nighttime $N0_3$ column using visible absorption spectroscopy, preferably simultaneously with measurements of other nitrogen-containing constituents.

(4) Dinitrogen Pentoxide (N_20_5)

(a) Rationale for Monitoring

Dinitrogen Pentoxide is expected to be an important reservoir molecule for odd nitrogen, especially in and near polar night, where there is little or no sunlight to photodissociate it. It is expected to strongly reflect dynamical processes, and should therefore have large longitudinal and temporal variability during winter. It will have strong diurnal variation over nearly the entire globe. Its concentration may also be affected by the presence of aerosols or polar stratospheric clouds, as there is evidence that there is a heterogeneous process leading to $HN0_3$ formation in winter; the reaction of $N_20_5 + H_20 \rightarrow 2HN0_3$ is suspected (Evans, et al., 1985; Austin, et al., 1986; Jackman, et al., 1987). N_20_5 should also respond to variations in total odd nitrogen described above for $N0_2$.

All these sources of variation combine to make determination of average concentrations of N_20_5 difficult in the absence of a large number of measurements. Long-term monitoring would therefore be of great use. Since a fundamental quantity of interest in the atmosphere (and one directly addressed by photochemical models) is the total amount of available odd nitrogen (e.g., $NO + N0_2 + N0_3 + HN0_3 + HN0_4 + ClON0_2 + 2N_20_5$), determination of the N_20_5 amount is important, as it may constitute an important fraction of that quantity.

(b) Monitoring Requirements

Monitoring of N_20_5 will be complicated by strong diurnal, short-term (dynamical), and seasonal variability described above, which will combine to make high measurement frequency important. Because of the small scale height at N_20_5 at higher altitudes, good vertical resolution will be very important for accurate determination of N_20_5 concentrations.

(c) Equipment Qualified for Monitoring

The only unambiguous measurements of stratospheric N_20_5 are those made recently by the ATMOS (Russell, et al., 1988) and Stratospheric Infrared Interferometer Spectrometer (SIRIS) experiments (a measurement using a pressure modulator radiometer had been reported previously, but was considered tentative by its investigator). The ATMOS measurement, based on infrared solar absorption at occultation, was successful only for sunrise, when N_20_5 concentrations are expected to be at their maximum; a measurement at sunset, when they should be at their minimum, was unsuccessful. Such measurements could be used for monitoring if an appropriate satellite-based spectrometer could be constructed and flown - although the nature of the occultation measurement (only one latitude per day for sunrise measurements) could make interpretation of these measurements very difficult. A carefully scheduled series of regular shuttle flights for ATMOS could provide some information on long-term trends in N_20_5, but the interpretation of results from such a series could be complicated by the dynamically induced variations of N_20_5 at high latitudes in winter (when N_20_5 concentrations are expected to be largest). The SIRIS experiment, which is balloon borne, is not well-suited for monitoring of constituent concentrations in its present form, although improvements in technology may make a satellite-borne version possible towards the end of the 10-year time frame considered in this document.

The CLAES and ISAMS spectrometers on UARS are being developed to have the capability to measure stratospheric N_20_5 concentrations. These instruments, based on infrared thermal emission, have the advantage of allowing for measurement at all latitudes. Even so, interpretation of these measurements, coming at different local times as a function of time (due to the inclination of the UARS orbit) could make trend determination for this diurnally and seasonally varying constituent complicated. Use of a polar orbiting satellite or a series of ground-based stations would probably be preferable.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Carry out occasional ATMOS flights or SIRIS-type balloon measurements to help improve the database of N_20_5 vertical profiles and diurnal variations. Make similar measurements from ground-based ATMOS if possible.

(ii) (4-8) Make N_20_5 measurements using ISAMS and CLAES instruments on UARS.

(iii) (8-10) Investigate satellite.based detection methods which might be used on Eos.

(5) Nitric Acid ($HN0_3$)

(a) Rationale for Monitoring

Nitric Acid is one of the most important nitrogen-containing reservoir molecules in the stratosphere. Its maximum concentration at high latitudes is in winter in the lower stratosphere. It can have large longitudinal gradients, which arise from large meridional and vertical gradients in the presence of strong dynamics. Its chemistry had been thought to be well-understood; formation was via reaction of OH with $N0_2$, while loss was by photolysis and reaction with OH. There clearly are problems associated with its chemistry, however, as one-dimensional models have difficulty obtaining correct vertical dependence and two-dimensional models incorrectly predict the seasonal dependence of high-latitude $HN0_3$. Correction of the latter problem requires an additional mechanism for conversion of N_20_5 to $HN0_3$, probably involving heterogeneous reactions as described above.

Since concentrations of $HN0_3$ are large and variable, and the chemistry is not fully understood, monitoring of $HN0_3$ is important. But because $HN0_3$ does not play a direct role in most of the chemical processes occurring in the stratosphere, monitoring of $HN0_3$ is of less importance than that of $N0_2$, for instance. Simultaneous measurement of $N0_2$ and $HN0_3$ would be of great use, however, since at night these two molecules account for some 75 percent of total odd nitrogen.

(b) Monitoring Requirements

Like the other nitrogen-containing constituents, $HN0_3$ has strong short-term and seasonal variation over much of the stratosphere. Thus, many frequent measurements must be made if long-term trends are to be reliably resolved. Unlike the other constituents, it has no appreciable diurnal variation over most of the stratosphere, so there is no major constraint on signal integration time beyond that required by consideration of short-term variation. Since $HN0_3$ mixing ratios peak in the winter pole near 30 mb and fall off rapidly above and below, good vertical resolution (on the order of the scale height for $HN0_3$, which may be 3 km) is necessary if its vertical profile is to be reliably determined.

(c) Equipment Qualified for Monitoring

The success of the LIMS experiment on the Nimbus-7 satellite suggests that monitoring of $HN0_3$ concentrations by satellite-based remote sensing is the preferred technique for long-term monitoring. The CLAES and ISAMS instruments on UARS are both designed to detect $HN0_3$, covering the altitude range from 10-40 and 15-45 km, respectively. The ISAMS instrument, which does not require the use of solid cryogen, is an especially attractive one for long-term monitoring if long-term stability can be assured.

Aircraft-based measurement of the $HN0_3$ column above flight altitude may also be made using infrared solar absorption techniques as well as by infrared emission. Numerous such measurements have been made, giving useful information about the latitudinal and seasonal variation of the stratospheric $HN0_3$ column. Development of improved ground-based techniques that would allow for the determination of $HN0_3$ vertical profiles could be an attractive alternative to satellite measurements. Measurement of the total $HN0_3$ column from the ground would be less useful, although still helpful.

(d) Strategy for Monitoring

(i) (0-2) Make periodic measurements of stratospheric $HN0_3$ column from aircraft until ground-based techniques are available.

(ii) (2-5) Consider development of ground-based methods for detection of $HN0_3$ column or vertical profile. When these become available, use them routinely and continue aircraft measurements only until correlation between total column and stratospheric column is established (if total column is measured).

(iii) (4-8) Make measurements of $HN0_3$ using ISAMS and CLAES instruments on UARS.

(iv) (8-10) Consider implementation of satellite-borne measurement techniques for Eos, such as the potential NOAA GOMR instrument.

(6) Peroxynitric Acid ($HN0_4$)

(a) Rationale for Monitoring

Peroxnyitric Acid is a reservoir species for both hydrogen and nitrogen, most importantly in the lower stratosphere. The major role of $HN0_4$ in stratospheric chemistry is as a reactant in the reaction $OH + HN0_4 \rightarrow H_20 + N0_2 + 0_2$, which is a major contributor to odd hydrogen loss in the lower stratosphere. The concentration of $HN0_4$ is expected to be everywhere less than that of $HN0_3$, however, so it is of less importance, and the necessity of monitoring is limited. As a reservoir species, measurement of its concentration could have great usefulness as the verification of photochemical models, although a small set of measurements should be sufficient for this purpose.

(b) Monitoring Requirements

Monitoring of $HN0_4$ will be difficult because of its low concentrations; the largest mixing ratio expected in the stratosphere is on the order of 0.6 ppbv. Such concentrations occur only in a relatively narrow altitude range from 25 to 30 km, with very rapid decreases above and below. Extremely good vertical resolution is necessary if the $HN0_4$ vertical profiles are to be obtained. Like $HN0_3$, $HN0_4$ is expected to have little or no diurnal variation, therefore long signal integration times are possible. Large meridional gradients in the winter hemisphere may lead to fairly substantial short-term variability at low altitudes. Relatively frequent measurements may be needed to determine long-term trends in mid-latitude and polar winter, while less frequent measurements are probably necessary at other latitudes and seasons.

(c) Equipment Qualified for Monitoring

There appear to be no techniques currently available that could be used for routine monitoring of $HN0_4$. The only clear measurement of its vertical profile in the stratosphere was by the ATMOS experiment on Spacelab 3, and because of the occultation-nature of the measurement, this provided information on only two latitudes (31°N, 47°S). A satellite-borne version of ATMOS could in principle be used for $HN0_4$ monitoring, as could a series of ATMOS shuttle flights. Due to the expected seasonal and latitudinal variability of $HN0_4$, such flights would need to be made at similar times of the year and with similar orbits for their use to be appropriate for monitoring. Improving technology might allow a satellite-borne infrared emission spectrometer capable of detecting $HN0_4$ to be constructed towards the end of the ten-year period discussed here.

No ground-based techniques for measurement of $HN0_4$ have been implemented, although consideration of the use of infrared solar absorption measurements from high-altitude ground stations is underway. If feasible, such measurements could be quite useful in monitoring stratospheric $HN0_4$ concentrations.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Consider possibility of in situ measurements of $HN0_4$.

(ii) (2-5) Consider possibility of making regular ground-based measurements of total $HN0_4$ column.

(iii) (2-5) Make additional ATMOS observations from occasional flights.

(iv) (8-10) Consider improvements in infrared technology which would make satellite-based measurements possible. Implement on Eos if possible.

6.2.3. Chlorine-Containing Species

(1) Chlorine Monoxide (ClO)

(a) Rationale for Monitoring

Chlorine Monoxide is the major form of chlorine which is catalytically active in stratospheric ozone destruction, especially at mid-high latitudes. This destruction occurs by the cycle

$$\begin{array}{c} Cl + 0_3 \text{ -> } 0_2 + ClO \\ 0 + ClO \text{ -> } Cl + 0_2 \\ \hline 0 + 0_3 \text{ -> } 0_2 + 0_2 \end{array}$$

Its concentration is simply related to that of Cl, (the other form of chlorine which is active in ozone destruction) by a photochemical equilibrium approximation

$$\frac{[Cl]}{[ClO]} = \frac{[O]k(O + ClO \text{ -> } Cl + 0_2) + [NO]k(NO + ClO \text{ -> } Cl + N0_2)}{[0_3]k(Cl + 0_3 \text{ -> } ClO + 0_2)}$$

in daytime; at night [Cl] may be assumed to be zero throughout the stratosphere. ClO serves as the precursor of the reservoir chlorine, containing species HOCl and $ClON0_2$, which are formed by reaction with $N0_2$ and $H0_2$, respectively, and plays a minor role in the interconversion of NO and $N0_2$. It has a diurnal cycle associated with its interconversion with the reservoir molecule $ClON0_2$. In the lower stratosphere its concentrations at night will be exceedingly small unless $ClON0_2$ formation has been inhibited by removal of much or all of the stratospheric $N0_2$, as has been suggested for Antarctic spring (Solomon, et al., 1986; McElroy, et al., 1986; Crutzen and Arnold, 1986). Observations of enhanced lower stratospheric South Polar ClO have recently been reported (P. Solomon, et al., 1987).

The importance of ClO in the destruction of stratospheric ozone and the probability that total stratospheric chlorine concentrations are increasing with time make the monitoring of stratospheric ClO one of the most important tasks in any long-term program studying the composition of the stratosphere. The significant role suggested for ClO in Antarctic ozone depletion makes its measurement in the polar regions in winter and spring especially important.

(b) Monitoring Requirements

Because of its importance, ClO measurements should be made with high frequency and precision at several sites. It has a strong diurnal variation, therefore short signal integration times are important. Its meridional gradients are weak except near the winter pole, and there only near its 40 km mixing ratio peak. There are strong vertical gradients above and below that altitude, however, so good vertical resolution in any measurement technique is essential. If the predicted increase of stratospheric Cl (about 5 percent per year) is to be observed, measurement frequency and accuracy need not be too high, even given the expected short-term and seasonal variability of ClO. The day-to-night ratio of ClO is a particularly important quantity (and one that may vary with time if there are changes in stratospheric nitrogen content) and thus any monitoring method should work well throughout the diurnal cycle if it is to be truly useful.

(c) Equipment Qualified for Monitoring

Ground-based millimeter-wave techniques have been extensively used for the study of the total column, vertical profile, and diurnal variation of ClO in the stratosphere and appear to be the method of choice for its long-term monitoring. These methods are not ideal, however, as they are of limited vertical resolution (approximately one atmospheric scale height) and have difficulty determining ClO concentrations in the lower stratosphere. This is not a major problem under typical conditions, as ClO concentrations are quite small (0.1 ppbv) below 30 km. In areas where ClO may occur in larger amounts in the lower stratosphere, as has been suggested for the Antarctic spring stratosphere, the millimeter-wave techniques are less useful.

Ground-based measurements have also been made by infrared laser heterodyne techniques, but these have suggested smaller ClO abundances than are expected based on the millimeter-wave or in situ measurements. Exact calibration of this technique requires an accurate knowledge of the infrared line strength parameters for ClO, which is a difficult problem. Use of this technique in trend measurement, where absolute accuracy is of less importance, may be worthwhile. It does have the advantage of being more sensitive to ClO in the lower stratosphere, so it may prove to be a useful complement to the millimeter-wave techniques if monitoring of lower stratospheric ClO becomes important.

Aircraft-based measurements of ClO have been made of lower stratospheric ClO using a chemical conversion/resonance fluorescence technique. This instrument was tested at mid-latitudes (Brune, et al., 1988) and flown on the ER-2 aircraft as part of the Airborne Antarctic Ozone Experiment in 1987.

Satellite-based measurement of ClO by two techniques should be made by UARS. ClO vertical profiles from 25 to 45 km will be made with the MLS experiment. These measurements should be quite accurate (to approximately 0.1 ppbv for profiles made with one minute time resolution and 0.01 for global zonal monthly maps). Detection of ClO over a broader altitude range has also been planned for the CLAES experiment, but the difficulty of this detection makes it probable that only very limited data on ClO will become available from this experiment.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Make frequent measurements of ClO vertical profile and total column from several stations simultaneously. Improve instrument sensitivity (so that shorter signal integration times are possible. Improve bandwidth and baseline stability of instrument for measurements of lower stratospheric ClO.

(ii) (0-2, 2-5) Better understand the discrepancy between the heterodyne infrared and milliter-wave techniques. Obtain good experimental infrared line strengths for ClO to allow for unambiguous conversion of absorption to concentrations. Test for agreement with ClO from millimeter-wave methods in lower stratosphere.

(iii) (4-8) Make ClO measurements from UARS using MLS instruments, and if possible, the CLAES instrument.

(iv) (4-8) Consider possible non-LTE effects that may affect infrared state-to-state chemistry of ClO, including vibrational state distribution of $Cl + 0_3 \rightarrow ClO + 0_2$ reaction and ClO quenching by 0_2.

(v) Work to improve satellite-based techniques planned for UARS to allow for better sensitivity and resolution on EOS.

(2) Hydrogen Chloride (HCl)

(a) Rationale for Monitoring

Hydrogen Chloride serves as a reservoir species for chlorine in the stratosphere. Under normal conditions it is expected to have the largest concentration of any odd chlorine species in the upper stratosphere. Its chemistry is relatively straightforward, being formed from active chlorine primarily by reaction of Cl with CH_4 and being lost by reaction with OH, although other reactions make minor contributions to its budget. The amount of HCl in the stratosphere is believed to depend on both latitude and season and may also have short-term variability due to meteorological processes.

Its role as a repository of much of the active stratospheric chlorine makes its monitoring important, because measurement of HCl may provide a more complete idea of the total chlorine burden in the stratosphere than would measurements of ClO, even though the latter plays a more active chemical role. Since the total amount of chlorine in the stratosphere is believed to be increasing with time, measurements of HCl may therefore be the most direct method of confirming such increases. Trends may not be monotonic, however, as volcanic eruptions may inject large amounts of HCl into the stratosphere over short periods of time. Aircraft measurements made so far have been interpreted as showing an average annual increase of 5 percent per year in HCl column above 12 km, while ground-based measurements suggest a considerably smaller increase

(Zander, et al., 1987a; Ozone Trends Panel, 1988) in the total column. Long-term monitoring of HCl should therefore be a very important part of any monitoring program.

(b) Monitoring Requirements

A monitoring program for HCl should be constructed to allow for accurate determination of long-term trends associated with increasing chlorine content in the stratosphere. It should also ideally focus on the stratosphere. Column measurements from the ground are less desirable than measurements of the vertical profile or the stratospheric column. Frequent measurements will be needed if trends are to be accurately determined, because HCl has strong vertical and meridional gradients, especially in the winter hemisphere, and should vary both in the short-term and seasonally. Short signal integration time is not required as HCl should have little or no diurnal variation.

(c) Equipment Qualified for Monitoring

A variety of techniques appear to be available for the monitoring of stratospheric HCl concentrations, although none may prove to be perfect. Ground-based measurements of the total HCl column have been successfully made by several groups at different locations, including the South Pole (Goldman, et al., 1987). But these have the disadvantage of including a potentially non-negligible component of tropospheric HCl, which is believed to be highly variable. Thus, long-term measurements of the total HCl column may not allow for the unambiguous determination of stratospheric HCl column amounts.

Aircraft measurements of the column amount of HCl above some reference altitude (typically 12 km) have also been made routinely. These have the advantage of being above nearly all of the troposphere so that one can neglect the contribution of tropospheric HCl. Aircraft measurements are more difficult and expensive than ground-based ones, and the variability in stratospheric HCl makes it important that a large number of measurements be made if small long-term trends are to be sorted out from the data.

Ground-based measurements of the vertical profile of stratospheric HCl have also been reported (Goldman, et al., 1986). This method has been demonstrated to be reasonably insensitive to the assumed contribution of tropospheric HCl. It appears to have great potential for the retrieval of information about the vertical profile of HCl in the stratosphere, and may be exceedingly useful in long-term monitoring.

Until now no satellite-borne measurements of HCl have been made. Two measurements of HCl on the UARS experiment are being planned, however. One, by the CLAES experiment, will use infrared thermal emission and should be able to obtain HCl vertical profiles over the altitude range from nearly 10 to 50 km while covering nearly all latitudes. These measurements may have non-LTE effects (Mergenthaler and Kumer, 1986) which will need to be incorporated into the data inversion algorithm. The other, using the HALOE experiment, will cover only the 10 to 40 km range and will obtain information on only two latitudes per day (sunrise, sunset) because of the occultation nature of the measurement. Such a technique could operate for a longer period of time than the CLAES technique, which relies on a solid cryogen for cooling of its infrared detector. Balloon-borne far-infrared determinations of the vertical profile of stratospheric HCl appear feasible

(Abbas et al., 1984), and extension of this technique to space-borne platforms in the time frame of this document is quite possible.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue ground-based measurements of total HCl column from Jungfraujoch observatory and elsewhere with sufficient frequency to characterize long-term trends and seasonal cycles; make regular measurements of HCl vertical profile where possible.

(ii) (0-2) Continue aircraft and shuttle (ATMOS) measurements of stratospheric HCl column. Some aircraft measurements should be co-located and simultaneous with selected ground-based column measurements.

(iii) (0-2, 2-5) Better understand tropospheric HCl column amounts and variability, with some measurements made in conjunction with ground-based column measurements.

(iv) (4-8) Make HCl measurements from UARS using HALOE and CLAES instruments. Non-LTE effects which might influence CLAES results should be understood.

(v) (8-10) Consider improved satellite-based detection of HCl including (but not limited to) far-infrared techniques for implementation on or prior to Eos.

(3) Chlorine Nitrate ($ClON0_2$)

(a) Rationale for Monitoring

Chlorine Nitrate is, after HCl, the most important chlorine-containing reservoir species in the stratosphere. It has strong diurnal variability because of its interconversion with ClO (see section 6.2.3.(a)) and can be expected to reflect dynamical activity in winter in the lower and middle stratosphere, where its concentrations are relatively large and its photochemical lifetime is fairly long. Thus, it will have temporal and longitudinal variabilities, which together make a large number of measurements necessary if its average concentration is to be well determined. Monitoring of $ClON0_2$ is of less importance than that of ClO or HCl, but would still be very useful, as it can include a major portion of the available odd chlorine in the stratosphere.

(b) Monitoring Requirements

$ClON0_2$ is expected to be present in, at most, the 1-1.5 ppbv range for current chlorine levels, with strong diurnal variation at most altitudes and latitudes in the stratosphere, so monitoring techniques should be sensitive and require short signal integration times. Frequent measurements are needed, especially in the winter hemisphere when $ClON0_2$ distributions are expected to reflect the dynamical processes in the stratosphere. The expected mixing ratio peak is between 20 and 30 km, requiring that any monitoring technique be sensitive in the middle and lower stratosphere. A small vertical scale height above and below the peak necessitates good vertical resolution for determining accurate vertical profiles.

(c) Equipment Qualified for Monitoring

Measurement of vertical profiles of $ClON0_2$ in the stratosphere has proven to be quite difficult. Only recently, with the ATMOS experiment on Spacelab 3 (Raper, et al., 1987) and the balloon-borne SIRIS experiment (Massie, et al., 1987), has its unambiguous detection been carried out and its vertical profile determined. The same principle used in the ATMOS experiments (infrared solar absorption measurements by solar occultation during sunrise and sunset) could, in principle, be carried out on a satellite. Alternatively, a series of flights of the ATMOS spectrometer could be used to obtain $ClON0_2$ profiles on a regular basis (e.g., annually). Use of such measurements for monitoring purposes would require that they be made at comparable times of the year with similar orbits, and this might be logistically difficult. Such occultation measurements also have the disadvantage of providing only two latitudes -- one at sunrise and one at sunset (in opposite hemispheres). For species with diurnal variation due to photochemical processes, comparison between these two sets of measurements must be made carefully.

Measurements of stratospheric $ClON0_2$ are being planned for the CLAES experiment on UARS, which should cover the 20 to 30 km altitude range (below and near the peak of mixing ratios). These have the potential for being more global, depending on the signal strength for $ClON0_2$.

Some thought is being given to the use of solar absorption measurements from the Jungfraujoch station in the Swiss Alps to determine stratospheric $ClON0_2$ concentrations. If Practical, such measurements could be extremely useful in monitoring of $ClON0_2$.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Make additional ATMOS or SIRIS measurements to get additional information about $ClON0_2$ distribution and variability.

(ii) (2-5) Further investigate possibility of making column measurements from the ground.

(iii) (4-8) Make measurements of $ClON0_2$ using CLAES instrument on UARS.

(iv) (8-10) Further investigate satellite-based techniques for measurement with an aim of inclusion on Eos.

(4) Hypochlorous Acid (HOCl)

(a) Rationale for Monitoring

Hypochlorous Acid is also a reservoir species for chlorine in the stratosphere, but it is of less importance than HCl and $ClON0_2$. Its chemistry is straightforward, being produced by the reaction of ClO and $H0_2$, and being lost primarily by photolysis. Its photochemical lifetime is shorter than that of $ClON0_2$, and its concentration is expected to be smaller (unless heterogeneous processes have removed stratospheric $N0_2$, as has been suggested for Antarctic spring). In many cases its concentration may be inferred from simultaneous measurements of ClO and $H0_2$ or their precursors, so that actual measurements may not be needed to obtain reasonably accurate information about its concentration. Of the chlorine species mentioned so far, its monitoring is the least important.

(b) Monitoring Requirements

Sensitive techniques will be necessary for monitoring HOCl because of its estimated small concentrations (below 0.3 ppbv) and its complicated diurnal variation. Its mixing ratio peak is relatively high in the stratosphere (35 to 40 km), but its mixing ratio decreases rapidly with altitude above and below the peak, so good vertical resolution is necessary if accurate vertical profiles are to be retrieved. Its meridional gradients are relatively weak and its photochemical lifetime is fairly short, which suggest that short-term variability might be less than that of other chlorine-containing species. Therefore, reduced measurement frequency might be possible for HOCl monitoring.

(c) Equipment Qualified for Monitoring

There appear to be no measurement techniques currently available that could be routinely applied to the measurement of stratospheric HOCl. The only published measurement of stratospheric HOCl is an upper limit vertical profile, based on balloon-borne infrared spectroscopy. Major advances in measurement capability appear necessary before monitoring of HOCl is possible.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Develop techniques for unambiguous detection of HOCl concentrations by any available methods, including in situ methods.

(5) Chlorine Dioxide (OClO)

(a) Rationale for Monitoring

Chlorine Dioxide is not expected to be very abundant over much of the stratosphere, but it has been suggested that it reflects the peculiar chemistry that may be associated with Antarctic ozone depletion. Its monitoring is probably only called for in polar regions in winter, and then is still of less interest than that of ClO and HCl.

(b) Monitoring Requirements

Monitoring of OClO columns requires the ability to measure relatively small columns at large solar zenith angles. High measurement frequency is useful for all near-polar measurements, as the rapid motion of the polar vortex implies that the meteorological conditions associated with the air over any such station may vary with time.

(c) Equipment Qualified for Monitoring

Ground-based visible absorption techniques have been used for measuring the total OClO column amount (S. Solomon, et al., 1987). Most of these measurements have been made from Antarctica as part of the National Ozone Expedition (NOZE) expedition; additional spectra have been taken for comparison purposes elsewhere. The current instrumentation appears adequate for the monitoring of OClO amounts from Antarctica and other high latitude stations in the future. More sensitive techniques would probably be needed if monitoring were desired at lower latitudes, where abundances of OClO are substantially smaller.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue measurements of OClO column near South Pole at high zenith angles. Make some measurements at high northern latitudes if possible. Improve methodology to solve baseline problem at low OClO concentrations at other latitudes.

6.2.4. Aerosols

(1) Aerosols

(a) Rationale for Monitoring

Aerosols can scatter solar radiation, and may be especially important in that they may interfere with ultraviolet measurements of ozone from the ground and from satellites. It can be difficult to unambiguously correct such data for interference from aerosols, which can be highly variable (see below), so the accurate monitoring of aerosols is necessary if ultraviolet techniques (ground-based or satellite-based) are to be used for ozone measurement.

Concentrations and properties of aerosols in the stratosphere may have enormous temporal and vertical variation. Aerosols may be formed as a result of injection of volcanic material directly into the stratosphere as in the El Chichon eruption of 1982. As volcanic clouds spread, they may form thin layers localized in altitude and latitude until breaking up into smaller parts.

Aerosols (and polar stratospheric clouds) have been implicated as having an important role in Antarctic ozone depletion (Solomon, et al., 1986; McElroy, et al., 1986; Crutzen and Arnold, 1987), and any detailed understanding of that phenomena will require that the concentrations and properties of aerosols be understood. Aerosols may serve as a catalyst for heterogeneous chemistry and may also have important radiative effects leading to changes in the dynamical properties of the polar stratosphere. Catalysis of heterogeneous chemistry by aerosols has also been suggested to be important in affecting the chemistry of nitric acid in the winter stratosphere.

(b) Monitoring Requirements

Information about the amount and preferably the optical properties of aerosols should ideally be obtained with sufficient frequency and spatial coverage so that it can be used in the analysis of ultraviolet data on ozone composition.

(c) Equipment Qualified for Monitoring

Several different satellite-based systems have been used effectively for determination of information concerning stratospheric aerosols. These include the SAGE and SAGE II instruments on the Applications Explorer Mission-2 satellite (AEM-2) and ERBS, respectively, the Stratospheric

Aerosol Measurement II (SAM-II) instrument on Nimbus-7, and infrared emission spectrometer on the Solar Mesosphere Explorer (SME) Satellite. The techniques for aerosol detection used by SAGE, SAGE II, and SAM-II require solar occultations, so only one or two latitudes per day were accessible. SME gave information on only a limited longitudinal region, mostly over North America. SAGE, SAGE II, and SAM-II have been very useful in the study of stratospheric aerosol and polar stratospheric cloud amounts (Brogniez and Ignoble, 1987; Kent, 1986; McCormick and Trepte, 1987) and either technique would be suitable for monitoring.

A ground-based technique which also appears suitable for monitoring involves LIDAR (laser radar). This has been used extensively to study aerosols associated with the El Chichon (Thomas et al., 1987) and Nevado del Ruiz (DeFoor and Robinson, 1987) eruption clouds. Altitude ranges from 5 to 40 km are accessible by this technique, although the 15 to 30 km region appears to be the most interesting one.

Airborne LIDARS have also been flown with some success, and used to obtain data on mid-latitude aerosols and clouds and polar stratospheric clouds in the Arctic (Poole and McCormick, 1988) and most recently in the Antarctic as part of the Airborne Antarctic Ozone Expedition (Browell, 1987).

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue satellite-based measurements being made by SAGE-II and SAM II.

(ii) (2-5) Further develop ground-based and airborne lidar techniques so that vertical Profiles of backscatter associated with aerosols can be measured routinely at several locations.

(iii) (0-2, 2-5) Develop technology and theoretical understanding so that aerosol backscatter profiles can be unambiguously converted to number densities and size distributions.

(iv) (4-8) Make measurements using ISAMS instrument on UARS.

(v) (8-10) Develop new techniques for measurement of aerosols from satellite, including infrared measurements for proposed NOAA GOMR instrument.

6.2.5. Additional Species

(1) Bromine Monoxide (BrO)

(a) Rationale for Monitoring

Bromine Monoxide should be one of the major, if not the dominant, bromine-containing molecules in the stratosphere. It participates in a catalytic ozone-destroying cycle, as does ClO, and it may interact with the chlorine chemistry in the stratosphere. The reaction of ClO and BrO to form OClO + Br in the Antarctic stratosphere in spring has been suggested to be important in the observed spring ozone depletion there (Tung, et al., 1986) and to be responsible for the high levels of OClO also observed there (S. Solomon, et al., 1987). Since amounts of atmospheric bromine are believed to be increasing at about the same rate as those of chlorine (Ozone Trends Panel, 1988), it would be very helpful to have some long-term measurements of bromine-containing molecules. Because of its expected large concentrations and its active chemical role, BrO would be the molecule of choice. Alternatively, in the 30 to 35 km region, where BrO is expected to be the dominant inorganic bromine compound, measurements of total inorganic bromine could be made without excessive loss of information, although such measurements are less suitable for monitoring purposes than for straightforward measurement.

(b) Monitoring Requirements

The concentrations of BrO expected in the stratosphere are quite small (15 to 25 ppv) and as a result will require exceedingly sensitive techniques. Measurement frequency should be such that any secular trend in BrO can be detected. This trend might be sufficiently large that a modest monitoring program could suffice. As mentioned above, measurements of total inorganic bromine would be a reasonable, but less desirable, surrogate for those of BrO.

(c) Equipment Qualified for Monitoring

The only published observation of BrO reported to date is an in situ measurement based on a chemical conversion/resonance fluorescence technique (Brune and Anderson, 1986). Additional measurements have been made over Antarctica as a part of the Airborne Antarctic Ozone Experiment. Because this is an in situ technique, it is not an ideal one for long-term monitoring. Any attempts at monitoring BrO must therefore await development of appropriate techniques, Preferably ground- or satellite-based. Measurements of total inorganic bromine also require in situ methods, either aircraft-based for the lower stratosphere (Sedlacek, et al., 1984) or balloon-based for the middle stratosphere (Sedlacek, et al., 1984; Gallagher, 1987). The disadvantage of these measurements is that it is difficult to determine the collection efficiency of the sampling filters for the different bromine compounds, especially BrO.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Make additional in situ measurements of BrO to further clarify amount present, vertical profile, and expected variability.

(ii) (2-5) Develop ground-based techniques that are sufficiently sensitive to measure the low concentrations of BrO expected.

(iii) (8-10) Develop remote sensing techniques that will allow BrO to be determined from Eos.

(2) Hydrogen Fluoride (HF)

(a) Rationale for Monitoring

Hydrogen Fluoride is the repository for nearly all stratospheric fluorine formed after the destruction of chlorofluorocarbons. It is a very stable molecule, lost only by removal into the troposphere by rainout. Both ground-based and aircraft-based measurements of the HF column amount suggest that HF has been increasing exceedingly rapidly in recent years; increases of 5 to 10 percent per year are indicated (Zander et al., 1987b; Ozone Trends Panel, 1988). This increase is superimposed on substantial daily and monthly variability.

Long-term monitoring of HF concentrations would be very useful not only because of its necessity in determining any secular trends in stratospheric HF, but because it would allow for better understanding of stratospheric chlorine measurements. Increases of both HF and HCl would, for example, imply that chlorine increases may be derived primarily from chlorofluorocarbon emissions, while an increase in HCl unaccompanied by an HF increase would suggest that chlorine changes are due to natural emission (e.g. CH3Cl) or other anthropogenic sources (e.g. CH_3CCl_3).

(b) Monitoring Requirements

The large projected increase in stratospheric HF concentrations [organic fluorine in the troposphere is increasing at a rate of 5.4 percent per year (Ozone Trends Panel, 1988)] and the clear existence of a measured trend in the existing data suggest that only a relatively small monitoring effort should be necessary for the determination of secular trends. Nevertheless, the observed short-term and seasonal variability will make year-round measurements necessary if a secular trend is to be clearly isolated. Reduction of uncertainties of both ground-based and aircraft-based techniques is important due to the present discrepancy between the two.

(c) Equipment Qualified for Monitoring

The same ground-based and aircraft-based techniques used for measurement of the HCl column amount may also be used for the HF amount. Some of the same limitations apply to their use, specifically the importance of considering short-term variability and the possible contribution of tropospheric HF to the column observed in the ground-based measurements. Vertical profiles of HF in the 10-40 km altitude region will be obtained by the HALOE instrument on UARS, and these would be helpful for monitoring purposes.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Continue ground-based measurements of total HF column from Jungfraujoch and other observatories over an extended period of time; attempt to increase number of ground-based stations.

(ii) (0-2) Make additional aircraft- and shuttle-(ATMOS) based measurements of stratospheric HF column, some of which should be collocated and simultaneous with the ground-based measurements. Resolve apparent discrepancy between aircraft, and ground-based measurements.

(iii) (4-8) Make measurements of HF using HALOE instrument on UARS.

(3) Sulfur Dioxide ($S0_2$)

(a) Rationale for Monitoring

Sulfur Dioxide is at the center of all sulfur chemistry in the stratosphere. It may be directly injected into the stratosphere by volcanos or formed in the stratosphere by oxidation of other sulfur-containing molecules. $S0_2$ is converted in the stratosphere to sulfuric acid ($H2S0_4$), which makes up the major part of the stratospheric aerosol layer. Thus, knowledge of $S0_2$ concentrations and their variation is important in the understanding of observations of stratospheric aerosols and polar stratospheric clouds. $S0_2$ also absorbs in the ultraviolet, and high levels of $S0_2$ in the stratosphere can influence concentrations of 0_3 remotely sensed using ultraviolet spectroscopic techniques. Accurate knowledge of $S0_2$ would therefore be helpful in better understanding 0_3 concentrations observed in this way, such as with SBUV, SBUV/2 and the Total Ozone Mapping Spectrometer (TOMS) on Nimbus-7, as well as with ground-based Dobson measurements.

(b) Monitoring Requirements

The major need for $S0_2$ measurements is at times of large volcanic eruptions (expected to be the source of most stratospheric $S0_2$), since ultraviolet measurements of ozone are most difficult at these times. Thus, what is especially needed for $S0_2$ is the ability to quickly begin to make measurements of $S0_2$ anywhere over the globe on short notice for short periods of time (from the time of an eruption until $S0_2$ concentrations have been reduced to their background values).

(c) Equipment Qualified for Monitoring

Both the SBUV (McPeters et al., 1984) and TOMS (Krueger, 1983, 1985) instruments on Nimbus-7 have been successfully used to measure column amounts of $S0_2$ in the stratosphere after the eruption of El Chichon. Both are still operating and can be used for $S0_2$ measurement. In addition, SBUV/2 has the capability for making these measurements, although none have been made so far.

(d) Strategy for Monitoring

(i) (0-2,2-5) Continue analysis of TOMS observations of stratospheric $S0_2$ as needed.

(ii) (0-2,2-5) Test ability of SBUV/2 to determine concentrations of $S0_2$ and implement along with periodic background measurements on an as needed basis, thereafter, consistent with adequate determination of ozone concentrations.

(iii) (8-10) Initiate development of new detection techniques for $S0_2$ with sufficient sensitivity so that background concentrations of stratospheric $S0_2$ and the high concentrations of tropospheric $S0_2$ associated with polluted urban areas can be remotely determined from space.

(4) Metals

(a) Rationale for Monitoring

Metals are believed to be present in the stratosphere in very small concentrations (on the order of ten parts per trillion by volume), it has been suggested that metal atoms, most importantly sodium (Na), but also magnesium (Mg) and iron (Fe), may play an important role in the partitioning of chlorine between reservoir and active forms, or in affecting the gas-phase concentration of $HN0_3$, and thus affect ozone concentrations in the upper stratosphere (Rodriguez, et al., 1986; Aikin and McPeters, 1986; Prather and Rodriguez, 1988). As stratospheric chlorine concentrations increase in the future, metal atom chemistry may become more important because of the important role of metal chlorides (e.g., NaCl) as reservoir species.

Metal atoms enter the atmosphere primarily by meteor ablation in the upper mesosphere and lower thermosphere, and are transported downward in the atmosphere, being lost eventually by washout in the troposphere. Since meteor impacts and vertical transport rates can both vary with time, large metal-atom induced perturbations to chlorine and/or nitrogen chemistry may lead to irregular variation of chlorine species concentrations in the stratosphere. This variation could complicate the detection of trends in concentrations of chlorine containing species.

The chemistry of metal atoms in the stratosphere is not completely understood, and in the case of Na may even have little effect on stratospheric chlorine chemistry (Ager and Howard, 1986, so any monitoring program for stratospheric metals, especially Na, should be accompanied by laboratory measurements and theoretical analysis designed to increase understanding of their stratospheric importance.

(b) Monitoring Requirements

The metal-containing compound whose measurement would be most important is NaCl, especially in the upper stratosphere where its effect on chlorine chemistry is expected to be largest. NaCl is expected to be much more abundant than other Na-containing reservoir species in the upper stratosphere ($Na0_2$, NaOH), and is expected to undergo little diurnal variation. A technique suitable for routinely measuring NaCl near 50 km (where concentrations on the order of 10 pptv are expected) is needed. Information on the concentrations of Mg and Fe in polar stratospheric clouds in the Antarctic would also be very useful.

(c) Equipment Qualified for Monitoring

No techniques currently exist for the measurement of stratospheric metal atoms or compounds, including NaCl. Such techniques would need to be developed as part of the monitoring plan.

(d) Strategy for Monitoring

(i) (0-2, 2-5) Do laboratory work to better resolve possible effects of metal atoms in stratosphere, especially on formation and reactivity of clusterions of NaO, NaOH, and $Na0_2$ which may be formed in upper atmosphere.

(ii) (8-10) Develop techniques for use in measurement of stratospheric metals in upper stratosphere.

6.3. Conclusions

It is clear that if the causes of any long-term trends in stratospheric ozone composition or temperature are to be understood, the long-term behavior of the concentrations of a number of trace stratospheric constituents must also be understood. If such understanding is to be obtained, a long series of measurements of these constituents, starting with ground-based and aircraft-based techniques and then being enlarged to include satellite-based monitoring (with UARS and Eos), will be needed.

Any ranking of the order of "importance" of the constituents for which long-term concentration data are needed will be somewhat subjective. It is also impossible to create such a list without consideration if what measurements are possible in the immediate and short term. We, therefore, include here a priority list that takes into account the possibility of desired measurements being made. The list is somewhat subjective in that it reflects the views of the authors of this chapter. It does draw heavily on the priority list developed at the NASA/NOAA/CMA workshop on the Network for the Detection of Stratospheric Change held in Boulder, Colorado, in March 1986 [NASA, 1986]. It differs somewhat from that list in that it includes only those species discussed in this Chapter and includes several species not included in the workshop summary list.

Of particular importance is the fact that many closely-spaced measurements must be made from several locations if long-term trends in the concentrations of a given species are to be determined, as most of these vary on several scales (e.g., short-term due to meteorological processes; seasonally and other long-term variation due to special events such as volcanic eruptions or El Ninos, and possibly due to the 11-year solar cycle; in addition, some constituents have diurnal variations).

Another crucial component of a monitoring program is that one cannot simply switch from one measurement technique to another as new ones become available, even if the newer one is more accurate than the older one. There must be overlaps between measurement periods with different techniques. These periods must be long enough that differences in calibration and precision are very well understood and that any differences in trends between instruments would have a chance to manifest themselves. Furthermore, it is important that several different techniques be used for each constituent.

The ideal monitoring program includes both ground-based and satellite-based techniques. Ground-based techniques have several positive features, including relative ease of long-term calibration (which is absolutely crucial if small secular trends are to be determined); ease of maintenance in case of failure or degradation; and the ability to measure concentrations of species which cannot be measured by existing satellites. Satellite-based techniques offer the advantage of global coverage and the simplicity of using a single instrument for one or more constituents. In the absence of a ground-based measurement network and/or a regular series of shuttle flights of accurately calibrated instruments designed for comparison with satellite-based instruments, such as the planned Shuttle/Solar Backscattered Ultraviolet (SSBUV) missions, ensuring the long-term stability of satellite-based measurement devices unambiguously enough so that small trends may be determined is nearly impossible.

Pairs or groups of measurements can be far more useful than individual ones. For example, an observed trend in daylight or twilight measurements of NO or $N0_2$ may not reflect a change in the stratospheric odd nitrogen budget. A trend in either could be due to changes in the partitioning between NO and $N0_2$, which is controlled by temperature and concentrations of 0_3 and ClO. Simultaneous measurement of NO and $N0_2$ removes this ambiguity. Similarly, measurements of total odd nitrogen ($NO_y = NO + N0_2 + N0_3 + HN0_3 + NNO_4 + ClON0_2 + 2N_20_5$) remove any ambiguity associated with unknown partitioning of nitrogen among its different compounds. An additional advantage of simultaneous measurement is that it can allow for tests of photochemical theory, as well as for the inference of concentrations of trace species whose measurement may prove to be difficult. The obtaining of simultaneous and collocated measurements of related species is an important part of any monitoring program.

The ability to understand and intelligently interpret the results obtained from the proposed monitoring program requires that the atmospheric science community have sufficient modeling capability and an accurate physical and chemical data base. Models play an especially important role in helping to separate cause from effect, as well as in pointing out topics which need further research. Any monitoring plans implemented should be done in a way which ensures extensive interaction between modelers and observers, including access to models and data for those in need.

The constituents are divided into three groups; highest priority, moderate priority, and others. Within each group no rank by priority is given, because the distinctions become quite subjective and, in many cases, arbitrary.

6.3.1. Group I - Highest Priority

(1) ClO vertical profiles. As this is the active form of stratospheric chlorine and as chlorine is the element whose concentration is both very likely to be rapidly increasing and to be very efficient in destroying ozone, measurement of ClO is absolutely central to any monitoring program. Since ground-based techniques for measuring ClO in the upper stratosphere already exist, this is a practical measurement.

(2) H_20 vertical profiles. Besides being radiatively important, H_20 serves as the source of the hydrogen radicals responsible for destroying much of the ozone in the upper stratosphere and most in the mesosphere. It also plays a crucial role in the partitioning of nitrogen and chlorine compounds between active forms, which destroy ozone, and reservoir species, which do not. Its measurement by a variety of techniques has been made for some time, and new technology is being developed to improve measurement capability.

(3) Aerosol vertical distribution. Any understanding of ozone measurements by ultraviolet techniques will require information about the number density and size distributions of stratospheric aerosols. Aerosol distributions also may clearly demonstrate the effect of volcanic eruptions on the stratosphere as well as of changes in temperature fields. Aerosol measurements by several techniques are currently being made.

(4) NO_2 vertical profile or column. As an active and abundant form of odd nitrogen, which is responsible for much of the catalytic destruction of ozone in the stratosphere, NO_2 is a very important constituent. It also plays a role in reducing the effectiveness of chlorine in destroying ozone, so a knowledge of its concentration is mandatory for the understanding of efficiency of chlorine-catalyzed ozone destruction. Since there is some evidence that NO_2 concentrations may vary non-linearly with time on the time scale of years, long-term measurements are crucial. Column measurements have been made for some timely vertical profile measurements have been made from satellites.

(5) HCl vertical profile or column. HCl serves as the reservoir for much of the chlorine in the stratosphere, and should provide a good indicator of the total growth of the stratospheric chlorine content. Measurement of columns has been made for some time although the interpretation of ground-based measurements is difficult; ground-based measurement of vertical profiles appears to be possible.

6.3.2. Group II - Moderate Priority

(1) OH column or vertical profile. OH is at the center of nearly all stratospheric chemistry. It plays a role in the hydrogen-catalyzed destruction of stratospheric ozone, it controls the partitioning of chlorine compounds by reacting with HCl and CH_4, and controls the partitioning of nitrogen compounds between ozone-destroying NO_2 and the inactive HNO_3. Column measurements made from the ground for some time have the disadvantage of having a large mesospheric contribution, so vertical profile measurements would be quite useful. The column measurements also show some unexplained variability with time and location, so additional measurements would be helpful. Technology for ground-based measurements of vertical profiles is slowly being developed, but may not be available for some time.

(2) HNO_3 column or vertical profile. As the most abundant nitrogen- containing reservoir molecule in the stratosphere, its measurement, together with that of nighttime NO_2, would provide a good indicator of the total odd-nitrogen burden of much of the stratosphere. Column measurements of HNO_3 can be made from aircraft, while vertical profile measurements have been made from satellites. If NO_2 measurements are not part of a particular aspect of the monitoring program, such as one satellite mission, HNO_3 measurements increase in priority, as they would then provide the greatest possible information about odd nitrogen concentrations in the stratosphere.

(3) HF column. Measurement of HF, which should be the dominant F-containing molecule in the stratosphere, would be useful in combination with measurements of HCl to provide information about the source of chlorine in the stratosphere. Ground-based and aircraft-based measurements of the HF column have been made in the past.

(4) NO column or vertical profile. Measurement of NO concentrations may be combined with those of NO_2 for both day and night to infer the importance of N_2O_5 and $ClONO_2$, both of which are difficult to measure. In the daytime NO is the dominant nitrogen-containing species in the upper stratosphere, and thus may provide a better indication of the daytime nitrogen partitioning than may NO_2. Ground-based and aircraft-based measurements of NO columns have been made.

(5) $H0_2$ column or vertical profile. $H0_2$, like OH, plays an important role in hydrogen-catalyzed ozone destruction and in the partitioning of nitrogen and chlorine containing compounds. Its measurement together with OH would more or less completely define stratospheric odd hydrogen chemistry. Some ground-based measurements of upper stratospheric $H0_2$ have been made, although technique improvement would be useful, and development of techniques for routinely measuring lower stratospheric $H0_2$ remains an important problem.

6.3.3. Group III - Others

(1) $ClON0_2$ column or vertical profile. $ClON0_2$ is an important reservoir species for Cl, and may become one for N as the amount of chlorine in the stratosphere increases. Routine measurement may occur some time in the future, but its measurement would be useful in that it could account for a sizable fraction of stratospheric Cl and N and is hard to infer indirectly.

(2) BrO column or vertical profile. Bromine is known to be very effective in catalyzing ozone destruction, it may be rapidly increasing in the stratosphere due to the use of anthropogenic bromine-containing compounds. It has been suspected of playing a very important role in the chemistry associated with the Antarctic spring ozone minimum. Measurement techniques suitable for monitoring need to be developed for this species.

(3) N_20_5 column or vertical profile. N_20_5 is an important nitrogen- containing species in the polar stratosphere in winter, and its concentration can reflect the influence of meteorological processes. Thus, its inference from other species is difficult and there is no substitute for measurement. The current capability for ground-based measurement is minimal, however, so monitoring must await technological development.

(4) H_20_2 column or vertical profile. H_20_2 is a reservoir species whose concentration will reflect that of OH and $H0_2$. It is expected to be strongly variable. Its measurement can be very important in assessing our understanding of stratospheric chemistry due to the sensitivity of its predicted values to quantities in photochemical models. Measurement techniques need to be developed for the measurement of its concentration.

(5) HOCl column or vertical profile. HOCl is a reservoir for stratospheric chlorine, but should contain a much smaller fraction of it than does HCl or $ClON0_2$. It may play a more important role in the Antarctic spring, however, and monitoring of its concentration would provide a sensitive test of ideas about the chemistry there. As HOCl has not been definitively detected in the stratosphere, marked improvement in techniques needs to be made before such measurements can be carried out.

(6) $N0_3$ column or vertical profile. $N0_3$ serves as a crucial intermediate in the conversion of $N0_2$ to N_20_5. Its concentration is not very well understood (there is evidence of chemistry missing from photochemical models); therefore, monitoring would be useful in understanding the source and magnitude of this discrepancy. Ground-based measurements of the column have been made in the past.

(7) $S0_2$ column or vertical profile. $S0_2$ is the source of the sulfate in the stratospheric aerosol layer. When present in large amounts in the stratosphere, such as after large volcanic eruptions, it can affect remotely sensed 0_3 measurements made in the ultraviolet. Measurement of $S0_2$ at and shortly thereafter these times would be very useful in assessing any impact of $S0_2$ on observed 0_3 and aerosol amounts.

(8) OClO column or vertical profile. OClO has been implicated as being evidence of the peculiar chemistry suggested to be associated with the Antarctic spring ozone minimum. Measurements of OClO columns have been useful in better understanding such chemistry. Continuation of measurements at high latitudes in winter and spring would further assist in the development and assessment of ideas about that chemistry.

(9) $HN0_4$ column or vertical profile. $HN0_4$ is probably the least important of the nitrogen-containing reservoir species mentioned so far. Nevertheless, its measurement would be useful in providing information for the testing of photochemical models predicting its concentration and variability.

(10) Metal Atoms/Compounds vertical profile or single altitude. Metal atoms, especially sodium (Na), have been suggested as having a potentially large effect on partitioning of chlorine between inactive and active forms in the upper stratosphere. Since this is where Cl-catalyzed ozone decomposition is most important, it is possible that metal atoms might affect ozone concentrations there. The methodology to measure metal compounds at very low levels in the stratosphere must be developed, so monitoring of the compounds is a very long-term goal at best.

APPENDIX A REFERENCES

Abbas, M., J. Guo, I. G. Nolt, and B. Carli, 1984: Far infrared remote sounding of stratospheric temperature and trace gas distributions. J. Atmos. Chem., 2, 145-162.

Abbas, M. M., J. Guo, B. Carli, F. Mencaraglia, A. Bonetti, M. Carlotti, and I. G. Nolt, 1987: Stratospheric 0_3, H_20, and HDO observations from balloon-based far infrared observations, J. Geophys. Res., 92, 8354-8364.

Ager, J. W., III and C. J. Howard, 1986: The kinetics of $Na0+0_2+M$ and $NaO+C0_2+M$ and their role in atmospheric sodium chemistry, Geophys. Res. Lett., 13, 1395-1398.

Aikin, A. C. and R. D. McPeters, 1986: Meteoric material and the behavior of upper stratospheric polar ozone, Geophys. Res. Lett., 13, 1300-1303.

Angell, J. K. and J. Korshover, 1983: Global variations in total ozone and layer-mean ozone: an update through 1981, J. Clim. Appl. Meteor., 22, 1611-1627.

Austin, J., R. R. Garcia, J. M. Russell III, S. Solomon, and A. F. Tuck, 1986: On the atmospheric photochemistry of nitric acid, J. Geophys. Res., 91, 5477-5485.

Blake, D. R., E. W. Mayer, S. C. Tyler, Y. Makide, D. C. Montague, and F. S. Rowland, 1982: Global increase in atmospheric methane concentrations between 1978 and 1980, Geophys. Res. Lett., 9, 477-480.

Bojkov, R., 1986: Surface ozone during the second half of the nineteenth century, J. Clim. Appl. Meteor., 25, 343-352.

Boville, B. A., 1987: The validity of the geostrophic approximation in the winter stratosphere and troposphere, J. Atmos. Sci., 44, 443-457.

Brogniez, C. and J. Lenoble, 1987: Modeling of the stratospheric background aerosols from zonally averaged SAGE profiles, J. Geophys. Res., 92, 3051-3060.

Browell, E. V., 1987: Ozone and Aerosol Dial System, in Airborne Antarctic Ozone Experiment, NASA/Ames Research Center, p. 19.

Brune, W. H. and J. G. Anderson, 1986: In situ observations of midlatitude stratospheric ClO and BrO, Geophys. Res. Lett., 13, 1391-1394.

Brune, W. H., E. M. Weinstock, and J. G. Anderson, 1988: Midlatitude ClO below 22 km altitude, measurements with a new aircraft-borne instrument, Geophys. Res. Lett., 15, 144-147.

Burnett, C. R., K. R. Minschwaner, and E. B. Burnett, 1988: Vertical column abundance measurements of atmospheric hydroxyl from 26N, 40N, and 65N, J. Geophys Res., in press.

Callis, L. B. and M. Natarajan, 1986: The Antarctic ozone minimum: relationship to odd nitrogen, odd chlorine, the final warming, and the 11-year solar cycle, J. Gephys. Res., 91, 10771-10796.

Callis, L. B., R. E. Boughner, and J. D. Lambeth, 1987: The stratosphere: Climatologies of the radiative heating and cooling rates and the diabatically diagnosed net circulation fields, J. Geophys. Res., 92, 5585-5608.

Chance, K. V. and W. A. Traub, 1987: Evidence for stratospheric hydrogen peroxide, J. Geophys. Res., 92, 3061-3066.

Chandra, S., 1986: The solar and dynamically induced oscillations in the stratosphere, J. Geophys. Res., 91, 2719.

Chanin, M..L. and A. Hauchecorne, 1987: Lidar sounding of the structure and dynamics of the middle atmosphere. A review of recent results relevant to transport processes, to appear in Transport Processes in the Middle Atmosphere, D. Reidel Pub. Co.

Charlson, R. J., J. E. Lovelock, M. 0. Andreae, and S. G. Warren, 1987: Oceanic albedo and climate, Nature, 326, 651-656.

Craig, H., and C. C. Chou, 1982: Methane, the record in polar ice cores, Geophys. Res. Lett., 9, 1221-1224.

Crutzen, P., 1976: The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73-76.

Crutzen, P. J. and L. T. Gidel, 1983: A two-dimensional photochemical of the atmosphere; 2, The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4CH_3Cl, and the effect of various NO_x sources on tropospheric ozone, J. Geophys. Res., 88, 6641-6661.

Crutzen, P. J. and F. J. Arnold, 1986: Odd nitrogen incorporation in polar stratospheric clouds: a possible cause for the spring time ozone decay in Antarctica, Nature, 324, 651-655.

Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, A. J. Crawford, P. J. Fraser, and R. D. Rosen, 1983a: The atmospheric lifetime experiment, 3, Lifetime methodology and application in 3 years of $CFCl_3$ data, J. Geophys. Res., 88, 8379-8400.

Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, C. A. Cardelino, and A. J. Crawford, 1983b: The atmospheric lifetime experiment, 4, Results for CF_2Cl_2 based on 3 years of data, J. Geophys. Res., 88, 8401-8414.

DeFoor, T. and E. Robinson, 1987: Stratospheric lidar profiles from Mauna Loa observations, Winter 1985-1986, Geophys. Res. Lett., 14, 618-621.

Dickerson, R. R., 1984: Measurements of reactive nitrogen compounds in the free troposphere, Atmos. Environ., 18, 2585-2593.

Dignon, J. and S. Hameed, 1985: A model investigation of the impact of increases in anthropogenic NO_x emissions between 1967 and 1980 on tropospheric ozone, J. Atmos. Chem., 3, 491-506.

Douglass, A. R., R. B. Rood, and R. S. Stolarski, 1985: Interpretation of ozone temperature correlations 2. Analysis of SBUV ozone data, J. Geophys. Res., 90, 10693-10708.

Douglass, A. R. and R. B. Rood, 1986: Derivation of photochemical information near 1 mb from ozone and temperature data, J. Geophys. Res., 91, 13153-13166.

Elson, L. S., 1986: Ageostrophic motions in the stratosphere from satellite observations, J. Atmos. Sci, 43, 409-418.

Evans, W. F. J., C. T. McElroy, I. E. Galbally, 1985: The conversion of N_20_5 to $HN0_3$ at high latitudes in winter, Geophys. Res. Lett., 12, 825-828.

Fabian P., R. Borchers, S. A. Penkett, and N. J. D. Prosser, 1981: Halocarbons in the stratosphere, Nature, 294, 733-735.

Fahey, D. W., C. S. Eubank, G. Hubler, and F. C. Fehsenfeld, 1985: Evaluation of a catalytic reduction technique for the measurement of total reactive odd - nitrogen NO, in the atmosphere, J. Atmos. Chem., 3, 435-468.

Finger, F. G., M. E. Gelman, F. J. Schmidlin, R. Leviton, and B. W. Kennedy, 1975: Compatibility of meteorological rocketsonde data as indicated by international comparison tests, J. Atmos. Sci., 32, 1705-1714.

Fishman, J. and W. Seiler, 1983: Correlative nature of ozone and carbon monoxide in the troposphere: Implications for the tropospheric ozone budget, J. Geophys. Res., 88, 3662-3670.

Fishman, J., F. M. Vukovich, and E. V. Browell, 1985: The photochemistry of synoptic-scale ozone synthesis: Implications for the global tropospheric ozone budget, J. Atmos. Chem., 3, 299-329.

Fishman, J., P. Minnis, and H. G. Reichle, Jr., 1986: Use of satellite data to study tropospheric ozone in the tropics, J. Geophys. Res., 91, 14,451-14,465.

Galloway, J. N., G. E. Likens, W. C. Keene, and J. M. Miller, 1982: The compositions of precipitation in remote areas of the world, J. Geophys. Res., 87, 8771-8786.

Gallagher, C. C., C. A. Forsberg, and R. V. Pieri, 1983: Stratospheric N_20, CF_2Cl_2 and $CFCl_3$ composition studies utilizing in situ cryogenic, whole air sampling methods, J. Geophys. Res., 88, 3798-3808.

Gallagher, C. C., 1987: Inorganic bromine in the lower stratosphere, J. Atm. Terr. Phys., 49, 299-302.

Gammon, R. H., W. D. Komhyr, and J. T. Peterson, 1985: The global atmospheric $C0_2$ distribution 1968-83; Interpretation of the results of the NOAA/GMCC measurement program, in The Global Carbon Cycle: Analysis of the Natural Cycle and Implications of Anthropogenic and Alterations for the Next Century, edited by J. R. Trabalka and D. E. Reichle, Springer-Verlag, New York.

GMCC, 1985: Geophysical Monitoring for Climatic Change, No. 14, Summary Report, NOAA/ARL, Boulder, CO, Dec. 1986.

Goldman, A., F. J. Murcray, R. D. Blatherwick, and D. G. Murcray, 1986: Quantification of HCl from high-resolution, ground-based, infrared solar spectra in the 3000 cm-l region, J. Quant. Spec. Rad. Trans., 36, 385-387.

Goldman, A., F. J. Murcray, F. H. Murcray, D. G. Murcray, 1987: Quantification of HCl from high resolution infrared solar spectra obtained at the south pole in December 1986, Geophys. Res. Lett., 14, 622-623.

Heath, D. F., T. P. Repoff, and R. F. Donnelly, 1984: Nimbus-7 SBUV observations of solar UV spectral irradiance variations caused by solar rotation and active region evolution for the period November 7, 1978-November 1, 1980, NOAA Tech. Memo., ERL ARL-129, Natl. Oceanic and Atmos. Admin., Boulder, Colo.

Heath, D. F., and B. M. Schlesinger, 1986: The Mg 280 nm doublet as a monitor of changes in solar ultraviolet irradiances, J. Geophys. Res., 91, 8672.

Jackman, C. H., and P. D. Guthrie, and J. A. Kaye, 1987: An intercomparison of nitrogen-containing species in Nimbus-7 LIMS and SAMS data, J. Geophys. Res., 92, 995-1008.

Kavanaugh, M., 1987: Estimates of future CO, N_20, and NO_x, emissions from energy combustion, Atmos. Environ., 21, 463-468.

Kaye, J. A. and C. H. Jackman, 1986: Concentrations and uncertainties of stratospheric trace species inferred from Limb Infrared Monitor of the stratosphere data 1. Methodology and Application to OH and $H0_2$, J. Geophys. Res., 91, 1117-1135.

Kaye, J. A. and J. B. Kumer, 1987: Non-LTE Effects in stratospheric NO and implications for infrared remote sensing, Appl. Opt., 26, 4747-4754.

Keating, G. M., 1981: The response of ozone to solar activity variations: a review, Solar Phys., 74, 321.

Keating, G. M., M. C. Pitts, G. Brasseur, and A. De Rudder, 1987: Response of middle atmosphere to short-term solar ultraviolet variation: I. Observations, J. Geophys. Res., 92, 889.

Keeling, C. D., 1983: The global carbon cycle: What we know and could know from atmospheric, biospheric, and oceanic observations, in Proceedings of the $C0_2$ Research Conference: Carbon dioxide, Science and Consensus, DOE CONF - 820970, pp. II.3-II.62, U. S. Dept. of Energy, Washington, DC.

Kent, G. S., 1986: Dispersion characteristics of volcanically injected aerosol as seen by SAGE I, SAM II, and SAGE II, in Abstracts from 6th AMS Conference on Atmospheric Radiation, Williamsburg, VA, pp. J54-J55.

Kerridge, B. and Remsberg, E. E., 1987: Evidence for non-local thermodynamic equilibrium in the mode of mesospheric H_20 and the mode of stratospheric $N0_2$, EOS, 68, 372.

Khalil, M. A. K., and R. A. Rasmussen, 1983: Increase and Seasonal Cycles of Nitrous Oxide in the Earth's Atmosphere, Tellus, 35B, 161-169.

Khalil. M. A. K. and R. A. Rasmussen, 1984: Carbon monoxide in the Earth's atmosphere; Increasing trend, Science, 224, 54-56.

Khalil, M. A. K., R. A. Rasmussen, 1985: Causes of increasing atmospheric methane: depletion of hydroxyl radicals and the rise of emissions, Atmos. Environ., 19, 397-407.

Khalil, M. A. K. and R. A. Rasmussen, 1986: Trichlorotrifluoroethane (F-113): Trends at Pt. Barrow, Alaska, Geophysical Monitoring for Climatic Change, No. 13, Summary Report 1984, E. C. Nickerson, Ed., pp. 91-93.

Kiehl, J. T. and S. Solomon, 1986: On the radiative balance of the stratosphere, J. Atmos. Sci., 43, 1525-1534.

Komhyr, W. D., S. J. Oltmans, and R. D. Grass, 1987: Atmospheric ozone at South Pole, Antarctica, in 1986, J. Geophys. Res., submitted for publication.

Krueger, A. J., 1983: Sighting of El Chichon sulfur dioxide clouds with the Nimbus-7 Total Ozone Mapping Spectrometer, Science, 220, 1377-1379.

Krueger, A. J., 1985: Detection of Volcanic Eruptions from Space by their Sulfur Dioxide Clouds, in Abstracts from AIAA 23rd Aerospace Sciences Meeting, Reno, Nevada.

Lal, S., R. Borchers, P. Fabian, and B. C. Kruger, 1985: Increasing abundance of $CBrClF_2$ in the atmosphere, Nature, 316, 135-136.

Larsen, J. C., L. R. McMaster, M. P. McCormick, and W. P. Chu, 1986: Measurements of lower stratospheric/upper tropospheric water vapor by the SAGE II instrument, in Abstracts from 6th AMS Conference on Atmospheric Radiation, Williamsburg, VA, pp. J56-J58.

Logan, J. A., 1985: Tropospheric ozone: Seasonal behavior, trends and anthropogenic influence, J. Geophys. Res., 90, 10,463-10,482.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, 1981: Tropospheric chemistry: A global perspective, J. Geophys. Res., 86, 7210- 7254.

Massie, S. T., J. A. Davidson, C. A. Cantrell, A. H. McDaniel, J. C. Gille, V. G. Kunde, J. C. Brasunas, W. C. Maguire, A. Goldman, and M. M. Abbas, 1987: Atmospheric infrared emission of $ClON0_2$ observed by a balloon-borne Fourier spectrometer, J. Geophys. Res., 92, 14806-14814.

McCormick, M. P. and Trepte, C. R., 1987: Polar stratospheric optical depth observed between 1978 and 1985, J. Geophys. Res., 92, 4297-4306.

McElroy, M. B., R. J. Salawitch, and S. C. Wofsy, 1986: Antarctic 0_3: chemical mechanisms for the spring decrease, Geophys. Res. Lett., 13, 1296- 1299.

McInturff, R. M. and F. G. Finger, 1968: The compatibility of radiosonde data at stratospheric levels over the northern hemisphere. ESSA Technical Memorandum WBTM DATAC 2, 61 pp.

McNeal, R. J., 1987: The NASA Global Tropospheric Experiment: Chemical Instrumentation Test and Evaluation (GTE/CITE 7): Preface, J. Geophys. Res., 92, 1976-1987.

McPeters, R. D., D. F. Heath, and B. M. Schlesinger, 1984: Satellite observation of $S0_2$ from El Chichon: Identification and Measurement, Geophys. Res. Lett., 11, 1203-1206.

Mergenthaler, J. L. and J. B. Kumer, 1986: An assessment of OH airglow interference on the remote sensing of stratospheric HCl via limb sounding in the near-IR, Int. J. Rem. Sens., 7, 1203-1211.

NASA, 1986: Network for the Detection of Stratospheric Change, Report of the Workshop, Boulder, CO, March 5-7, 1986, NASA, Washington, D.C.

NASA, 1987: Space opportunities for tropospheric chemistry research, ed. J. S. Levine, NASA CP-2450, 90 pp., NASA, Washington, DC.

Nash, J. and G. F. Forrester, 1986: Long term monitoring of stratospheric temperature trends using radiance measurements obtained by the TIROS-N series of NOAA spacecraft, Adv. Space Res., V, 37-44.

Nash, J. and F. J. Schmidlin, 1987: Final report of the WMO international radiosonde intercomparisons, WMO Report No. 30.

National Research Council (NRC), 1984; Global Tropospheric Chemistry, A Plan for Action, National Academy Press, Washington, DC.

NOAA, 1982: The National Plan for Stratospheric Monitoring and Early Detection of Change, 1981-1986, FCM-P17-1982, 79, Federal Coordinator for Meteorological Services and Supporting Research, NOAA, Rockville, MD.

Oltmans, S. J., 1986: Water vapor profiles for Washington, DC; Boulder, CO; Palestine, TX; Laramie, WY; and Fairbanks, AK; during period 1974 to 1985, NOAA Data Report ERL ARL-7, NOAA, Silver Spring, MD.

Oltmans, S. J. and W. D. Komhyr, 1986: Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climatic Change Baseline Observations, J. Geophys. Res., 91, 5229-5236.

Ozone Trends Panel, 1988: Executive Summary, NASA, Washington, DC. Poole, L. R. and M. P. McCormick, 1988: Airborne lidar observations of Arctic polar stratospheric clouds, Geophys. Res. Lett., 15, 21-23.

Prather, M., M. Elroy, S. Wofsy, G. Russell, and D. Rind, 1987: Chemistry of the global troposphere: fluorocarbons as tracers of air motion, J. Geophys. Res., 92, 6579-6613.

Prather, M. J. and J. M. Rodriguez, 1988: Antarctic Ozone: Meteoric control of $HN0_3$, Geophys. Res. Lett., 15, 1-4.

Prinn, R. G., P. G. Simmonds, R. A. Rasmussen, R. D. Rosen, F. N. Alyea, C. A. Cardelino, A. J. Crawford, D. M. Cunnold, P. J. Fraser, and J. E. Lovelock, 1983a: The atmospheric lifetime experiment, 1. Introduction, instrumentation and overview, J. Geophys. Res., 88, 8353-8367.

Prinn, R. G., R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, D. M. Cunnold, B. C. Lane, C. A. Cardelino and A. J. Crawford, 1983b: The atmospheric lifetime experiments, 5, Results for CH_3CCl_3 based on three years of data, J. Geophys. Res., 88, 8415-8426.

Prinn, R. G., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, R. Rosen, 1987: Atmospheric trends in methylchloroform and the global average for the hydroxylradical, Science, 238, 945-950.

Quiroz, R. S. and M. E. Gelman, 1972: Direct determination of thickness of stratospheric layers from single channel satellite radiance measurements, Mon. Wea. Rev., 100, 788-795.

Ramanathan, V. R., J. Cicerone, H. B. Singh, and J. T. Kiehl, 1985; Trace gas trends and their potential role in climate change, J. Geophys. Res., 90, 5547-5566.

Ramanathan, V., L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lacis, F. Luther, J. Mahlman, R. Reck, and M. Schlesinger, 1987: Climate-chemical interactions and effects of changing atmospheric trace gases, Rev. Geophys., 25, 1441.1482.

Raper, 0. F., C. B. Farmer, R. Zander, and J. H. Park, 1987: Infrared spectroscopic parameters of halogenated sink and reservoir gases in the stratosphere with the ATMOS instrument, J. Geophys. Res., 92, 9851-9858.

Rasmussen, R. A. and M. A. K. Khalil, 1986: Atmospheric Trace Gases: Trends and distributions over the last decade, Science, 232, 1623-1624.

Reichle, H. G., Jr., V. S. Conners, J. A. Holland, W. D. Hypes, H. A. Wallio, J. C. Casas, B. B. Gormsen, M. S. Saylor, and W. D. Hasketh, 1986: Middle and upper tropospheric carbon monoxide mixing ratios as measured by a satellite borne remote sensor during November 1981, J. Geophys. Res., 91, 10,865-10,888.

Remsberg, E. E., 1986: The accuracy of the Nimbus 7 LIMS temperatures in the mesosphere, Geophys. Res. Lett., 13, 311-314.

Rinsland, C. P. and J. S. Levine, 1985: Free tropospheric carbon monoxide concentrations in 1950 and 1951 deduced from infrared total column amount measurements, Nature, 318, 250-254.

Rinsland, C. P. and J. S. Levine, 1986: Identification and measurement of atmospheric ethane (C_2H_6) from a 1951 infrared solar spectrum, Appl. Optics, 25, 4522-4525.

Rinsland, C. P., J. S. Levine, and T. Miles, 1985: Concentration of methane in the troposphere deduced from 1951 infrared solar spectra, Nature, 318, 245-249.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, 1986: Possible impact of sodium species on ClO and 0_3 in the upper stratosphere. Geophys. Res. Lett., 13. 499-502.

Rood, R. B., D. J. Allen, W. G. Baker, D. J. Lamich. and J. A. Kaye, 1988; The use of assimilated stratospheric data in constituent transport calculations, submitted to J. Atmos. Sci.

Rosenfield, J. E., M. R. Schoeberl, and M. A. Geller, 1987: A computation of the stratospheric diabatic circulation using an accurate radiative transfer model, J. Atmos. Sci. 44, 859-876.

Russell, J. M. III, C. B. Farmer, C. P. Rinsland, R. Zander, L. Froidevaux, G. C. Toon, B. Gao, J. Shaw, and M. Gunson, 1988: Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on Spacelab 3, J. Geophys. Res., 93, 1718-1736.

Schmidlin, F. J., 1981: Repeatability and measurement uncertainty of U.S. meteorological rocketsondes, J. Geophys. Res., 86, 9599-9603.

Schmidlin, F. J., J. R. Duke, A. I. Ivanovsky, and Y. M. Chernyshenko, 1980; Results of the August 1977 Soviet and American meteorological rocketsonde intercomparison held at Wallops Island, Virginia, NASA Reference Publication 1053.

Sedlacek, W. A., A. L. Lazarus, and B. W. Gandrud, 1984: Measurements of stratospheric bromine, J. Geophys. Res., 89, 4821-4825.

Simmonds, P. G., F. N. Alyea, C. A. Cardelino, A. J. Crawford, D. M. Cunnold, B. C. Lane, J. E. Lovelock, P. G. Prinn, and R. A. Rasmussen, 1983: The atmospheric lifetime experiment, 6, Results for carbon tetrachloride based on three years data, J. Geophys. Res., 88, 8427-8441.

Solomon, S., P. J. Crutzen, and R. G. Roble, 1982: Photochemical coupling between the thermosphere and the lower atmosphere 1. Odd nitrogen from 50 to 120 km, J. Geophys. Res., 88, 5229-5239.

Solomon, S. and R. R. Garcia, 1983; On the distribution of nitrogen dioxide in the high latitude stratosphere, J. Geophys. Res., 88, 5229-5239.

Solomon, S., R. R. Garcia, F. S. Rowland, and D. J. Wuebbles, 1986: On the depletion of Antarctic ozone, Nature, 321, 755-758.

Solomon, P., B. J. Connor, R. DeZafra, A. Barnett, J. W. Parrish. and M. Jaramillo, 1987: High concentrations of chlorine monoxide at low altitudes in the Antarctic spring stratosphere secular variation, Nature, 328, 411-413.

Solomon, S., G. H. Mount, R. W. Sanders, and A. L. Schmeltekopf, 1987: Visible spectroscopy at McMurdo station, Antarctica 2. Observations of OClO, J. Geophys. Res., 92, 8329-8338.

Stauffer, B., G. Fischer, A. Neftel, and H. Oeschger, 1985: Increase of atmospheric methane recorded in Antarctic ice core, Science, 229, 1386-1388.

Steele, L. P., P. J. Fraser, R. A. Rasmussen, M. A. K. Khalil, T. J. Conway, A. J. Crawford, R. H. Gammon, K. A. Masarie, and K. W. Thoning, 1987: The global distribution of methane in the troposphere, J. of Atmos. Chem., 5, 125-171.

Thomas, A. and F. G. Finger, 1974: Technical attachment 74-8, National Meteorological Center Newsletter 74-6.

Thomas, L., D. B. Jenkins, D. P. Wareing, G. Vaughan, and M. Farrington, 1987: Lidar observations of stratospheric aerosol associated with the El Chichon eruption, Ann. Geophys., 5A, 47-56.

Thompson, A. M. and R. J. Cicerone, 1986: Atmospheric CH_4, CO, and OH from 1860 to 1985, Nature, 321, 148-150.

Torr, M. R., D. G. Torr, W. Swift, P. Bhatt, and G. Liu, 1987: Measurements of OH in the stratosphere by high resolution UV spectroscopy, Geophys. Res. Lett., 14, 937-940.

Tung, K..K., M. K. W. Ko, J. M. Rodriguez, and N. D. Sze, 1986: Are Antarctic ozone variations a manifestation of dynamics or chemistry?, Nature, 322, 811-814.

UCAR, 1986: Global Tropospheric Chemistry: Plans for the U. S. Research Effort, December 1986, UCAR-OIES, Boulder, CO.

Wang, W., Y. Yung, A. Lacis, T. Mo, and J. Hansen, 1976: Greenhouse effects due to manmade perturbations of trace gases, Science, 194, 685-687.

Weiss, R. F., 1981: Tropospheric N_20: Distribution in space and time, J. Geophys. Res., 86, 7185-7195.

WMO, 1982: Catalog of radiosondes in use by members, WMO Report No. 11 (1986 update in press)

WMO, 1986: Atmospheric Ozone 1985: Assessment of our understanding of the processes controlling its present distribution and change, World Meteorology Organization, Geneva.

Zander, R., G. Roland, L. Delbuoille, A. SaUVal, C. B. Farmer, and R. H. Norton, 1987a: Column abundance and long-term trend of hydrogen chloride (HCl) above the Jungfraujoch station, J. Atmos. Chem., 5, 395-404.

Zander, R., G. Roland, L. Delbuoille, A. SaUVal, C. B. Farmer, and R. H. Norton, 1987b: Monitoring of the integrated column of hydrogen fluoride above the Jungfraujoch station since 1977 . The HF/HCl column ratio, J. Atmos. Chem., 5, 385-394.

APPENDIX B LIST OF ACRONYMS

AAOE - Airborne Antarctic Ozone Experiment
ABLE - Atmospheric Boundary Layer Experiment
AEM-2 - Applications Explorer Mission-2
ALE - Atmospheric Lifetime Experiment
AMSU - Advanced Microwave Sounding Unit
ART - Automatic Radiosonde Tracking
ATMOS - Atmospheric Trace Molecule Spectroscopy
ATN - Advanced TIROS-N
BUV - Backscattered Ultraviolet Radiometer
CLAES - Cryogenic Limb Array Etalon Spectrometer
CMA - Chemical Manufacturers Association
DMSP - Defense Meteorological Satellite Program
ECC - Electrochemical Concentration
Eos - Earth Observing System
ERBS - Earth Radiation Budget Satellite
ESIRE - European Solar Irradiance Experiment
FAA - Federal Aviation Administration
GAGE - Global Aerosols and Gases Experiment
GLS - GOMR Limb Sounder
GMCC - Geophysical Monitoring for Climatic Change
GNS - GOMR Nadir Sounder
GOMR - Global Ozone Monitoring Radiometer
GPCP - Global Precipitation Chemistry Program
GTCP - Global Tropospheric Chemistry Program
GTE - Global Tropospheric Experiment
HALOE - Halogen Occultation Experiment
HRDI - High Resolution Doppler Imager
HIRS - High Resolution Infrared Sounder
ICSU - International Council for Scientific Unions
IRIS - Infrared Interferometer Spectrometer
ISAMS - Improved Stratospheric and Mesospheric Sounder
LIDAR - Light Detection and Ranging System
LIMS - Limb Infrared Monitor of the Stratosphere
LRIR - Limb Radiance Inversion Radiometer
MAPS-CO - Measurement of Air Pollution by Shuttle - Carbon Monoxide
MAS - Millimeter-Wave Atmospheric Sounder
MFR - Multiple Filter Radiometer
MLS - Microwave Limb Sounder
MST - Mesospheric, Stratospheric, Tropospheric
MSU - Microwave Sounding Unit
NADP - National Acid Deposition Program
NAS - National Academy of Sciences
NASA - National Aeronautics and Space Administration
NBS - National Bureau of Standards

NDSC - Network for Detection of Stratospheric Change
NMHC - Nonmethane Hydrocarbons
NOAA - National Oceanic and Atmospheric Administration
non-LTE - non-Local Thermodynamic Equilibrium
NOZE - National Ozone Expedition
OGC - Oregon Graduate Center
PCE - Photochemical Equilibrium
RITS - Radiatively Important Trace Species
SAGE - Stratospheric Aerosol and Gas Experiment
SAM-II - Stratospheric Aerosol Measurement II
SBUV - Solar Backscattered Ultraviolet Radiometer
SBUV/2 - Solar Backscattered Ultraviolet Radiometer version 2
SIRIS - Stratospheric Infrared Interferometer Spectrometer
SME - Solar Mesospheric Explorer
SSBUV - Shuttle Solar Backscattered Ultraviolet Radiometer
SSU - Stratospheric Sounding Unit
STEP - Stratosphere-Troposphere Exchange Program
SUSIM - Solar Ultraviolet Spectral Irradiance Monitor
TIROS - Television and Infrared Observing Satellite
TOMS - Total Ozone Mapping Spectrometer
TOVS - TIROS Operational Vertical Sounder
UCAR - University Corporation for Atmospheric Research
UNEP - United Nations Environmental Program
UARS - Upper Atmosphere Research Satellite
WCRP - World Climate Research Program
WMO - World Meteorological Organization

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