NASA Contractor Report 145309

The Capability of Satellite Borne Remote Sensors to Measure Stratospheric Trace Constituents

Volume II: Ozone and Aerosol Related Missions

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ABSTRACT

This document is Volume II of a three volume report issued as MITRE/METREK Technical Report, MTR-7519. The three volumes cover the following principal subjects:

Volume I contains a synthesis of the results of two previous MITRE/METREK studies {1,2} and an update of the information contained in them. The update was made during the Summer and Fall of 1977. These studies deal with a comprehensive review of stratospheric trace constituent measurement requirements. The scope of the study was restricted to those constituents which fall into the general category of "air pollutants."

Volume II separates stratospheric trace constitutent measurement requirements into two somewhat overlapping areas. In the first area, it is assumed that the only problem of interest is ozone; its chemistry chain, environmental effects and measurement requirements. In like manner, in the second area it is assumed that the only problem of interest is stratospheric aerosols; their chemistry, effects and measurement requirements.

Volume III contains material of a supportive nature not considered to be of sufficient importance to be included in the other two volumes. This material is of two types:

- Information and numerical evaluations used in the development of mission evaluations for stratospheric trace constituent measurement.

- Various spatial and temporal distributions for those stratospheric trace species having sufficient measurements available to warrant their presentation.

The reader is advised to note that the results and conclusions presented here are based on the specific combination of remote sensors, Shuttle orbits and analysis values selected to exemplify the technique presented. Although these sensors and orbits are typical, extension of the study to include all available sensors and many orbits, or to another specific small combination could result in different results and conclusions.

ACKNOWLEDGEMENTS

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LIST OF CHEMICAL SYMBOLS*

Symbol	Name
A	Argon
Al^{++++}	Aluminum ion
nAl_2O_3	Aluminum oxide aerosol
Br	Atomic bromine
Br^-	Bromide ion aerosol
BrO	Bromine oxide
Ca^{++}	Calcium ion aerosol
CBr_4	Tetrabromomethane (carbon tetrabromide)
$CCl_2=CHCl$	Trichloroethylene
CCl_4	Tetrachloromethane (carbon tetrachloride)
$CFCl_2^+$	Dichlorofluoromethane radical
$CFCl_3$	Trichlorofluomethane (F-11)
CF_2Cl^+	Chlorodifluoromethane radical
$CF_2ClCFCl_2$	Trichlorotrifluoroethane (F-113)
CF_2Cl_2	Dichlorodifluoromethane (F-12)
$CHClF_2$	Chlorodifluoromethane (F-22)
$CHCl_2F$	Dichlorofluoromethane
$CHCl_3$	Trichloromethane (chloroform)
$CH_2:CHCl$	Vinyl chloride
CH_2Cl_2	Dichloromethane (methyl dichloride)

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*Common name given in parentheses where appropriate. Unless specifically stated, species is assumed to be in gaseous state.

Symbol	Name
CH_2O	Methanal.(formaldehyde)
CH_3	Methyl radical
CH_3Br	Bromomethane (methyl bromide)
CH_3CCl_3	Trichloroethane (methyl chloroform)
CH_3Cl	Chloromethane (methyl chloride)
CH_3O	Methyl oxy radical
CH_3O_2	Methyl peroxy radical
$(CH_3)_2S$	Methyl sulfide
CH_4	Methane
CO	Carbon monoxide
$COCl$	Carbonyl monochloride
COS	Carbonyl sulfide
CO_2	Carbon dioxide
nCO_2	Carbon dioxide in cluster formation; quasi aerosol
CS_2	Carbon disulfide
$C_2H_4Cl_2$	Dichloroethane
C_2H_5Cl	Chloroethane (ethyl chloride)
C_xH_y	Non-methane hydrocarbons (NMHC)
Cl	Atomic chlorine
Cl^-	Chloride ion aerosol
$Cl_2C:CCl_2$	Tetrachloroethene (perchloroethylene)
$ClFCO$	Fluoroformyl chloride

Symbol	Name
ClO	Chlorine monoxide
$ClONO_2$	Chlorine nitrate
ClO_2	Chlorine dioxide
ClO_x	"Odd" chlorine
Cu^{++}	Copper ion aerosol
F_2CO	Carbonyl fluoride
Fe^{++} or Fe^{+++}	Iron ion aerosol
H	Atomic hydrogen
HBr	Hydrogen bromide
HCl	Hydrogen chloride
HF	Hydrogen fluoride
HNO_2	Nitrous acid
HNO_3	Nitric acid
$nHNO_3$	Nitric acid aerosol
HO or OH	Hydroxyl
HO_2	Hydroperoxyl
HSO_3^-	Bisulfite radical
H_2	Molecular hydrogen
H_2O	Water vapor
nH_2O	Liquid water or ice (as aerosol or in cluster formation)
H_2O_2	Hydrogen peroxide

Symbol	Name
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
$H_2SO_4 \cdot nH_2O$	Sulfuric acid aerosol
$H_x C_y O_z$	Unspecified organic compound
I^-	Iodide ion aerosol
K^+	Potassium ion aerosol
M	Unspecified third body
Mg	Magnesium aerosol
Mn^{++} or Mn^{+++}	Manganese ion aerosol
N	Atomic nitrogen
N_2	Molecular nitrogen
nN_2	Molecular nitrogen in cluster formation; quasi aerosol
NH_3	Ammonia
NH_4^+	Ammonium ion
nNH_4^+	Ammonium ion aerosol
$NH_4HSO_4 \cdot nH_2O$	Ammonium bisulfate aerosol
$(NH_4)_2SO_4$	Ammonium sulfate aerosol
$(NH_4)_2S_2O_8$	Ammonium peroxydisulfate aerosol
NO	Nitric oxide
nNO	Nitric oxide in cluster formation; quasi aerosol
NO_2	Nitrogen dioxide

Symbol	Name
NO_2^-	Nitrite ion aerosol
NO_3	Nitrogen trioxide
NO_3^-	Nitrate ion aerosol
NO_x	"Odd" nitrogen (nitrogen oxides)
N_2O	Nitrous oxide
N_2O_5	Nitrogen pentoxide
Na^+	Sodium ion aerosol
O	Atomic oxygen, unspecified
$O(^1D)$	Atomic oxygen, excited state ^1D
$O(^3P)$	Atomic oxygen, normal state
$O(^1S)$	Atomic oxygen, excited state ^1S
O_2	Molecular oxygen
$O_2(^1\Delta)$	Molecular oxygen, excited state $^1\Delta$
O_3	Ozone
SF_6	Sulfur hexafluoride
SO_2	Sulfur dioxide
nSO_2	Sulfur dioxide in cluster formation; quasi aerosol
SO_3	Sulfur trioxide
$SO_4^=$	Sulfate ion aerosol
Si^{++++}	Silicon ion aerosol

1.0 INTRODUCTION AND CONCLUSIONS

1.1 General Objectives

Planned Shuttle missions provide another opportunity for NASA to evaluate and utilize stratospheric remote sensors. This unique platform will allow larger payloads than have been possible while permitting the man-machine interface which has been lacking. The key goals of any remote sensing experiment are the optimization of sensors to the mission and the timely communication of the results to the intended users.

In recent studies [1,2] for NASA/LaRC, MITRE/METREK has examined the sensor/constitutent/platform problems for the case of multi-purpose space missions. In the first of these, an assessment of the capabilities of specific NASA remote sensing systems to provide appropriate measurements of stratospheric parameters was made. This study emphasized the roles of the aerosol, the nitrogen oxide/ozone chemistry cycle and the chlorine/ozone chemistry cycle in the stratsophere. It also evaluated the capabilities of six specific instruments to provide required measurements of stratospheric constituents.

In the second study a more comprehensive view of all stratospheric trace constituents was taken. This included:

- development of a prioritized list of requirements for stratospheric trace constituent measurement;

- a comprehensive summary of present knowledge of stratospheric trace constituents;

- development of a detailed structured constituent/instrument/mission evaluation technique; and

- application of the technique to a specific set of instrument/
  orbit combinations.

Since the completion of the two original studies a need has

been recognized to synthesize the previous studies and combine this

synthesis with additional updated information to produce a single

document having the following principal objectives:

- providing the scientific community with a concise view
  of the current status of knowledge of stratospheric trace
  constituents and generating the impetus for frank and in-
  depth discussions of future requirements;

- providing the instrument development community with an
  information set which would guide them in selecting optimum
  directions for new instrument development based on the
  combination of scientific needs and instrument capabilities.

Volume I of this document presents the results of this synthesis

and updating.

In the current volume the fact is recognized that for a variety

of reasons concern may focus on one particular aspect of the strat-

osphere such as the ozone cycle or the role of aerosols. The reasons

for this specific concern may be political, scientific, economic or

involve public concern over current issues such as supersonic aircraft

or chlorofluoromethanes. These basic nontechnical concerns may

result in limiting the scope of any stratospheric measurement program.

Two such logical limitations would involve studies restricted to:

- the ozone chemistry cycle

- the role of aerosols in the stratosphere

It is these two limited measurement programs which are of

concern in the present study. Each significant component of the

chemistry chains for both ozone and aerosols is identified and

prioritized. The approach to this prioritization will be similar to

that used in Volume I for the overall stratospheric study. This will

yield two separate prioritized lists of constituents with some

species appearing on both lists. From this point the analysis will

proceed as in the previous study. The same instrument and orbit

combinations will be used but evaluations will be limited to those

species involved in either the ozone or aerosol chains. Two sets of

results will be produced one giving the optimum instrument/orbit

combinations for ozone chemistry and the other the optimum instrument/

orbit combinations for measuring aerosols.

In most areas covered by this study, considerable effort has

already been expended by many groups, not only within NASA but

also among other government agencies, the private sector and in the

two previous MITRE studies. MITRE's principle role in the present

study was to integrate and reconcile these sometimes disparate

sources and to provide informed opinions in the areas where either

no data existed or a concensus was absent. The following subsections

summarize the major sections of this report.

1.1.1. The "Natural" and "Perturbed" Stratosphere

The purpose of this section (2.0) is threefold. The first is

to provide a readily available short summary of the general charac-

teristics of the stratosphere. The temperature regime and circulation

are discussed in terms of the general dynamic processes to illustrate

the formation of the unperturbed stratosphere. This leads to a summary of the stratospheric constituents and their role in atmospheric chemistry. The later two parts of the section present summaries of ozone chemistry and the role of stratospheric aerosols. This section is intended only as a supporting base of information for understanding the various topics covered later.

1.1.2 User Requirements for Stratospheric Measurements

In volume I of this report the results of an extensive user requirements study are presented. That presentation discussed some general features of NASA's interaction with users of stratospheric data and presented the two major examples (ultraviolent radiation* and climate) of pressing atmospheric pollution problems which demand of NASA a careful and effective program of development. The emphasis was placed on who uses the data and how they use it in order to develop the specifics of the measurement requirements. In the present section (3.0) this work is summarized with emphasis placed on the distinction in requirements to satify users concerned with ultraviolet radiation (UV) and those concerned with climate. The general assumption is made that ozone chemistry primarily affects UV while aerosols primarily affect climate.

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*Biologists divide the ultraviolet spectrum into three wavelength regions: UV-A: 0.32 to 0.4 μm; UV-B: 0.28 to 0.32 μm; UV-C: less than 0.28 μm. Unless specifically stated the term UV when used in this report refers to all three regions.

1.1.3 Science Requirements

In this section (4.0) the analysis of user needs and general measurement requirements developed in the previous setioh (3.0) are used in combination with present knowledge of stratospheric chemistry and with the results of many other recent studies to develop two sets of prioritized scientific requirements for stratospheric trace constituent measurements. The first set focuses on ozone chemistry and the second on aerosols.

1.1.4 Mission Evaluations

This section (5.0) presents the results of the application of a method for the evaluation of various stratospheric species measurement missions. The method itself was developed during previous MITRE effort [2] and is presented in detail as Appendix A in both Volumes I and II of this report. Much of the supporting data used in these evaluations has been assembled in several of the appendices of Volume III of this report. Separate evaluations are made for ozone and aerosol applications. The evaluations include all possible combinations of three orbits (a 30° shuttle type, a 56° shuttle type and a polar type) with one or more of four remote instruments,

- Limb IR Monitor for the Stratosphere (LIMS)

- Stratospheric Aerosol and Gas Experiment (SAGE)

- Correlation Interferometer for the Measurement of Atmospheric Trace Species (CIMATS)

- Halogen Occultation Experiment (HALOE)

1.2 Conclusions

Many of the generalized conclusions contained in Volume I of this report apply equally well to specific ozone or aerosol missions. The following sections will present the more significant of these conclusions along with specific points relating to the ozone and aerosol mission evaluations.

1.2.1 Current and Projected Measurement Capability

Analysis of the material presented here and in Volume I indicates three key conclusions:

(1) The performance of current remote stratospheric sensors, in some cases, compares quite well with identified measurement requirements. Their ability to measure other species has not been demonstrated. A number of in-situ methods also exist with comparable sensitivity and accuracy but whose measurements are of a limited utility, given their spatial and temporal sampling characteristics.

(2) None of the current, in-situ methods have the capability to satisfy the requirements for global monitoring and the temporal constraints derived from the users needs portion of the study.

(3) Existing, non-remote techniques will continue to play an important role in stratospheric investigations for both corroboration of remotely collected data and in the evolutionary development of future remote sensors.

All of the measurment techniques discussed have their strengths and weaknesses. The in-situ methods are extremely sensitive and accurate but suffer from limited coverage and local contamination problems. Remote sensing techniques offer wide area coverage and relatively long mission lifetimes. Their disadvantages lie in the

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reduced senstivity to low concentration levels and the requirements for auxiliary data to invert the integrated path measurements which most utilize. Indeed, the masses of data which must be processed in order to yield the desired information is at least a temporary disadvantage of remote sensing methods. The development of better models and improved data handling techniques is expected to minimize these problems.

The general features of remote sensors of the stratosphere aboard a satellite platform reveal two key features:

(1) nadir-viewing instrumentation provides superior performance in the areas of horizontal resolution and measurement time per orbit

(2) limb-viewing instrumentation provides superior sensitivity, and vertical resolution

In most other areas, the two basic monitoring methods are equally capable. The science requirements include the need for vertical profiles and data of fairly high quality. Limb-viewing instrumentation appears to satisfy these needs but provides limited temporal sampling for solar occultation when certain orbits are used. As a result, instrumentation of the limb emission type represents the optimum choice. In general, this type of instrument has the potential of satisfying scientific requirements for vertical profiles as well as those for spatial and temporal sampling.

Orbital considerations emerge as a key element in the applicability of various sensor systems to specific measurement roles. Sunsynchronous orbits provide optimum coverage for nadir-viewing, thermal source sensors and limb-viewing emission source sensors. High angle non-sunsynchronous

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orbits are preferred to nadir-viewing reflected solar source or limb-viewing solar occultation sensors, if geographical coverage is to be maximized.

1.2.2 Requirements for Stratospheric Measurements

Material utilized in the selection of requirements for strato-spheric monitoring has been derived from the user needs survey as well as the detailed investigation of data needed for a better understanding of stratospheric chemistry. In addition, a review of current measurement methods examined the quality of data currently available for a variety of gases of interest. The proposed accuracy requirements reflect improvements, where required, over current limitations.

In many cases no specific requirements have been expressed for spatial or temporal sampling. In view of the generally infrequent and localized nature of current measurements, any satellite monitoring system will represent an improvement in these categories. It is anticipated that the need will exist for global coverage at a rate which provides data on diurnal and seasonal variations as well as longer term trends.

Based on the measurement requirements expressed by various categories of users and numerous other specific studies, prioritized lists of properties and species have been developed for ozone and aerosol oriented missions (Tables 4-II and 4-III respectively). Both lists give the highest priority for measurement of three basic properties:

- stratospheric temperature

- solar irradiance

- earth radiance

In addition the ozone oriented list stresses measurements in the following categories:

- pure oxygen forms, O_x

- hydrogen oxides, HO_x

- nitrogen oxides, NO_x

- chlorine oxides, ClO_x

The aerosol related list places the highest priority on measurements of:

- total aerosols

- total sulfate aerosols

- sulfuric acid aerosols

- ammonium sulfate, and

- major sulfate aerosol precursor gases

It must be remembered that these lists have been developed on a purely scientific basis, without regard to present knowledge or potential measurment capability. Later in the report application of the evaluation methodology presented indicates that many of the high priority properties and species do not receive the highest priority for planned satellite missions since their distributions are much more understood than most of the other important stratospheric species. Those species which show high priority for satellite missions are typically the

components of the basic reactions involving the direct production or depletion of ozone or the formation of sulfuric acid or ammonium sulfate aerosols.

As our understanding of the stratosphere matures, various constituents will receive more or less emphasis with respect to sampling and data quality. While these lists are presently current, changes should be anticipated, particularly when measurements exceed the current minimum requirements.

It should be noted that these requirements have been generated independently of any instrument considerations. Therefore, this material represents a set of performance goals for contact or remote sensors placed on airborne, orbiting, or terrestrial platforms. In the case of those species not yet measured, airborne measurements should receive considerable attention in order to establish background levels and to corroborate proposed remote sensing techniques.

1.2.3 <u>Selected Instrument/Orbit Evaluations</u>

Within the constraints imposed by the sensor complement examined and the choice of three orbits selected, the various sensor-orbit combinations were evaluated for each species of interest. For stratospheric study, the limb-scanners scored significantly higher than either the nadir-viewing or the solar occultation class of instruments. This is attributable to the direct vertical profiles which the limb-scanners provide.

Among the three orbits investigated, the polar orbit does not automatically give the best coverage. This tends to be a function of instrument type. For limb emission instruments, the higher the inclination angle the greater the global coverage. However, the poorest latitudinal coverage of all the combinations examined is obtained in the case of solar occultation from polar orbits.

It must be emphasized that the present evaluation was performed for a limited number of instruments and orbits. The methodology is sufficiently flexible to allow new instruments to be included in subsequent analyses of this type. If any of the instruments considered should prove incapable of all the measurements for which they are credited, their relative standing in a later analysis would suffer proportionately.

Evaluation of the various instrument/orbit combinations for an ozone related mission does not yield as clear a distinction among the combinations as in the evaluation of the total stratospheric program done in Volume I. The results (Table 5-XXII) indicate some preference for the three instrument mission containing the LIMS, CIMATS and HALOE. In addition a two instrument mission which contains LIMS and CIMATS scores favorably. The reasons for the superiority of these missions lies primarily in the number of species measured and secondarily in the relative importance of those measurements. For all of the eleven ozone mission combinations examined, the 56° orbit is seen to be capable of satisfying the greatest number

of scientific requirements. This is due to the preponderance of
solar occultation measurements in these ozone missions.

In contrast with the ozone results, orbit selection for com-
binations of instruments for aerosol missions does not consistently
show the 56° orbit to score the highest. The polar orbit tends to
prevail in combinations containing the LIMS instrument while the 56°
orbit is superior when it is absent. In no case is the 30° orbit
shown to be superior.

As with the ozone results, aerosol missions tend to score
higher based on the number of species measured with the LIMS, CIMATS,
HALOE combination and the LIMS, CIMATS combination prevailing. The
relative distinction between the various combinations is somewhat
clearer than in the ozone case. Those instruments (i.e., LIMS and
CIMATS) measuring the high priority sulfate precursor gases, ammonia
and water vapor, give the best evaluation results.

2.0 THE "NATURAL" AND "PERTURBED" STRATOSPHERE

Many recent studies refer to the stratosphere in one of two ways, namely, "natural" or "perturbed". In general the exact meaning of these terms is assumed to be known rather than defined. In this report the term "natural" refers to the long term average characteristics of the stratosphere which existed before any significant anthropogenic activities. The term "perturbed" is used when refering to any significant change in the natural state whether temporary (months to years) or quasi-permanent. Stratospheric perturbations can be caused in several ways:

- natural disturbances such as volcanic eruptions

- direct anthropogenic disturbances such as chlorofluoro-carbon releases, fossil fuel burning or high altitude aircraft operation

- indirect anthropogenic activities such as massive changes in land use or the ordinary growth and progress of the human race

The purpose of the following subsections is to acquaint the reader with the object of satellite remote sensor measurements—the stratosphere. The temperature regime and circulation are discussed in terms of the general dynamic processes to illustrate the formation of the unperturbed stratosphere. This leads to a summary of the stratospheric constituents and their role in atmospheric chemistry.

The two major reasons for observing or monitoring the stratosphere are to gain a more complete understanding of the subject and to

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be able to predict changes in the environment. Inadvertent modifications of the atmosphere by pollutants can have far-reaching effects upon man's activities. Chemical and physical processes, in terms of both ozone destruction and aerosol formation, will be summarized below to provide a background for later discussions contained in this report.

2.1 The "Natural" Stratosphere

2.1.1 Physical Formation of the Tropopause

The earth's atmosphere may be divided into layers which are characterized by the average vertical temperature structure. The three layers closest to the earth's surface are:

- Troposphere,
- Stratosphere, and
- Mesosphere.

Averaged over reasonably long periods of time, the temperature of the troposphere decreases regularly with altitude. At an elevation that varies systematically with latitude and seasons, the temperature becomes isothermal. This property defines the tropopause, which lies between 8 and 16 km. The stratosphere is the region above the tropopause and below the stratopause. In this region, the temperature is typically constant or increasing with altitude. This increase is reversed at an altitude of about 45 to 50 km--the stratopause. The region immediately above the stratopause is the mesophere.
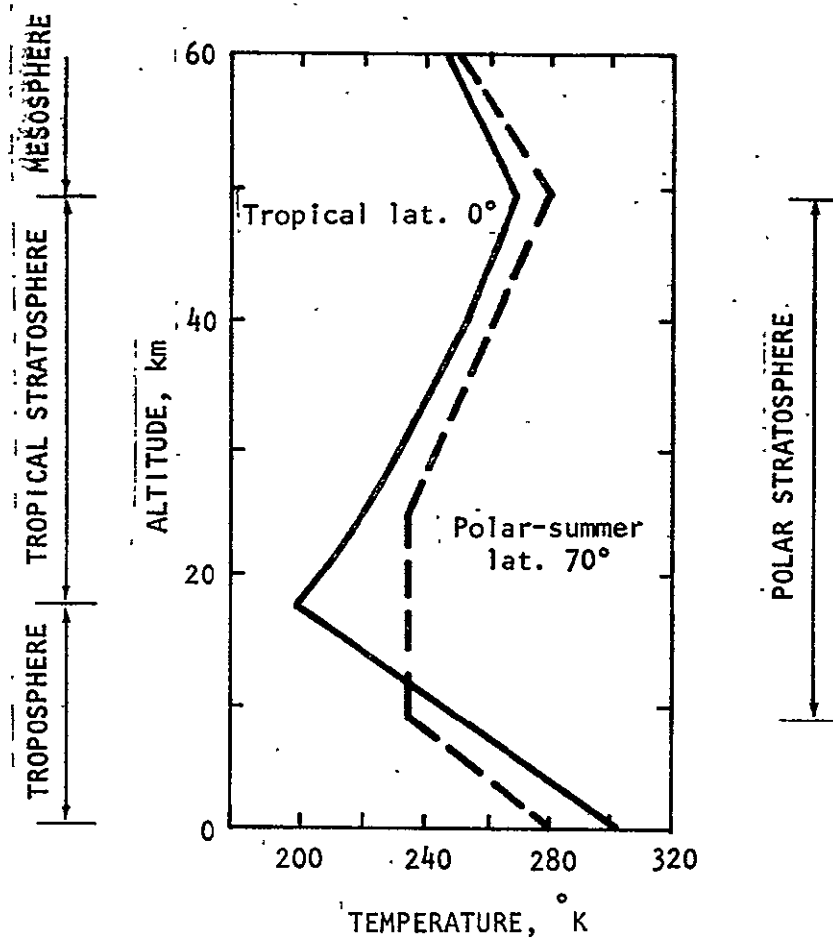
FIGURE 2-1

SAMPLE TEMPERATURE PROFILES IN TROPICAL AND POLAR ZONES [3]
(Troposphere, stratosphere, stratopause, and mesosphere
defined in terms of vertical temperature profiles)

The vertical distribution of temperature in the tropical and the polar zones is shown in Figure 2-1 [3]. The two temperature profiles of Figure 2-1 show substantial differences between polar and tropical regions.

The special properties of the stratosphere—its temperature inversion and the resulting slow vertical mixing—are a consequence of the presence of O_3, which is formed rapidly in the upper stratosphere. The formation of O_3 occurs at an altitude of 30 to 50 km by the photolysis of O_2, producing O, which in turn recombines with O_2 to form O_3. Some of the physical reasons behind the temperature inversions at the tropopause are discussed below.

If heat from the ground were the only source of energy in the atmosphere, the vertical temperature at a given location would decrease monotonically with altitude. In contrast, measurement of the vertical temperature profiles shows that beyond the tropopause, to a height of about 50 km, the temperature increases. At this height, the stratopause, the temperature undergoes an inversion and again starts to decrease.

One to three percent of the incoming solar radiation is absorbed by the O_3 layer in the stratosphere. The absorbed energy heats adjacent layers. The model now contains two sources of energy in the atmosphere, one at the surface and the other at an altitude of about 30 to 50 km. From this simplified picture, it is evident that a temperature inversion should occur at a height between the two

sources. The region where the inversion occurs defines the tropopause, which lies between 8 and 16 km depending on the season, latitude, and synoptic weather situation.

2.1.2 Transport Phenomena

Clouds, rain, and thunderstorms are strong evidence for the considerable vertical motion characteristic of the troposphere. In thunderstorms vertical velocities, which are generally 10 cm/sec in normal latitude cyclones and anticyclones, may reach 10 to 20 m/sec. In the stratosphere, however, the temperature increases with height providing an equilibrium condition. For this reason, the vertical motions rarely exceed a few centimeters per second and are often much smaller. In other words, an air parcel moves up or down more slowly in the stratosphere than it does in the troposphere. This is not true for horizontal motions in the stratosphere which are significantly more rapid than the vertical motions. Typical horizontal wind velocities in the stratosphere are of the order of 1 to 100 m/sec, whereas vertical velocities are in the range of 10^{-4} to 10^{-1} m/sec.

The overall structure of the wind field in the stratosphere has been investigated and shows a complicated latitudinal and seasonal dependence [5,6]. In general, there are some correlations between the meridional (N-S) and vertical wind fields at different times of the year [4]. No correlation seems to exist between the rapid zonal (E-W) circulation and vertical wind data.

In summary, because of the slow vertical mixing, the contaminants which are introduced into the stratosphere at a particular altitude will remain near that altitude for periods as long as several years [7]. This long residence time allows the contaminants to take part actively in the chemical and radiative processes of the stratosphere. In the case where a contaminant is capable of entering a catalytic process which would lead to the destruction of an important stratospheric constituent such as ozone, the consequences are of great importance and must be thoroughly investigated.

2.1.3 Stratospheric Constituents

The constituents of the stratosphere may be separated into four categories. These are:

- Major gaseous constituents,

- Minor gaseous constituents,

- Trace gaseous constituents, and

- Aerosols.

The major atmospheric constituents are N_2, O_2, A and CO_2. The accepted value for N_2 concentration is 78.08 percent by volume of dry air. Recent oxygen measurements show a concentration of 20.95 percent by volume when corrected to dry air conditions [4]. Argon has a stratospheric background concentration of 0.93 percent and carbon dioxide of 0.03 percent at about 20 km.

The minor constituents, such as O_3, H_2O, CH_4, etc.; have concentrations of a few parts per million in the stratosphere. Table 2-I

.summarizes some of the minor constituents at 20 km that are known to

be important in stratospheric chemistry and circulation. The number

of important trace gaseous constituents known to play a significant

role in stratosphere chemistry is very large and growing rapidly. A

complete development of the characteristics of these constituents is

given in later sections.

Besides these gaseous chemical constituents, a layer of particles

several kilometers thick, exists in the stratosphere. This layer,

called the "Junge layer," is located several kilometers above the

tropopause. The Junge, or sulfate layer, has a particle density of

two to ten times that exhibited above and below this layer. The

particle size is predominately in the 0.1 to 1.0 μm radius range. The

particle distribution shows a decreasing concentration with increasing

size. The particles consist mainly of sulfuric acid or sulfate solu-

tions and are probably in a supercooled liquid state. The characteris-

tics of this aerosol layer and of all stratospheric aerosols will be

covered in detail in later sections.

2.2 The "Perturbed" Stratosphere

As stated previously perturbations in the stratosphere may be

caused by either natural or anthropogenic changes. Natural changes

generally take the form of injection of gaseous, liquid or solid

materials through the tropopause into the stratosphere. Such changes

may be either abrupt as in the case of volcanic eruption or quasi-

continuous as in the case of the daily worldwide occurrence of thun-

derstorms. However, in this later case there is some question as to

TABLE 2-I

MINOR STRATOSPHERIC CONSTITUENTS

Species	Concentration at 20 km	Variability	Importance
O_3	6 ppmv	Factor of two or more diurnal, season, latitude and height.	UV-shield, radiative heating and cooling of stratosphere.
H_2O	3 ppmv	With latitude, season, and altitude.	Radiative balance, clouds, particle formation, O_3 chemistry.
CH_4	1 ppmv	Decreases with height above tropopause.	Chemical source of OH. Possible sink of Cl, indicator of tropopause interchange.
H_2	0.55 ppmv	Increases to a maximum of 0.8 ppmv at 28 km and decreases to 0.4 at 50 km.	O_3-chemistry.
N_2O	0.1 ppmv	Decreases with altitude, season, and latitude.	Source of stratospheric NO.
CO	0.05 ppmv	May decrease above tropopause, but actual profile and variations are unknown.	Indicator of troposphere-stratosphere exchange. By-product of CH_4 chemistry.

whether thunderstorms should be considered a perturbation or merely
one part of the natural stratosphere. For the purposes of this report
they will be treated as perturbations.

Injection of extraterrestrial material downward through the meso-
pause seems to occur but the characteristics of this mechanisms are
poorly understood. At present the total possible mass of such injec-
tions is thought to be small and would represent a negligible optical
perturbation [66].

Anthropogenically caused changes may take the form of direct
release of material in the stratosphere as with aircraft and rocket
exhaust or upward diffusion and transport through the tropopause of
material released into the troposphere. Table 2-II lists the major
categories of materials currently known to cause significant strato-
spheric perturbations along with the sources of each. The table
includes both natural and anthropogenic materials.

The ultimate stratospheric effects caused by these perturbations
belong to two chains, the UV chain and the climate chain. The direct
channels for production of these effects are three:

(1) Changes in UV transmission resulting from changes
     in ozone concentration.

(2) Changes in the radiative heat balance caused by
     formation of aerosols.

(3) Changes in the radiative heat balance caused
     directly by some gases such as carbon dioxide.

Since O_3 concentration controls the amount of UV-B radiation that
reaches the surface of the earth, a reduction in O_3 concentration will

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TABLE 2-II·

PRINCIPAL SOURCES OF STRATOSPHERIC PERTURBATIONS

TYPE OF PERTURBATION	TRANSPORTED FROM TROPOSPHERE	RELEASED BY AIRCRAFT IN-SITU
Liquid water or ice	√*	
Particles	√**	√
Gases		
Carbon Dioxide	√	√
Water Vapor	√	√
Nitrous Oxide	√	
Other Nitrogen Oxides		√
Ammonia	√	
Hydrogen Sulfide	√***	
Sulfur Dioxide	√***	√
Carbon Monoxide and Hydrocarbons	√	√
Chlorine Compounds including Chlorofluoromethanes	√	

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*   Major mechanism is thunderstorms and cumulonimbus clouds.

** Major mechanism is volcanic eruption.

*** Through ordinary transport and volcanic eruption.

increase the amount of this radiation, which has been shown to cause skin cancer and other biological effects [42]. The increase in aerosol concentrations (besides increasing the potential for hetrogeneous reactions whose effects are not well understood at present) will perturb the radiation balance of the earth's atmosphere and may lead to climatic changes, affecting sunshine, temperature, and precipitation. In addition to these, CO_2 and H_2O vapor introduced into the stratosphere by aircraft or Space Shuttle vehicles may increase the greenhouse effect and lead to stratospheric warming, which would perturb the natural circulation of the stratosphere.

Table 2-III shows which of the three channels for producing UV or radioactive heat balance changes are associated with the various categories of stratospheric perturbations. In the following subsections the mechanisms for ozone change and aerosol production are discussed in more detail. Direct radioative heat balance changes are not discussed since they are beyond the scope of this report.

2.3 Stratospheric Chemistry

The stratosphere contains many different kinds of reactive chemical species. Any one of these species can react with a number of others, or be generated by a variety of other reactions which are sometimes very complex and quite indirect.

As related to stratospheric chemistry in general, three types of reactions may be distinguished. These are:

● Photochemical reactions,

TABLE 2-III

PRINCIPAL CHANGES ASSOCIATED WITH STRATOSPHERIC PERTURBATIONS

TYPE OF PERTURBATION	CHANGES IN OZONE AND UV TRANSMISSION	CHANGES IN RADIATIVE HEAT BALANCE	
		VIA AEROSOLS	DIRECT
Liquid water or ice	✓	✓	✓
Particles		✓	
Gases			
Carbon Dioxide			✓
Water Vapor	✓	✓	✓
Nitrous Oxide	✓		
Other Nitrogen Oxides	✓		
Ammonia	✓	✓	
Hydrogen Sulfide		✓	
Sulfur Dioxide	✓	✓	
Carbon Monoxide and Hydrocarbons	✓		
Chlorine Compounds including Chlorofluoromethanes	✓		

- Homogeneous reactions, and

- Heterogeneous reactions.

Photochemical reactions involve the interaction of electro-
magnetic radiation of of varying wavelengths with constituents of the
stratosphere. Photochemical interactions are the only known source
of stratospheric ozone production.

Homogeneous reactions are those reactions in which both the
reactant species and the products are in a gaseous phase. If in
these reactions a "third body" is needed to carry off energy to
prevent dissociation of the product, that third body is a gas mole-
cule.

Heterogeneous reactions are those reactions in which a particle,
solid or liquid, interacts with gaseous species. The interaction may
be catalytic, or the particle itself may take part in the reaction.

In the following subsections a more detailed discussion of the
chemistry of ozone and aerosols will be presented.

2.3.1 Ozone Chemistry

As stated above many reactive trace gases from both natural
and anthropogenic sources are tansported into the stratosphere or
released in situ. Although the mass of the stratosphere is an order
of magnitude less than that of the troposphere, the rate of exchange
with the troposphere is slow and there is no significant washout by
precipitation. For these reasons relatively minor perturbations in
the stratospheric balance can have significant long term effects.

The most important trace constituent in the stratosphere is
ozone. Any possibility of decreasng or even increasing the ozone
content of the stratosphere by altering the natural chemical balance
must be viewed as potentially dangerous. Two major applied problems
exist in current studies of stratospheric ozone. These are the
effect of aircraft and rocket exhausts released in the stratosphere
and the transport of chlorofluoromethanes from the troposphere.
Other relatively less significant problems also exist as was shown
previous in Table 2-II. In regard to ozone chemistry, perhaps key
among these others are anthropogenic releases of nitrous oxide,
ammonia and various organic chemicals.

An assessment of the effects of these stratospheric perturba-
tions requires an understanding of the natural chemistry and atmos-
pheric dynamics of the ozone balance. This is the basic problem.
The chemistry which originally was thought to be relatively simple,
is now known to be quite complex and involving many species. In
fact, except for the inert gas Argon, every gas currently known to
exist in the stratosphere can be related either directly or indirect-
ly with either ozone chemistry, aerosol chemistry or both.

In order to describe the chemistry of ozone formation and
destruction the various reactions will be discussed in the following
sequence.

- pure oxygen reactions
- hydrogen-oxygen reactions

- methane and hydrocarbon reactions

- nitrogen reactions

- chlorine reactions

- chlorine-nitrogen reactions

- other chemicals

In discussing the various ozone chemistry chains, the various gases can be divided into three types, reactive, inactive and passive. The term reactive will refer to those gases which readily and vigorously participate in reactions leading to the increase or decrease of ozone. Examples of such are atomic oxygen, hydroxyl, nitric oxide and chlorine monoxide.

Inactive gases are those which when formed during some ozone related process are removed completely from further participation in ozone chemistry. The prime example of such is carbon dioxide usually formed from the reaction of carbon monoxide and hydroxyl. There is no known mechanism for the reentry of carbon dioxide into any stratospheric ozone chemistry chain.

Passive gases are less reactive gases formed from one or more reactive components which temporarily prevent the reactive components from vigorous participation in ozone chemistry. An example of such is hydrogen chloride gas. While in this state the chlorine atom is prevented from reacting with ozone. Since the rate of formation of hydrogen chloride gas by reaction of atomic chlorine with methane or HO_x is one or two orders of magnitude greater than the rate of

destruction of hydrogen chloride gas by hydroxyl or atomic oxygen the

hydrogen chloride gas serves as a quasi sink for chlorine atoms.

Such gases are referred to as passive (i.e., less reactive).

2.3.1.1 Pure Oxygen Reactions. The pure oxygen reactions

in ozone chemistry refer to those in which only some forms of oxygen

participate. These reactions may involve solar ultraviolet light or

the presence of a third body (typically N_2 or another O_2 molecule).

These reactions may be termed natural since they occur irregardless of

any stratospheric perturbations. The principal pure oxygen reaction

are:

$$O_2 + h\nu \ (\lambda < 0.242 \ \mu m) \longrightarrow 0 + 0 \quad\quad (1)$$

$$0 + O_2 + M \longrightarrow O_3 + M \quad\quad (2)$$

$$O_3 + h\nu \ (\lambda : 0.45\text{-}0.65 \ \mu m) \longrightarrow 0 + O_2 \quad\quad (3a)$$

$$O_3 + h\nu \ (\lambda : 0.31\text{-}0.34 \ \mu m) \longrightarrow O_2 \ (^1\Delta) + 0 \ (^3P) \quad\quad (3b)$$

$$O_3 + h\nu \ (\lambda < 0.31 \ \mu m) \longrightarrow 0 \ (^1D) + O_2 \quad\quad (3c)$$

$$O_3 + 0 \longrightarrow O_2 + O_2 \quad\quad (4)$$

$$0 + 0 + M \longrightarrow O_2 + M \quad\quad (5)$$
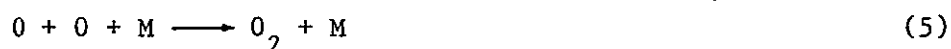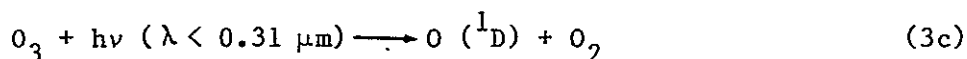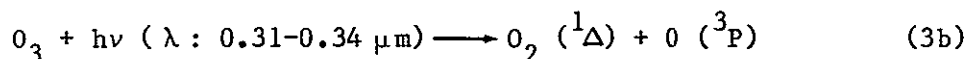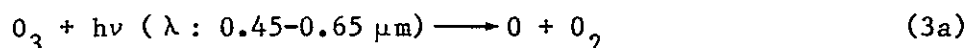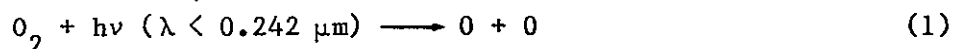
Reaction (1) is concentrated in the upper stratosphere and

provides the initial source of atomic oxygen. The reactions (2)

through (4) occur at lower altitudes in the stratosphere and reach

their maxima in the same altitude area as the ozone maximum. Reac-

tion (5) typically occurs in the mesosphere and can be neglected in

the stratosphere since reaction (2) predominates [75].

2.3.1.2 <u>Hydrogen-Oxygen Reactions</u>. Theoretically reactions involving hydrogen, oxygen and/or hydrogen oxides (HO_x) can occur via direct two body collision, three body collisions involving a neutral third body (M) or by photochemistry. The two body collision is the predominant one in the stratosphere with photochemical processes occurring in the mesosphere.

The principal reactions involving a single hydrogen atom are:

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (6)$$

$$H + O_3 \longrightarrow HO + O_2 . \qquad (7)$$

$$HO_2 + O \longrightarrow O_2 + HO \qquad (8)$$

$$HO + O \longrightarrow H + O_2 \qquad (9)$$

$$HO_2 + O_3 \longrightarrow HO + 2O_2 \qquad (10a)$$

$$HO + O_3 \longrightarrow HO_2 + O_2 \qquad (10b)$$

The first three of the above reactions principally occur in the upper stratosphere in the 35 km and above region. The atomic hydrogen involved initially in equation (6) is transported downward from higher levels in the mesosphere. These three reactions provide a mechanism for the production of hydroperoxyl and hydroxyl in the upper stratosphere. In the lower stratosphere (20 to 40 km) these two radicals which may be transported downward from the upper stratosphere or produced from other in situ reactions act as removal mechanisms for ozone and atomic oxygen (equations 7 through 10b).

Direct production and depletion of hydroxyl in the lower
stratosphere depends on the two principal reactions:

$$O\,(^1D) + H_2O \longrightarrow HO + HO \tag{11}$$

$$HO + HO_2 \longrightarrow H_2O + O_2 \tag{12}$$

Thus the presence or absence of water vapor in the lower stratos-
phere enters as a significant factor in the ozone balance.

The principal reactions which involve the production and
destruction of molecular hydrogen, H_2, are:

$$H + HO_2 \longrightarrow H_2 + O_2 \tag{13}$$

$$H_2 + O\,(^1D) \longrightarrow H + HO \tag{14}$$

Reaction 13 is important in the mesosphere and the hydrogen mole-
cules produced may be transported downward into the stratosphere
where they react with atomic oxygen to produce additional hydroxyls.

The extent to which hydrogen peroxide enters into the hydrogen/
oxygen chemistry cycle is poorly understood and requires more experi-
mentation [75]. The basic reaction for formation of hydrogen peroxide
involves the direct combination of 2 hydroperoxyl radicals:

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \tag{15}$$

Hydrogen peroxide is destroyed either through photodissociation,

$$H_2O_2 + h\nu \longrightarrow HO + HO \tag{16}$$

or by reaction with hydroxyl,

$$HO + H_2O_2 \longrightarrow H_2O + HO_2 \tag{17}$$

This entire chain of reactions should be the subject of further investigation.

2.3.1.3 Carbon Monoxide and Hydrocarbon Reactions. The role of carbon monoxide in the stratospheric ozone balance is indirect but nevertheless very important. One principal reaction dominates,

$$HO + CO \longrightarrow CO_2 + H \tag{18}$$

The hydrogen atoms released are thus available to react with molecular oxygen to produce the highly reactive hydroperoxyl as shown in reaction (6). In the upper troposphere and lower stratosphere reactions (17) and (6) combine to provide the principal pathway for conversion of hydroxyl to hydroperoxyl. It is therefore important to know the concentration and vertical distribution of carbon monoxide in the lower stratosphere. In the middle stratosphere the hydroxyl shows preference for reaction with ozone rather than carbon monoxide while in the upper stratosphere the atomic oxygen-hydroxyl reaction is favored.

The principal hydrocarbon involved in ozone chemistry is methane. Methane, which is transported upward from the troposphere, is photodissociated in the mesosphere and dissociated by oxidation in the stratosphere. The two principal reactions are with excited atomic oxygen, $O\ (^1D)$ or with hydroxyl,

$$O\ (^1D) + CH_4 \longrightarrow CH_3 + HO \tag{19}$$

$$HO + CH_4 \longrightarrow CH_3 + H_2O \tag{20}$$

In the stratosphere the methyl radicals which are produced in the above reactions have a preference for reaction with molecular oxygen in a three body manner,

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M \tag{21}$$

The methyl peroxy radicals produced usually enter into the nitrogen chemistry chain in a variety of ways as will be discussed later. These nitrogen chemistry reactions can yield formaldehyde which added to any formaldehyde transported from the troposphere can photodecompose yielding either atomic or molecular hydrogen,

$$CH_2O + h\nu \longrightarrow CHO + H \tag{22}$$

$$CH_2O + h\nu \longrightarrow CO + H_2 \tag{23}$$
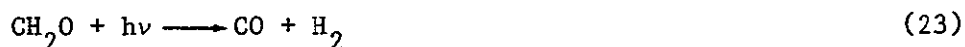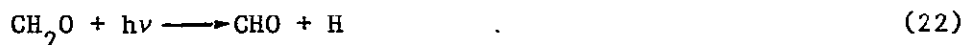
2.3.1.4 Nitrogen, Hydrogen and Oxygen Reactions

Although the nitrogen oxides chemistry cycle is extremely complex with many possible reactions, a simple description of the essential reactions indicates the basic cycle. Nitric oxide may be released into the stratosphere by high flying aircraft. However, the predominent source is through the reaction,

$$O(^1D) + N_2O \longrightarrow 2NO \tag{24}$$

N_2O is the principal nitrogen oxide transported upward from the troposphere where it is formed at the earth's surface through biological processes.

Once the NO is formed an equilibrium is established between NO and NO_2 through a series of reactions. The three principal ones are,

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{25}$$

$$NO_2 + O \longrightarrow NO + O_2 \tag{26}$$

$$NO_2 + h\nu \ (\lambda < 0.398 \ \mu m) \longrightarrow NO + O \qquad (27)$$
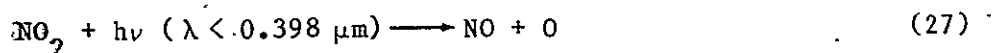
Reaction (25) is the same as that occurring in urban areas during smog production. Of the two reactions for $\cdot$ $\cdot$ ation of NO_2 reaction (26), as expected, occurs principally higher in the stratosphere where more atomic oxygen is available and reaction (27) occurs at lower altitudes. Due to the need for UV in reaction (27) the overall net effect of the three reactions is an increase in NO_2 at night and NO in the daytime.

At present the only know sink mechanism for stratospheric NO_x is conversion to one of the nitrogen oxide acids. This is followed by some type of aerosol formation and eventual settling into the troposphere where rainout can occur. The principal NO_x conversion reactions involve interaction with HO_x and a third body,

$$NO + HO_2 + M \longrightarrow HNO_3 + M \qquad (28)$$

$$NO_2 + HO + M \longrightarrow HNO_3 + M \qquad (29)$$

$$NO + HO + M \longrightarrow HNO_2 + M \qquad (30)$$

The conversion of NO_x to acids is also possible through a wide variety of reactions with organic compounds. Typical of these are reactions with methyl oxy or peroxy radicals,

$$CH_3O + NO_2 \longrightarrow CH_2O + HNO_2 \qquad (31)$$

$$CH_3O_2 + NO_2 \longrightarrow CH_2O + HNO_3 \qquad (32)$$

As noted earlier reactions of this type form a link between methane or hydrocarbon chemistry and NO_x chemistry.

2.3.1.5 Reactions Involving Chlorine

The potential for significant stratospheric ozone depletion

through reactions with odd chlorine has been clearly indicated by

many groups including the National Academy of Sciences [67,68]. The

basic source of stratospheric odd chlorine is through photodissocia-

tion of chlorine containing compounds transported upward from the

troposphere. These compounds may have natural origins such as some

of the CCl_4, CH_3Cl and HCL or they may be completely anthropogenic

as in the case of $CFCl_3$(F-11), CF_2Cl_2 (F-12) and the other chloro-

fluorocarbons. At the present time it is felt that the most prevalent

of these compounds in the atmosphere is CH_3Cl since its natural con-

centration is relatively high [75]. However the most controversial

compounds are the chlorofluorocarbons due to the enormous economic

impact associated with their utilization. Considerable doubt still

remains over the question of the possibility of tropospheric-sinks

for these compounds [114].

The basic mechanism for production of atomic chlorine in the

stratosphere is photolytic with the principal reaction at the present

time being,

$$CH_3Cl + h\nu \ (\lambda < 0.22 \ \mu m) \longrightarrow CH_3 + Cl \tag{33}$$
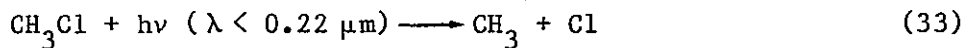
The amount of atomic chlorine produced in this reaction is probably

equal to that produced in the three following reactions [75].

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \tag{34}$$

$$CFCl_3 + h\nu \ (\lambda < 0.226 \ \mu m) \longrightarrow CFCl_2^+ + \cdot Cl \tag{35}$$

$$CF_2CL_2 + h\nu \ (\lambda < 0.215 \ \mu m) \longrightarrow CF_2Cl^+ + Cl \qquad (36)$$
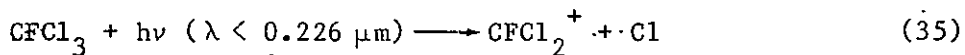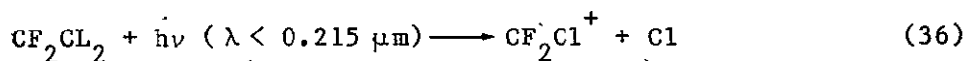
The dissociation of HCl is also of lesser magnitude,

$$HCl + h\nu \ (\lambda < 0.22 \ \mu m) \longrightarrow H + Cl$$
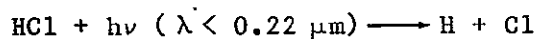
Thus methyl chloride is the most important overall source of stratospheric chlorine at the present.

Once formed atomic chlorine rapidly enters into catalytic chain decomposition of ozone in a two step reaction,

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (38)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (39)$$

The atomic chlorine may also be regenerated through reactions such as,

$$ClO + NO \longrightarrow Cl + NO_2 \qquad (40)$$

$$ClO + h\nu \longrightarrow Cl + O \qquad (41)$$

The principal sink for stratospheric chlorine is conversion into inactive hydrogen chloride followed by downward transport to the troposphere and rainout. The conversion into HCl generally occurs by reaction of chlorine monoxide with HO_x or possibly methane. For example,

$$Cl + HO_2 \longrightarrow HCl + O_2 \qquad (42)$$

$$Cl + CH_4 \longrightarrow HCl + CH_3 \qquad (43)$$

Recent reports [67,68] indicate that chlorine nitrate may serve as a passive chemical (temporary sink) for both Cl and NO_x. This is due to its apparent non-reaction with ozone and slow reaction with atomic oxygen. This slowly occurring cycle has three principal reactions [68],

2-23

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M \qquad (44)$$

$$ClONO_2 + h\nu \longrightarrow ClO + NO_2 \qquad (45)$$

$$ClONO_2 + O \longrightarrow ClO + NO_3 \qquad (46)$$

The role of chlorine nitrate in preventing ozone destruction has been studied [67,68] and found to reduce ozone depletion significantly. It concluded by the National Academy of Sciences [68] that, "unless there is some presently unknown process that quickly returns $ClONO_2$ into active ClO_x and NO_x species, the effect of chlorine nitrate formation is to decrease the projected ozone reductions by about a factor of 1.85 compared with the values calculated for the CFMs without this reaction."

2.3.1.6 Other Halogen Reactions

The possibility that bromine or fluorine compounds analogous to the chlorine compounds discussed in the previous section could play a role in ozone destruction has been studied [68]. Diametrically opposed results were reported for the two classes of chemicals.

The reactions for production of atomic bromine are very rapid. However the sink reactions for production of HBr are largely ineffective in producing this acid. Thus, an equivalent quantity of Br is much more effective than Cl in catalytic ozone destruction. It is fortunate that at the present time natural and anthropogenic releases of bromine compounds such as the fumigant CH_3Br appear to be an order of magnitude less than chlorine compounds.

.In contrast to the above it appears that although stratospheric production of atomic fluorine and catalytic destruction of ozone is possible, the sink reactions for production of HF are extremely rapid and dominate this cycle. Thus FO_x is unlikely to be a major factor in ozone chemistry.

2.3.2 Aerosol Chemistry

Of equal importance to stratospheric processes as the ozone chemistry cycle is the aerosol system which exists in the stratosphere. An aerosol is by definition [115], "a colloidal system in which the dispersed phase is composed of either solid or liquid particles, and in which the dispersion medium is some gas, usually air." This aerosol which varies significantly over time and space greatly influences stratospheric radiative transfer in both the incoming solar and outgoing infrared ranges. Changes in the nominal opacity of the stratosphere, which is about 2 percent [4], effect the passage of sunlight and heat to an extent which could result in variations in global mean temperature, general circulation and precipitation patterns. These climatic impacts are connected to a whole range of social, political and economic interdependence among nations [100].

Stratospheric aerosols have their origins from both natural and anthropogenic sources near the earth's surface and possibly somewhat from extraterrestial sources. In recent years the presence of aircraft and rockets in the stratosphere has also made a contribution.

Information on the global distribution of aerosols which varies considerably in time and space is given in volume III of this report. In the present discussion, only a brief summary of the vertical distribution is covered as a background for presentation of stratospheric aerosol chemistry.

In general the concentration of stratospheric aerosols shows a decrease with height. A depiction of this distribution is given in figure 2-2. The increase in concentration at an altitude of about 20km is called the Junge or sulfate layer. These aerosols are thought to be formed principally through the oxidation of hydrogen sulfide or sulfur dioxide which has been transported upward from the troposphere. The concentration of the aerosols can increase by as much as a factor of 10 to 100 after a volcanic eruption [66]. Study efforts during the Climatic Impact Assessment Program [4] have shown that the concentration of aerosols tends to decrease with time and the size distribution shifts toward smaller sizes between major volcanic eruptions.

At the 50km level another maximum is observed sporadically. These aerosols may be of extra-terrestial origin. In any event, their concentration is quite small and has a negligible effect on the total stratospheric system.

As stated above the principal mechanism for stratospheric aerosol formation appears to be oxidation of sulfur type gases and conversion to sulfuric acid or sulfate aerosols. In the following
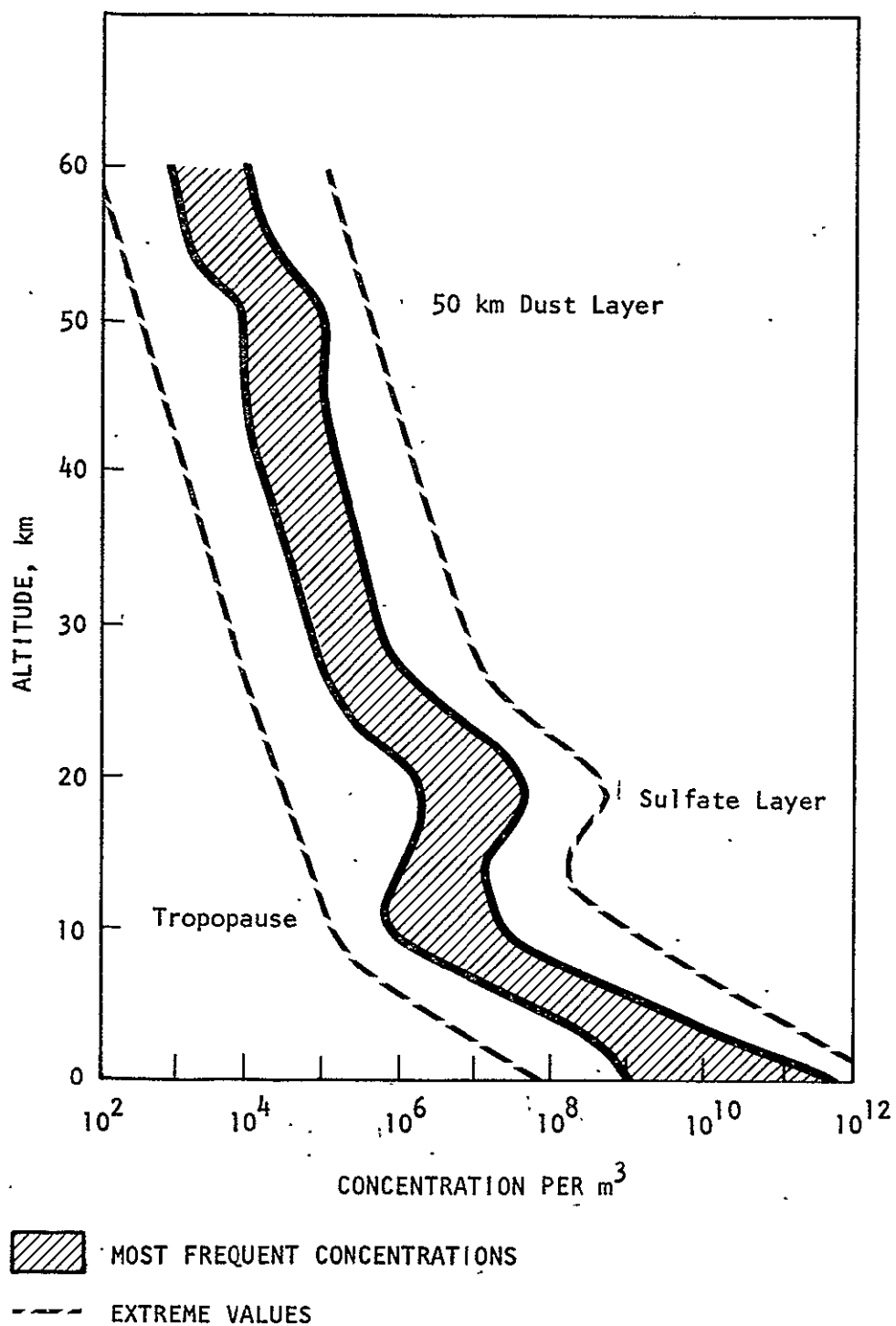
FIGURE 2-2
VERTICAL DISTRIBUTION OF AEROSOLS [66]

sections the discussion of aerosol chemistry will be divided into the
.sulfuric acid/sulfate cycle and other known mechanisms.

2.3.2.1 <u>Sulfate Aerosol Chemistry</u>. The mechanisms for con--
version of sulfur dioxide to sulfuric acid and sulfates are not well
understood even for tropospheric situations [116]. The most important
tropospheric sulfuric and sulfate formations identified to date [116]
are shown in table 2-IV. Of the five mechanisms shown only the first
two are likely to occur in the stratosphere. The lack of liquid
water in the stratosphere makes mechanisms 3 and 4 unlikely. In
addition, except for the possibility of carbon particles in aircraft
or rocket exhaust, mechanism 5 can be neglected.

However, the probability of occurrence of mechanisms 1 and 2 in
the stratosphere is increased by the ambient conditions, principally
the availability of atomic oxygen, HO_x and NO_x. The basic mechanisms
for direct photooxidation involves the availability of atomic_oxygen
from a photochemical reaction such as (1) or (3a, b or c),

$$SO_2 + O + M \longrightarrow SO_3 + M \tag{47}$$

which is followed by,

$$SO_3 + nH_2O \longrightarrow H_2SO_4 \cdot (n-1)H_2O \tag{48}$$
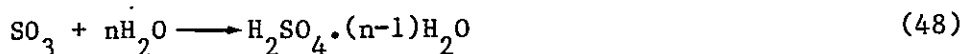
If HO_x enters the reaction rather than atomic oxygen the procedure
can be as follows,

$$SO_2 + HO_2 + h\nu \ (\lambda : 0.24 - 0.34 \ \mu m) \longrightarrow SO_3 + HO \tag{49}$$
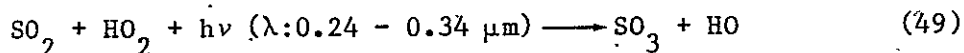
which then proceeds as in reaction (48).

TABLE 2-IV

TROPOSPHERIC MECHANISMS FOR CONVERTING SULFUR DIOXIDE
TO
SULFURIC ACID AND SULFATES[116]

MECHANISM	FACTORS CONTROLLING REACTION
1. Direct photo-oxidation	Sulfur dioxide concentration, sunlight intensity
2. Indirect photo-oxidation	Sulfur dioxide concentration, organic oxidant concentration, HO or NO_x concentration
3. Air oxidation in liquid droplets	Ammonia concentration, liquid water
4. Catalyzed oxidation in liquid droplets	Concentration of heavy metal (iron, $\cdots$, manganese) ions, liquid water
5. Catalyzed oxidation on dry surfaces	Carbon/particle concentration

Laboratory studies [117] have indicated the importance of ammonia in the growth of stratospheric aerosols. These studies concluded that a significant portion of stratospheric aerosols are composed of ammonium sulfate, ammonium bisulfate or possibly ammonium persulfate. A mechanism for the conversion to sulfate could be

$$NH_3 + H_2SO_4 \cdot nH_2O \longrightarrow NH_4HSO_4 \cdot nH_2O \qquad (50)$$

followed by

$$NH_3 + NH_4HSO_4 \cdot nH_2O \longrightarrow (NH_4)_2SO_4 \cdot nH_2O \qquad (51)$$
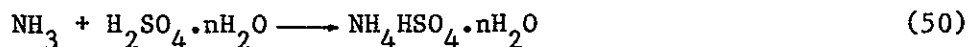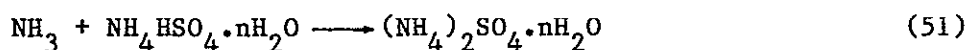
As soon as the ammonium sulfate salt is formed, it provides a medium for rapid catalytic oxidation of more SO_2,

$$2SO_2 + 2H_2O + O_2 \xrightarrow{\ \ NH_4 \ salt\ \ } 2H_2SO_4 \qquad (52)$$
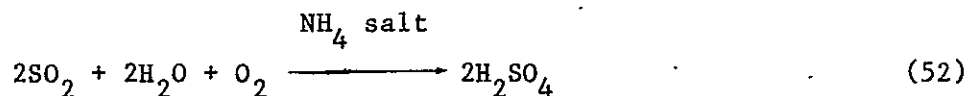
In summary the three main mechanisms for sulfate aerosol production are,

- Photolysis of O_3 to produce O atoms which oxidize SO_2 into sulfuric acid,

- Neutralization of sulfuric acid by ammonia and

- Rapid oxidation of additional SO_2 to sulfate through the catalytic action of ammonium ions

2.3.2.2 Other Aerosol Mechanisms

Some of the non-sulfate mechanisms for production of stratospheric aerosols wee indicated briefly in the introduction to this section. A listing of these and others indicates six possible pathways,

- Direct transport of particles from the troposphere

- Anthropogenic release in situ

- Conversion of non-sulfur stratospheric trace gases

- Extraterrestial matter

- Non-thunderstorm associated water or ice clouds

- Molecular clusters

Each of the above could contribute to the aerosol concentration in the stratosphere but none has shown any evidence of approaching the magnitude and scope of the sulfuric acid/sulfate aerosols.

The presence of stratospheric aerosols which have been transported upward from the troposphere is well substantiated by several factors. The first is the great increase in aerosols after volcanic activity. These eruptions probably contribute most of the basalt (aluminum, calcium, magnesium) type species which have been detected. The second factor indicating tropospheric to stratospheric transport is the relatively continuous decrease in concentration of aerosols with height and a third factor is the marked bimodal size distribution of the aerosols. It has been concluded from CIAP studies [4] that aerosols formed from gases in the lower stratosphere have a much larger mean size than those of tropospheric origin.

Anthropogenic releases of aerosols in the stratosphere occur from aircraft and rocket exhausts. Results of the Department of Transportation's High Altitude Pollution Program study [113] show

that current and projected aircraft operations in the lower stratosphere emit significant amounts of water, soot [carbon particles], lubricating oils and trace elements such as the heavy metals found in many crude oils. In addition to these releases, operation of propulsion systems such as the Space Shuttle booster could release a different set of chemicals such as aluminum oxides and hydrogen chloride.

In addition to the formation of sulfuric acid aerosols from sulfur dioxide and other sulfur gases, a lesser amount of aerosols appear to be formed during the NO_x and ClO_x cycles discussed previously in the ozone chemistry section. These aerosols serve as a sink for NO_x and chlorine in ozone chemistry. The main species appear to be nitric acid and hydrochloric acid. Other possible species include nitrous acid, nitrate and nitrite salts, chloride salts, hydrobromic and hydrofluoric acids, and their related halogen salts.

Non-thunderstorm associated water clouds are rare in the stratosphere. Two general types occur occasionally [115,118] from natural causes while aircraft contrails which transform into cirrus clouds have an anthropogenic origin. The first natural type called nacreous clouds occurs in polar regions at altitudes in the 21 to 30 Km range. They are presumed to be composed of supercooled water or ice. The second natural type called noctilucent clouds also occurs in polar regions at altitudes between 75 and 90km. These clouds may be

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composed of extra-terrestial dust possibly in combination with ice. Neither of these natural clouds has a significant impact on the stratospheric aerosol system. However, it has been shown that upper tropospheric and stratospheric aircraft contrails can cause a measurable change in radiative transfer.

During the CIAP study period [4] the possibility or speculation was indicated that certain gas molecules showed an affinity which caused small numbers of them to cluster together. These clusters are presumed to be much too small to be considered true aerosols but they should exhibit some non-gaseous characteristics. Among the gases speculated to cluster are sulfur dioxide, nitric oxide, molecular nitrogen, water vapor and carbon dioxide. The significance of clustering has not been theorized. This subject would require extensive investigation which does not appear to be warranted at present.

3.0 USER REQUIREMENTS FOR OZONE AND AEROSOL RELATED STRATOSPHERIC
     MEASUREMENTS

       In volume I of this report an extensive discussion of user

requirements for stratospheric measurements is presented. This dis-

cussion will be summarized here with emphasis placed on the distinc-

tion between the ozone problem which has changes in UV transmission

as its principal effect and the aerosol problem which effects

radiative transfer and hence global climate.

3.1 Identification of the Users

       The uses of both ozone and aerosol related data may be grouped

into three major categories, namely,

   • understanding stratospheric chemistry and physics

   • the effects of stratospheric change on the biosphere

   • monitoring for regulatory activities and long-term trends.

       The first function shown focuses on analysis and understanding

of the details of the various stratospheric cycles and is obviously

the most demanding in terms of the magnitude and scope of information

required.

       The second function focuses primarily on the results of strato-

spheric change namely changes in UV transmission and climate and how

they affect the earth's environment. Emphasis is not placed on the

particular cause of the change but rather on what results from the

change. Except for a few special cases such as direct intrusion of

ozone into high flying aircraft, in situ particulars are not of

concern to these users.

The third function of monitoring and regulation is of interest to a wide spectrum of users extending from governmental agencies to manufacturers or users of known or potentially hazardous materials. For example, an understandably large number of industrial organizations are known to be supporting studies of the chlorofluorocarbon/ozone problem. These users, both governmental and industrial, are concerned not only with the details of how ozone and aerosols alter the UV and radiative transfer but also with the effects of such alteration. The end goal of both groups is the formulation of equitable control and regulation when indicated.

3.2 Measurement Requirements for UV Studies

The predominant interest in the field of UV is in the interaction of biological systems with UV. As a result, it appears that this field is dominated by users far removed from effective utilization of observations which describe the state or variability of those features of the stratosphere which control UV transmission. However, at the same time, considerable interest has developed among scientific and regulatory groups in measurements of particular properties and species which will help clarify the physical and chemical processes which control the UV environment.

Specific measurement requirements are not generally clear since the largest potential group of users is not interested in detailed physics or chemistry of the stratosphere but rather with responses of biological systems to changes in the environment. However, some general comment can be made.

First, it is clear that a topic of primary concern is the intensity and wavelength distribution of ultraviolet radiation at the Earth's surface. Inference of this data from spacecraft measurements provides a unique opportunity to supplement present observations and provide more comprehensive coverage in space and time.

Secondary studies would include determination of the variability of radiation features, studies of the influence of polluting gases on the atmospheric transmission in the UV spectrum and data which relates the UV environment to biological variability.

Direct NASA contact with those studying the subject will begin the communication cycle so necessary if experiments are to be developed which satisfy these users.

3.3 Measurement Requirements for Climate Studies

Climate effects are much more pervasive than those defined previously for UV. In the case of UV, the chain of concern is traceable from the stratosphere directly to the well-defined set of users, both direct and indirect. For climate, the end point of such a consequence chain is much more diffuse. For this reason, the user community will be restricted to the primary users of remotely sensed data with the understanding that concern with climate is almost limitless.

The primary users of climatic data consist of those who are studying the physical processes of climate either through modeling or other approaches and those whose concern is monitoring the climate for indications of significant change.

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The total system which comprises the Earth's climate is extremely complex and highly interrelated. Stratospheric aerosols play only a small (but by no means insignificant) role in the total climate. However, in many cases perturbations in one or more of these smaller components of the climate system can have far reaching consequences throughout the world. With the full realization of the complexity of climate, it is still desirable to separate the system into various component processes,

- radiation
- water clouds
- surface
- atmospheric

Within these processes a set of parameters may be identified as being required for adequate characterization and monitoring of climate and in particular climate change. NASA [119] has proposed such a set of 40 parameters covering the full span of climatic component processes.

Those parameters involving atmospheric composition include:

- solar ultraviolet flux
- stratospheric aerosol optical depth
- tropospheric aerosol optical depth
- ozone
- stratospheric H_2O
- nitrous oxide and nitrogen oxides
- carbon dioxide

- chlorofluoromethanes

- methane

As can be seen in the above list many of the parameters also play key roles in the ozone chemistry cycle. Their roles in climate generally focus on their contribution to the radiative heat balance of the atmosphere. However, as stated earlier in this section this discussion is limited to aerosol related processes. The role of stratospheric gases in relation to climate has been discussed in Volume I.

Table 3-I shows NASA's proposed measurement requirements for stratospheric aerosol optical depth. In conjunction with the presentation of these requirements they indicate the need for satellite remote sensing as a key part of stratospheric aerosol monitoring.

The WMO-ICSU [47] has developed a set of requirements for the Global Atmospheric Research Program (GARP). Those requirements pertaining to atmospheric aerosol processes are shown in table 3-II. It is noteworthy that under the monitoring section the variables of concern are not only the number and mass of aerosols but also the concentration of precursor gases. It is unfortunate however that this and other studies do not provide sufficient detail to present the specifics of these precursor monitoring requirements. This again can be understood from the fact that most users are concerned with the effects of stratospheric aerosols rather than the detail chemical and physical processes.

TABLE 3-I

NASA'S PROPOSED MEASUREMENT REQUIREMENTS
FOR
STRATOSPHERIC AEROSOL OPTICAL DEPTH[119]

Desired accuracy	0.002
Spatial resolution	
North-South	250 km
East-West	1000 km
Vertical	3 km
Temporal resolution	1 month

TABLE 3-II

:ROSOL PROCESSES–SUMMARY OF TENTATIVE. OBSERVATIONAL: REQUIREMENTS[47]

-[. STUDY OF PROCESSES

a) Radiative effects of aerosols.

Required aerosol parameter for troposphere and stratosphere	Observational requirement and accuracy
Size distribution $\dfrac{dn}{dr\cdot}$ in cm^{-4} STP	5%
Vertical profile of size distribution	5% Required vertical resolution generally 0.5 to 1.0 kilometer
Real refractive index of bulk material n	1% over the range $1.0 \leq n < 2$
Imaginary part of the refractive index k	10% over the range $0.001 < k < 0.1$
Bulk density δ of aerosol particles, in g cm^{-3}	5% over the range $1.0 \leq \delta < 3.0$
Solubility of aerosol particles and/or growth characteristic with relative humidity	Use of 3 to 4 typical growth curves
For necessary data to calculate energy balance of the atmosphere	
b) Aerosol cloud interaction	Cannot be specified at this time.

[I. MONITORING

Variables to be monitored	Space Resolution	Time Resolution	Accuracy
1) Total number concentration 2) Concentration of optically important particles 3) Total mass concentration 4) Concentration of gaseous precursors	about 20 baseline stations distributed over the globe	daily	5%

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4.0 SCIENCE REQUIREMENTS

A number of recent major study groups (CIAP, GARP, NAS, etc.) and many smaller ones have addressed the general question of man's interaction with and impact on the stratosphere. A few of these groups have studied the entire stratospheric problem but in general the studies focus on one or more specific aspects of the stratospheric such as ozone, nitrogen oxides, chlorofluorocarbons or aerosols. In this section the results of these efforts are summarized and used to develop two sets of scientific requirements for stratospheric trace constituent measurements. The first set is developed on the assumption that user concern is only with the depletion of stratosphere ozone. The second assumes that user concern is only with stratospheric aerosols and associated chemistry.

In Volume I a listing is presented of those stratospheric measurements which would be desirable. The listing is presented without regard to involvement of any species or property in any specific chemical chain such as the ozone chain, the aerosol chain or others. Table 4-I presents the properties and gases from this list and indicates in capsule form the major or typical reasons why the measurement would be appropriate in a specific study of ozone or aerosols. If the term no direct involvement (NDI) is applied to any measurement it does not imply that no chain of reactions or events exists which would link the measurement with ozone or aerosol chemistry. It is intended to indicate any possible link is at least relatively remote.

4-1

TABLE 4-I
CAPSULE SUMMARY OF THE PARTICIPATION OF VARIOUS PROPERTIES AND GASES
IN OZONE AND AEROSOL CHEMISTRY

PROPERTY OR GAS	PARTICIPATION	
	OZONE CHEMISTRY	AEROSOL CHEMISTRY
Stratospheric Temperature	Changes with changes in ozone chemistry cycles	Change with aerosol changes
Solar Irradiance (inc UV)	UV-B increases with decreasing ozone	Radiation transmission affected by aerosol concentration
Earth Radiance	Many species associated with ozone absorb IR	Increase in aerosols create "greenhouse"
Water Vapor	Involved in production of H_2 and OH in upper stratosphere	Involved in $H_2SO_4 \cdot nH_2O$ formation
Ozone, O_3	a priori	Involved in oxidation of SO_2 and H_2S, through O and HO_x
Aerosols	NDI*	a priori
Carbon Dioxide, CO_2	Sink for CO through reaction with HO	NDI, except possible CO_2 cluster formation
Hydroxyl, HO	Involved in O_x, NO_x, ClO_x and CH_4 chemistry	Involved in SO_x chemistry
Atomic Oxygen, $O(^3P)$ or $O(^1D)$	Involved in O_x, HO_x, NO_x, and ClO_x chemistry	Involved in basic oxidation of SO_2
Ammonia, NH_3	Transport from troposphere and reaction with HO leads to NO_x chain	Neutralizes H_2SO_4 to produce $(NH_4)_2$ and related compounds
Nitric Oxide, NO	NO_x chemistry	NDI
Nitrogen Dioxide, NO_2	NO_x chemistry	NDI
Atomic Chlorine, Cl	ClO_x chemistry, catalytic ozone depletion	Formation of HCl and metal chlorides
Chlorine Monoxide, ClO	ClO_x chemistry	Formation of HCl and metal chlorides
Hydrogen, H_2 or H	O_x and HO_x chemistry, HCl equilibrium	Indirectly through HCl and metal chlorides
Hydroperoxyl, HO_2	O_x, HO_x, NO_x and Cl chemistry	Oxidation of SO_2
Nitrous Oxide, N_2O	NO_x chemistry	NDI
Nitrogen Pentoxide, N_2O_5	NO_x chemistry	NDI
Nitric Acid Vapor, HNO_3	NO_x chemistry	HNO_3 aerosols and nitrates
Chlorine Nitrate, $ClONO_2$	Reduces O_3 depletion; quasi sink for Cl_x and NO_x in lower stratosphere	NDI
Carbon Monoxide, CO	Involved in HO_x chemistry	NDI
Methane, CH_4	Reacts with O to produce HO and CH_3 radicals; also reacts with Cl to produce HCl and CH_3	NDI

TABLE 4-1 (CONTINUED)

PROPERTY OR GAS	PARTICIPATION	
	OZONE CHEMISTRY	AEROSOL CHEMISTRY
Hydrogen Chloride Gas, HCl	Cl chemistry	Chloride aerosol formation
Trichlorofluoromethane, F-11, $CFCl_3$	Cl chemistry, reacts with O and UV	NDI
Dichlorodifluoromethane, F-12, CF_2Cl_2	Cl chemistry, reacts with O and UV	NDI
Sulfur Dioxide, SO_2	Depletes O, HO, HO_2 etc., by oxidation to SO_3	Principal source for H_2SO_4 and sulfates
Tetrachloromethane, CCl_4	Cl chemistry, reacts with O and UV	NDI
Chloromethane, CH_3Cl	Cl chemistry, reacts with O and UV	NDI
Dichloromethane, CH_2Cl_2	Cl chemistry, reacts with O and UV	NDI
Trichloromethane, $CHCl_3$	Cl chemistry, reacts with O and UV	NDI
Formaldehyde, CH_2O	HO_x chemistry, reacts with UV to form H	NDI
Chlorodifluoromethane, F-22, $CHClF_2$	Cl chemistry, reacts with O and UV	NDI
Dichlorofluoromethane, F-21, $CHCl_2F$	Cl chemistry, reacts with O and UV	NDI
Methyl Bromide, CH_3Br	Br chemistry	NDI
Trichloroethylene, $CCl_2=CHCl$	Cl chemistry, reacts with O and UV	NDI
Methylchloroform, CH_3CCl_3	Cl chemistry, reacts with O and UV	NDI
Trichlorotrifluoroethane, F-113, $CF_2ClCFCl_2$	Cl chemistry, reacts with O and UV	NDI
Carbonyl Fluoride, F_2CO	Halogen chemistry	NDI
Fluoroformyl Chloride, ClFCO	Halogen chemistry	NDI
Tetrabromomethane, CBr_4	Br chemistry	NDI
Methyl Peroxy Radical, CH_3O_2	CH_4 and NO_x chemistry	NDI
Methyloxy Radical, CH_3O	CH_4 and NO_x chemistry	NDI
Chlorodifluoromethane Radical, CF_2Cl^+	Halogen chemistry	NDI
Dichlorofluoromethane Radical, $CFCl_2^+$	Halogen chemistry	NDI
Chlorine Dioxide, ClO_2	ClO_x chemistry	NDI
Methyl Sulfide, $(CH_3)_2S$	NDI	Sulfur and SO_x chemistry
Carbonyl Sulfide, COS	NDI	Sulfur and SO_x chemistry

TABLE 4-I (CONCLUDED)

PROPERTY OR GAS	PARTICIPATION	
	OZONE CHEMISTRY	AEROSOL CHEMISTRY
Carbon Disulfide, CS_2	NDI	Sulfur and SO_x chemistry
Dichloroethane, $C_2H_4Cl_2$	Cl chemistry	NDI
Chloroethane, C_2H_5Cl	Cl chemistry	NDI
Carbonyl Monochloride, COCl	Cl chemistry	NDI
Tetrachloroethene, $Cl_2C:CCl_2$	Cl chemistry	NDI
Vinyl Chloride, $CH_2:CHCl$	Cl chemistry	NDI
Hydrogen Sulfide, H_2S	NDI	Sulfur and SO_x chemistry
Hydrogen Fluoride, HF	Halogen chemistry	HF aerosol formation
Hydrogen Bromide, HBr	Halogen chemistry	HBr and bromide aerosol formation
Hydrogen Peroxide, H_2O_2	HO_x chemistry	HO_x/SO_x chemistry
Ammonium Ion, NH_4^+	Possible involvement with NH_3/OH reactions	Directly involved in $(NH_4)_2SO_4$ production
Sulfur Hexafluoride, SF_6	NDI, tracer in dispersion studies	NDI, tracer in dispersion studies
Sulfur Trioxide, SO_3	Product of HO_x/SO_2 reaction	Precursor of H_2SO_4 aerosol
Bisulfite Radical, HSO_3^-	Involved in possible depletion of HO	Possible precursor in H_2SO_4 and $SO_4^=$ aerosol formation
Nitrogen Trioxide, NO_3	NO_x chemistry	Precursor for HNO_3 and NO_3^- aerosols
Bromine Oxide, BrO	Br chemistry, analogous to ClO	Precursor for HBr and Br^- aerosols
Atomic Bromine, Br	Br chemistry	Precursor for HBr and Br^- aerosols
Atomic Oxygen, $O(^1S)$	Possibly involved in O_x chemistry	NDI
Molecular Oxygen, $O_2(^1\Delta)$	Possible involved in O_x chemistry	NDI
Non-Methane Hydrocarbon, C_xH_y	Possible reactions analogous to CH_4	NDI
Various Organics, $H_xC_yO_z$	Possible reactions analogous to CH_2O	NDI

Specific aerosols have not been included in the table since they are a priori involved in aerosol chemistry and as a group have no direct involvement in ozone chemistry. This is due to the quasi irreversable nature of aerosol formation. The only known sinks for aerosols are gravitational settling into the troposphere or possible washout in stratospheric thunderclouds.

4.1 Development of Scientific Criteria

The scientific criteria developed for stratospheric pollution measurements must have as their basis the major objectives of the entire stratospheric program. These objectives may be primary or secondary depending upon the nature of their interaction with man and his environment. The primary objectives are:

- Monitoring climatic changes caused by changes in the concentrations of the various stratospheric trace constituents, particularly aerosols; and,

- Monitoring changes in ultraviolet received at the earth's surface as a result of changes in the concentrations of the various stratospheric trace constituents, particularly ozone.

The secondary objectives may be considered as indirect objectives of the entire program. These are:

- Increased understanding of the chemistry and physics of the stratosphere and its constituents; and,

- Increased understanding of the meteorology and hydrodynamics of the stratosphere.

Obviously, there is considerable overlap between the primary and secondary objectives, since the latter have a much broader scope which includes the former.

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The following sections present discussions supporting the prioritization of ozone and aerosol related measurements into the various groupings shown.

4.2. Prioritization of Ozone Related Measurements

The list of stratospheric ozone related measurements has been presented in four groups which are considered to be of descending order of importance in terms of the absolute need for the measurement without regard to present knowledge or measurement capability. However, it must be emphasized at this point that none of these groups is considered unimportant. The groupings merely show the degree of importance, and relative placement within a group has no significance.

The rationale for placement of a required measurement in any one of the categories is given below:

Ozone Group 1. This group contains those properties and species which are considered to be directly related to changes in the untraviolet flux. For example, ozone is directly related to the major absorption of ultraviolet while the freon compounds are not.

Ozone Group 2. In this group are listed the components of the basic reactions involved in the direct production or depletion of the ozone concentration in the stratosphere. These species participate in the principal chemical equations which directly involve ozone. These equations are given below for each of the significant chemistry

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chains. The numbers in parentheses are the equation numbers as used previously in section 2.

Pure oxygen reactions:

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

$$O_3 + h\nu \ (\lambda :0.45\text{-}0.65 \ \mu m) \longrightarrow O + O_2 \qquad\qquad .(3a)$$

$$O_3 + h\nu \ (\lambda :0.31\text{-}0.34 \ \mu m) \longrightarrow O_2(^1\Delta) + O \ (^3P) \qquad (3b)$$

$$O_3 + h\nu \ (\lambda < 0.31 \ \mu m) \longrightarrow O \ (^1D) + O_2 \qquad\qquad (3c)$$

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

Hydrogen-oxygen reactions:

$$H + O_3 \longrightarrow HO + O_2 \qquad\qquad\qquad (7)$$

$$HO_2 + O_3 \longrightarrow HO + 2O_2 \qquad\qquad\qquad (10a)$$

$$HO + O_3 \longrightarrow HO_2 + O_2 \qquad\qquad\qquad (10b)$$
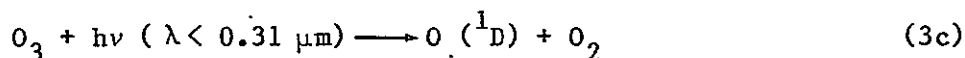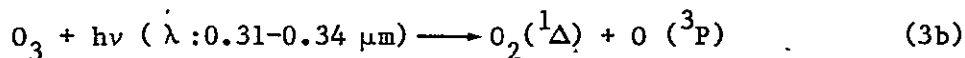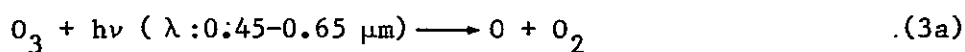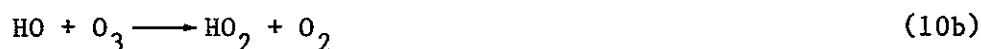
Nitrogen-oxygen reactions:

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad\qquad\qquad (25)$$

Chlorine-oxygen reactions:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad\qquad\qquad (38)$$
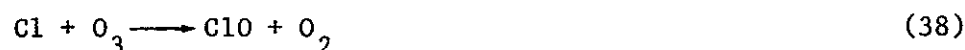
Ozone Group 3. This group contains those species considered to be the most important ones in the indirect chemistry chains; that is, those which result in the production or depletion of the major species discussed under Group 2.

Ozone Group 4. This group contains those species considered to be involved in a lesser but not unimportant way on the indirect chemistry chains discussed above.

Table 4-II presents the list of ozone related stratospheric measurements which should be made or would be of scientific interest. The measurements are grouped according to the criteria discussed above and placement was made after analyzing all available references that discuss the importance of the various species. The list also shows the major references supporting the selection of the measurement and its placement in the appropriate group. A number of other references [49, 57-61, 74-103, 113-120] were also consulted during preparation of the list.

4.3 Prioritization of Aerosol Related Measurements

The list of stratospheric aerosol related measurements has been presented in six groups which are considered to be of descending order of importance in terms of the absolute need for the measurement without regard to present knowledge or measurement capability. However, it must be emphasized at this point that none of these groups is considered totally unimportant. The groupings merely show the degree of importance, and relative placement within a group has no significance.

The rationale for placement of a required measurement in any one of the categories is given below:

Aerosol Group 1. This group contains those properties and species which are considered to be directly related to changes in climate and/or the stratospheric aerosol content. The group contains both stratospheric properties such as temperature and radiative flux and species such as total aerosols and sulfate aerosols.

TABLE 4-II

PRIORITIZED LIST OF DESIRED STRATOSPHERIC OZONE RELATED MEASUREMENTS

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
OZONE GROUP 1, MEASUREMENTS OF PROPERTIES AND SPECIES DIRECTLY ASSOCIATED WITH UV CHANGE														
Temperature	✓	✓	✓	✓	✓	✓				✓		✓	✓	✓
Solar Irradiance (including UV)	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Earth Radiance	✓	✓	✓		✓	✓				✓			✓	
Ozone, O_3	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓
OZONE GROUP 2, COMPONENTS OF THE BASIC REACTIONS INVOLVED IN THE DIRECT PRODUCTION OR DEPLETION OF OZONE														
Hydroxyl, HO	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓
Atomic Oxygen, $O(^3P)$	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
Atomic Oxygen, $O(^1D)$	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
Nitric Oxide, NO	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Nitrogen Dioxide, NO_2	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Atomic Chlorine, Cl	✓		✓	✓	✓			✓	✓	✓		✓	✓	✓
Chlorine Monoxide, ClO	✓	✓	✓	✓	✓	✓		✓	✓	✓		✓	✓	✓
Hydrogen, H_2 or H	✓	✓	✓	✓		✓		✓	✓	✓		✓		✓
Hydroperoxyl, HO_2	✓		✓	✓		✓	✓	✓	✓	✓		✓		✓

TABLE 4-II (Continued)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
OZONE GROUP 3, MAJOR COMPONENTS OF THE BASIC REACTIONS INDIRECTLY INVOLVED IN THE PRODUCTION OR DEPLETION OF OZONE														
Water Vapor, H_2O	✓	✓	✓		✓	✓	✓		✓	✓		✓	✓	✓
Ammonia, NH_3		✓			✓	✓	✓					✓		
Nitrous Oxide, N_2O	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓
Nitrogen Pentoxide, N_2O_5	✓		✓	✓	✓	✓		✓					✓	✓
Nitric Acid Vapor, HNO_3	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Chlorine Nitrate, $ClONO_2$								✓	✓			✓		✓
Carbon Monoxide, CO		✓	✓	✓		✓				✓		✓	✓	✓
Methane, CH_4	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Hydrogen Chloride Gas, HCl	✓	✓	✓	✓	✓			✓	✓	✓		✓	✓	✓
Trichlorofluoromethane, F-11, $CFCl_3$	✓	✓	✓	✓	✓			✓	✓	✓		✓	✓	✓
Dichlorodifluoromethane, F-12, CF_2Cl_2	✓	✓	✓	✓	✓			✓	✓	✓		✓	✓	✓
Sulfur Dioxide, SO_2	✓		✓		✓	✓	✓					✓	✓	
OZONE GROUP 4, OTHER SIGNIFICANT COMPONENTS OF THE OZONE CHEMISTRY CHAINS														
Carbon Dioxide, CO_2	✓	✓	✓					✓		✓	--	✓	✓	✓
Tetrachloromethane, CCl_4, (carbon tetrachloride)	✓	--		✓				✓	✓	✓		✓		✓

TABLE 4-II (Continued)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
<u>OZONE GROUP 4</u> (Continued)														
Chloromethane, CH_3Cl, (Methyl Chloride)					✓									
Dichloromethane, CH_2Cl_2, (Methyl Dichloride)					✓									
Trichloromethane, $CHCl_3$ (Chloroform)					✓									
Methanal, CH_2O, (Formaldehyde)			✓											
Chlorodifluoromethane, F-22, $CHClF_2$								✓	✓					
Dichlorofluoromethane, F-21, $CHCl_2F$								✓						
Bromomethane, CH_3BR, (Methyl Bromide)	✓							✓	✓	✓		✓		
Trichloroethylene, $CCl_2=CHCl$									✓	✓				✓
Methylchloroform, CH_3CCl_3									✓	✓				✓
Trichlorotrifluoroethane, F-113, $CF_2ClCFCl_2$									✓					
Carbonyl Fluoride, F_2CO									✓	✓		✓		✓
Fluoroformyl Chloride, $ClFCO$									✓	✓				✓
Tetrabromomethane, CBr_4	✓													
Methyl Peroxy Radical, CH_3O_2	✓													
Methyl Oxy Radical, CH_3O	✓													
Chlorodifluoromethane Radical, CF_2Cl^+	✓									✓				
Dichlorofluoromethane Radical, $CFCl_2^+$										✓				

TABLE 4-II (Continued)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
OZONE GROUP 4 (Continued)														
Chlorine Dioxide, ClO_2	✓													
Dichloroethane, $C_2H_4Cl_2$														✓
Ethyl Chloride, C_2H_5Cl														✓
Carbonyl Monochloride, $COCl$														✓
Tetrachloroethene, $Cl_2C{:}CCl_2$														✓
Vinyl Chloride, $CH_2{:}CHCl$														✓
Hydrogen Fluoride, HF			✓						✓	✓		✓	✓	✓
Hydrogen Bromide, HBr			✓									✓		✓
Hydrogen Peroxide, H_2O_2	✓	✓	✓			✓		✓				✓		✓
Ammonium Ion, NH_4^+		✓				✓	✓							
Sulfur Trioxide, SO_3	✓											✓		
Bisulfite Radical, HSO_3^-												✓		
Nitrogen Trioxide, NO_3	✓					✓						✓	✓	
Bromine Oxide, BrO												✓		
Atomic Bromine, Br												✓		✓
Atomic Oxygen, $O(^1S)$														✓
Oxygen, $O_2(^1\Delta)$														✓

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TABLE 4-II (Concluded)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
OZONE GROUP 4 (Concluded)														
Non-Methane Hydrocarbons, $C_x H_y$												✓		
Various Organics, $H_x C_y O_z$	✓													

Aerosol Group 2. In this group are listed the gaseous precursor components which are involved in the basic reactions for production of either sulfuric acid or ammonium sulfate aerosols. These reactions were shown in equations (47) through (52) in Section 2.3.2.1.

Aerosol Group 3. This group contains the major specific aerosols both in the sulfate and non-sulfate category. The latter includes aerosols such as nitric acid and hydrochloric acid.

Aerosol Group 4. This group contains all other aerosols which may be of significance in the stratosphere.

Aerosol Group 5. This group contains the precursor gases for non-sulfate aerosols along with the gases indirectly associated with sulfate aerosols.

Aerosol Group 6. This group contains those species suspected of being capable of forming molecular clusters as discussed in Section 2.3.2.1.

Table 4-III presents the list of aerosol related stratospheric measurements which should be made or would be of scientific interest. The measurements are grouped according to the criteria discussed above and placement was made after analyzing all available references that discuss the importance of the various species. The list also shows the major references supporting the selection of the measurement and its placement in the appropriate group. A number of other references [49, 57-61, 74-103, 113-120] were also consulted during preparation of the list.

TABLE 4-III

PRIORITIZED LIST OF DESIRED STRATOSPHERIC AEROSOL RELATED MEASUREMENTS

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
AEROSOL GROUP 1A, DIRECT MEASUREMENTS OF CLIMATIC CHANGE AND ULTRA-VIOLET CHANGE														
Temperature	✓	✓	✓	✓	✓	✓				✓		✓	✓	✓
Solar Irradiance (including UV)	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Earth Radiance	✓	✓	✓		✓	✓				✓			✓	
AEROSOL GROUP 1B, MAJOR AEROSOLS														
Total Aerosols		✓	✓	✓	✓	✓	✓					✓	✓	✓
Total Sulfate Aerosols	✓	✓	✓			✓	✓					✓		
Sulfuric Acid Aerosol, $H_2SO_4 \cdot nH_2O$	✓	✓	✓			✓	✓					✓		
Ammonium Sulfate, $(NH_4)_2 SO_4$		✓	✓			✓	✓					✓		
AEROSOL GROUP 2, MAJOR SULFATE AEROSOL PRECURSOR GASES														
Sulfur Dioxide, SO_2	✓		✓		✓	✓	✓					✓	✓	
Sulfur Trioxide, SO_3	✓						✓					✓		
Atomic Oxygen, O	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
Water Vapor, H_2O	✓	✓	✓		✓	✓	✓		✓	✓		✓	✓	✓
Hydroxyl, HO	✓	✓	✓		✓	✓	✓	✓	✓	✓		✓	✓	✓
Hydroperoxyl, HO_2	✓		✓	✓		✓	✓	✓	✓	✓		✓		✓

TABLE 4-III (Continued)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
AEROSOL GROUP 2 Concluded														
Ammonia, NH_3			✓		✓	✓	✓					✓		
Ammonium Ion, NH_4^+		✓				✓	✓							
AEROSOL GROUP 3, MAJOR SPECIFIC AEROSOLS														
Nitric Acid Aerosol, $nHNO_3$		✓	✓											
Chloride Aerosol, Cl^-														
Nitrate Aerosol, NO_3^-		✓	✓			✓	✓							
Ammonium Ion Aerosol, nNH_4^+		✓	✓			✓	✓							
Ammonium Peroxydisulfate, $(NH_4)_2 S_2O_8$			✓			✓								
AEROSOL GROUP 4, OTHER SPECIFIC AEROSOLS														
Aluminum Oxide Aerosol, nAl_2O_3	✓											✓		
Nitrite Aerosol, NO_2^-		✓					✓							
Liquid Water or Ice, nH_2O	✓	✓	✓											
Aluminum Ion, Al^{+++}		✓												
Bromide Ion, Br^-		✓	✓				✓							
Calcium Ion, Ca^{++}		✓					✓							
Copper Ion, Cu^{++}		✓	✓											

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TABLE 4-III (Continued)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
AEROSOL GROUP 4 Concluded														
Iodide Ion, I^-		✓	✓											
Iron Ion, Fe^{++} or Fe^{+++}			✓											
Magnesium, Mg		✓												
Manganese Ion, Mn^{++} or Mn^{+++}			✓											
Potassium Ion, K^+		✓	✓											
Silicon Ion, Si^{++++}		✓	✓											
Sodium Ion, Na^+		✓	✓				✓							
AEROSOL GROUP 5, OTHER PRECURSOR GASES														
Ozone, O_3	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Atomic Chlorine, Cl	✓		✓	✓	✓			✓	✓	✓		✓	✓	✓
Chlorine Monoxide, ClO	✓	✓	✓	✓	✓	✓		✓	✓	✓		✓	✓	✓
Hydrogen, H_2 or H	✓	✓	✓	✓		✓		✓	✓	✓		✓		✓
Nitric Acid Vapor, HNO_3	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
Hydrogen Chloride Gas, HCl	✓	✓	✓	✓	✓			✓	✓	✓		✓	✓	✓
Hydrogen Sulfide, H_2S					✓	✓	✓					✓		
Methyl Sulfide, $(CH_3)_2S$												✓		

TABLE 4-III (Concluded)

NAME OF SPECIES/PROPERTY AND SYMBOL	MAJOR REFERENCES WHERE CITED													
	39	40	62	63	64	65	66	67	68	69	70	71	72	73
AEROSOL GROUP 5 Concluded														
Carbonyl Sulfide, COS														✓
Carbon Disulfide, CS_2														✓
Hydrogen Fluoride, HF				✓					✓	✓		✓	✓	✓
Hydrogen Bromide, HBr				✓								✓		✓
Hydrogen Peroxide, H_2O_2	✓	✓	✓			✓		✓				✓	✓	✓
Bisulfite Radical, HSO_3^-							✓					✓		
Nitrogen Trioxide, NO_3	✓					✓						✓	✓	
Bromine Oxide, BrO												✓		✓
Atomic Bromine, Br												✓		✓
AEROSOL GROUP 6, QUASI AEROSOLS														
Sulfur Dioxide, nSO_2, (in cluster formation)		✓	✓											
Nitric Oxide, nNO, (" " ")			✓											
Nitrogen, nN_2 (" " ")			✓											
Liquid Water or Ice, nH_2O (" " ")			✓											
Carbon Dioxide, nCO_2 (" " ")			✓											

4-18

5.0 MISSION EVALUATIONS

This section presents the results of the application of a method for the evaluation of various stratospheric species measurement missions. The method was developed previously [2] and is presented in detail as Appendix A in both Volumes I and II of this report. In the current application the method has been revised and updated to evaluate the same set of missions and instruments from two standpoints,

- the monitoring of stratospheric ozone and related processes,

- the monitoring of stratospheric aerosols and related precursor gaseous processes.

5.1 Evaluation of Specific Missions

The missions selected for evaluation were:

- A Shuttle-type mission with a 30° inclination and a four-to six-month duration,

- A Shuttle-type mission with a 56° inclination and a four-to six-month duration,

- A polar-type mission with a one- to two-year duration.

Several instruments under development were evaluated for each of these missions. The instruments evaluated are shown in Table 5-I along with the generic type of each of the species evaluated.

Tables 5-II through 5-XVII show the results of these evaluations for each species/instrument/mission combination. Included with each parameter value for the three missions is the performance used to determine the value. The values (V) shown in each table for present, required and mission capability are taken from the value matrices presented in Volume III of this report. The values represent the

5-1.

TABLE 5-I

STRATOSPHERIC INSTRUMENTS AND SPECIES EVALUATED
FOR
OZONE AND AEROSOL MISSIONS

INSTRUMENT	GENERIC TYPE	SPECIES	OZONE MISSION	AEROSOL MISSION
LIMS[*]	Limb scanning	CO_2	✓	
		O_3	✓	✓
		H_2O	✓	✓
		NO_2	✓	
		HNO_3	✓	✓
SAGE	Solar occultation	O_3	✓	✓
		Aerosols		✓
CIMATS	Solar occultation	H_2O	✓	✓
		CH_4	✓	
		N_2O	✓	
		NH_3	✓	✓
		CO	✓	
HALOE	Solar occultation	HF	✓	✓
		CH_4	✓	
		HCl	✓	✓
		NO	✓	

[*]Instrument descriptions are given in Section 6.2 of Volume I.

TABLE 5-II

EVALUATION OF CARBON DIOXIDE, CO_2, LIMS WITH 80° AZIMUTH SCAN

Parameter	WF 0-1	Present Knowledge V	Present Knowledge VXWF	Required Capability V	Required Capability VXWF	Shuttle 30° V	Shuttle 30° VXWF	Shuttle 56° V	Shuttle 56° VXWF	Sun-Sync Noon V	Sun-Sync Noon VXWF
Latitude	0.1	8	0.8	9	0.8	5 90°	0.5	8 140°	0.8	10 170°	1.0
Duration of Program	0.3	8	2.4	8	2.4	5 4-6 mos	1.5	5 4-6 mos	1.5	7 1-2 yrs	2.1
Diurnal Coverage	0.1	8	0.8	8	0.8	10 Full	1.0	10 Full	1.0	9 Part D&N	1.0
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	0.2	10	2.0	10	2.0	10 Full	2.0	10 Full	2.0	10 Full	2.0
Vertical Profile Resolution	0.2	8	1.6	9	1.8	10 <1Km	2.0	10 <1Km	2.0	10 <1Km	2.0
Longitude	0.1	8	0.8	8	0.8	10 Full	1.0	10 Full	1.0	10 Full	1.0
	1.0		8.4		8.6		8.0		8.3		9.1
Total Value			8		9		8		8		9
Incremental Gain Over Present							<1		<1		<1	1

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-III

EVALUATION OF OZONE, LIMS WITH 80° AZIMUTH SCAN

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.25	10	2.5	10	2.5	5 90°	1.25	6 140°	1.5	10 170°	2.5
Duration of Program	.25	7	1.75	10	2.5	4 4-6 mos	1.0	4 4-6 mos	1.0	6 1-2 yrs	1.5
Diurnal Coverage	.15	2	.3	8	1.2	10 Full	1.5	10 Full	1.5	8 Part D&N	1.2
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.1	7	.7	10	1	10 Full	1.0	10 Full	1.0	10 Full	1.0
Vertical Profile Resolution	.15	5	.75	10	1.5	10 <1Km	1.5	10 <1Km	1.5	10 <1Km	1.5
Longitude	.1	10	1	10	1	10 Full	1.0	10 Full	1.0	10 Full	1.0
	1.0		7.0		9.7		7.25		7.5		8.7
Total Value		7		10		7		8		9	
Incremental Gain Over Present				3		<1		1		2	

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-IV

EVALUATION OF OZONE, SAGE, SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.25	10	2.5	10	2.5	4 90° sparse at extremes	1.0	7 150° sparse at extremes	1.75	0	0 5
Duration of Program	.25	7	1.75	10	2.5	4 4-6 mos	1.0	4 4-6 mos	1.0	6 1-2 yrs	1.5
Diurnal Coverage	.15	2	.3	8	1.2	2 Part Day 2 points	0.3	2 Part Day 2 points	0.3	2 Part Day 2 points	0.3
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.1	7	.7	10	1	10 Full	1.0	10 Full	1.0	10 Full	1.0
Vertical Profile Resolution	.15	5	.75	10	1.5	7 ~10 points	1.05	7 ~10 points	1.05	7 ~10 points	1.05
Longitude	.1	10	1	10	1	10 Full	1.0	10 Full	1.0	10 Full	1.0
	1.0		7.0		9.7		5.35		6.1		4.85
Total Value		7		10		5		6		5	
Incremental Gain Over Present				3		<1		<1		<1	

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-V

EVALUATION OF WATER VAPOR, H_2O, CIMATS SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge V	VXWF	Required Capability V	VXWF	Shuttle 30° V	VXWF	Shuttle .56° V	VXWF	Sun-Sync Noon V	VXWF
Latitude	.3	6	1.8	9	2.7	6	1.8 90° sparse at extremes	8	2.4 150° sparse at extremes	0	0 5°
Duration of Program	.2	5	1.0	9	1.8	6	1.2 4-6 mos	6	1.2 4-6 mos	9	1.8 1-2 yrs
Diurnal Coverage	.1	7	0.7	8	0.8	2	0.2 Part Day 2 points	2	0.2 Part Day 2 points	2	0.2 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	5	0.75	10	1.5	10	1.5 Full	10	1.5 Full	10	1.5 Full
Vertical Profile Resolution	.15	7	1.05	10	1.5	5	0.75 ~20 points	5	0.75 ~20 points	5	0.75 ~20 points
Longitude	.1	0	0	8	0.8	10	0.1 Full	10	0.1 Full	10	0.1 Full
	1.0		5.3		9.1		5.55		6.15		4.35
Total Value			5		9		6		6		4
Incremental Gain Over Present					4		1		1		<1

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-VI

EVALUATION OF WATER VAPOR, H_2O, LIMS WITH 80° AZIMUTH SCAN

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.3	6	1.8	9	2.7	7 90°	2.1	9 140°	2.7	10 170	3.0
Duration of Program	.2	5	1.0	9	1.8	6 4-6 mos	1.2	6 4-6 mos	1.2	9 1-2 yrs	1.8
Diurnal Coverage	.1	7	0.7	8	0.8	10 Full	1.0	10 Full	1.0	9 Part D&N	0.9
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	5	0.75	10	1.5	10 Full	1.5	10 Full	1.5	10 Full	1.5
Vertical Profile Resolution	.15	7	1.05	10	1.5	10 <1Km	1.5	10 <1Km	1.5	10 <1Km	1.5
Longitude	.1	0	0	8	0.8	10 Full	1.0	10 Full	1.0	10 Full	1.0
	1.0		5.3		9.1		8.3		8.9		9.7
Total Value			5		9		8		9		10
Incremental Gain Over Present					4		3		4		5

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-VII

EVALUATION OF AEROSOLS, SAGE SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.15	9	1.35	10	1.5	4	0.6 90° sparse at extremes	7	1.05 150° sparse at extremes	0	0 5
Duration of Program	.15	8	1.2	9	1.35	7	1.05 4-6 mos	7	1.05 4-6 mos	9	1.35 1-2 yrs
Diurnal Coverage	.05	9	0.45	9	0.45	6	.3 Part Day 2 points	6	.3 Part Day 2 points	6	.3 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.25	8	2.0	10	2.5	10	2.5 Full	10	2.5 Full	10	2.5 Full
Vertical Profile Resolution	.15	7	1.05	10	1.5	7	1.05 ~10 points	7	1.05 ~10 points	7	1.05 ~10 points
Longitude	.25	6	1.5	10	2.5	10	2.5 Full	10	2.5 Full	10	2.5 Full
	1.0		7.55		9.8		8.00		8.45		7.7
Total Value			8		10		8		8		8
Incremental Gain Over Present					2		<1		<1		<1

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-VIII

EVALUATION OF AMMONIA, NH_3, CIMATS SOLAR OCCULTATION

Parameter	WF	Present V	Present VXWF	Required V	Required VXWF	Shuttle V	Shuttle VXWF	Shuttle V	Shuttle VXWF	Sun-Sync V	Sun-Sync VXWF
Latitude	.2	0	0	7	1.4	7	1.4 90° sparse at extremes	8	1.6 150° sparse at extremes	0	0 ~5°
Duration of Program	.1	0	0	6	0.6	8	0.8 4-6 mos	8	0.8 4-6 mos	9	0.9 1-2 yrs
Diurnal Coverage	.15	0	0	6	0.9	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.25	0	0	7	1.75	10	2.5 Full	10	2.5 Full	10	2.5 Full
Vertical Profile Resolution	.25	0	0	7	1.75	9	2.25 ~20 points	9	2.25 ~20 points	9	2.25 ~20 points
Longitude	.05	0	0	8	0.4	10	0.5 Full	10	0.5 Full	10	0.5 Full
	1.0		0.		6.8		8.05		8.25		6.75
Total Value		0		7		8		8		7	
Incremental Gain Over Present				7		8		8		7	

LEGEND:

V = Value

VXWF = Value x weighting factor

TABLE 5-IX

EVALUATION OF NITROGEN DIOXIDE, NO_2, LIMS WITH 80° AZIMUTH SCAN

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.15	4	.6	10	1.5	7	1.05	9	1.35	10	1.5
							90°		140°		170°
Duration of Program	.15	5	.75	9	1.35	7	1.05	7	1.05	9	1.35
							4-6 mos		4-6 mos		1-2 yrs
Diurnal Coverage	.35	5	1.75	9	3.15	10	3.5	10	3.5	8	2.8
							Full		Full		Part D&N
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	6	0.9	10	1.5	10	1.5	10	1.5	10	1.5
							Full		Full		Full
Vertical Profile Resolution	.15	4	0.6	10	1.5	10	1.5	10	1.5	10	1.5
							≤1Km		≤1Km		≤1Km
Longitude	.05	0	0	8	0.4	10	.5	10	.5	10	.5
							Full		Full		Full
	1.0		4.6		9.4		9.1		9.4		9.15
Total Value			5		9		9		9		9
Incremental Gain Over Present					4		4		4		4

LEGEND:

V = Value

VXWF = Value x weighting factor

TABLE 5-X

EVALUATION OF NITRIC ACID VAPOR, NHO_3, LIMS WITH 80° AZIMUTH SCAN

Parameter	WF 0-1	Present Knowledge V	VXWF	Required Capability V	VXWF	Shuttle 30° V	VXWF	Shuttle 56° V	VXWF	Sun-Sync Noon V	VXWF
Latitude	.3	5	1.9	10	3.0	7 90°	2.1	9 140°	2.7	10 170°	3.0
Duration of Program	.25	3	.75	9	2.25	7 4-6 mos	1.75	7 4-6 mos	1.75	9 1-2 yrs	2.25
Diurnal Coverage	.1	7	.7	8	.8	10 Full	1.0	10 Full	1.0	8 Part D&N	0.8
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	7	1.05	10	1.5	10 Full	1.5	10 Full	1.5	10 Full	1.5
Vertical Profile Resolution	.1	8	.8	10	1.0	10 ≤1Km	1.0	10 ≤1Km	1.0	10 ≤1Km	1.5
Longitude	.1	0	0	8	.8	10 Full	1.0	10 Full	1.0	10 Full	1.0
	1.0		4.8		9.35		8.35		8.95		9.55
Total Value		5		9		8		9		10	
Incremental Gain Over Present				4		3		4		5	

LEGEND:

V = Value
VXWF = Value x weighting factor
D & N = Day & Night

TABLE 5-XI

EVALUATION OF HYDROGEN CHLORIDE GAS, HCl, HALOE SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge V	Present Knowledge VXWF	Required Capability V	Required Capability VXWF	Shuttle 30° V	Shuttle 30° VXWF	Shuttle 56° V	Shuttle 56° VXWF	Sun-Sync Noon V	Sun-Sync Noon VXWF
Latitude	.35	4	1.4	9	3.15	6	2.1 90° sparse at extremes	8	2.8 150° sparse at extremes	0	0 5°
Duration of Program	.1	5	.5	8	.8	8	0.8 4-6 mos	8	0.8 4-6 mos	9	0.8 1-2 yrs
Diurnal Coverage	.1	0	0	7	.7	3	0.3 Part Day 2 points	3	0.3 Part Day 2 points	3	0.3 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.2	6	1.2	9	1.8	9	1.8 10-40Km	9	1.8 10-40Km	9	1.8 10-40Km
Vertical Profile Resolution	.2	7	1.4	9	1.8	9	1.8 2Km	9	1.8 2Km	9	1.8 2Km
Longitude	.05	0	0	8	.4	10	0.5 Full	10	0.5 Full	10	0.5 Full
	1.0		4.5		8.65		7.35		8.0		5.2
Total Value			5		9		7		8		5
Incremental Gain Over Present					4		2		3		<1

LEGEND:
V = Value
VXWF = Value x weighting factor

EVALUATION OF METHANE, CH_4, CIMATS SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge V	VXWF	Required Capability V	VXWF	Shuttle 30° V	VXWF	Shuttle 56° V	VXWF	Sun-Sync Noon V	VXWF
Latitude	.4	0	0	8	3.2	7	2.8 90° sparse at extremes	8	3.2 150° sparse at extremes	0	0 5°
Duration of Program	.1	0	0	6	0.6	8	0.8 4-6 mos	8	0.8 4-6 mos	9	0.9 1-2 yrs
Diurnal Coverage	.15	0	0	6	0.9	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	6	0.9	8	1.2	10	1.5 Full	10	1.5 Full	10	1.5 Full
Vertical Profile Resolution	.15	3	0.45	9	1.35	9	1.35 ~20 points	9	1.35 ~20 points	9	1.35 ~20 points
Longitude	.05	0	0	8	0.4	10	0.5 Full	10	0.5 Full	10	0.5 Full
	1.0		1.35		7.65		7.55		7.95		4.85
Total Value			1		8		8		8		5
Incremental Gain Over Present					7		7		7		4

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-XIII

EVALUATION OF METHANE, CH_4, HALOE SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.4	0	0	8	3.2	7	2.8 90° sparse at extremes	8	3.2 150° sparse at extremes	0	0 ~5
Duration of Program	.1	0	0	6	0.6	8	0.8 4-6 mos	8	0.8 4-6 mos	9	0.9 1-2 yrs
Diurnal Coverage	.15	0	0	6	0.9	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points	4	0.6 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	6	0.9	8	1.2	10	1.5 Full	10	1.5 Full	10	1.5 Full
Vertical Profile Resolution	.15	3	0.45	9	1.35	9	1.35 2Km	9	1.35 2Km	9	1.35 2Km
Longitude	.05	0	0	8	0.4	10	0.5 Full	10	0.5 Full	10	0.5 Full
	1.0		1.35		7.65		7.55		7.95		4.85
Total Value			1		8		8		8		5
Incremental Gain Over Present					7		7		7		4

LEGEND:
V = Value
VXWF = Value x weighting factor

EVALUATION OF NITROUS OXIDE, N_2O, CIMATS SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge V	Present Knowledge VXWF	Required Capability V	Required Capability VXWF	Shuttle 30° V	Shuttle 30° VXWF	Shuttle 56° V	Shuttle 56° VXWF	Sun-Sync Noon V	Sun-Sync Noon VXWF
Latitude	.25	4	1.0	10	2.5	7	1.75 90° sparse at extremes	9	2.25 150° sparse at extremes	0	0 ~5°
Duration of Program	.15	5	0.75	9	1.35	7	1.05 4-6 mos	7	1.05 4-6 mos	9	1.35 1-2 yrs
Diurnal Coverage	.1	8	0.8	8	0.8	1	0.1 Part Day 2 points	1	0.1 Part Day 2 points	1	0.1 Part Day 2 points
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	6	0.9	10	1.5	10	1.5 Full	10	1.5 Full	10	1.5 Full
Vertical Profile Resolution	.15	4	0.6	10	1.5	9	1.35 ~20 points	9	1.35 ~20 points	9	1.35 ~20 points
Longitude	.05	0	0	8	0.4	10	0.5 Full	10	0.5 Full	10	0.5 Full
	1.0		4.05		8.05		6.25		6.75		4.8
Total Value			4		8		6		7		5
Incremental Gain Over Present					4		2		3		1

LEGEND:

V = Value

VXWF = Value x weighting factor

TABLE 5-XV

EVALUATION OF CARBON MONOXIDE, CO, CIMATS SOLAR OCCULTATION

Parameter	WF. 0-1	Present Knowledge V	Present Knowledge VXWF	Required Capability V	Required Capability VXWF	Shuttle 30° V	Shuttle 30° VXWF	Shuttle 56° V	Shuttle 56° VXWF	Sun-Sync Noon V	Sun-Sync Noon VXWF
Latitude	.4	0	0	8	3.2	7 2.8 90° sparse at extremes		8 3.2 150° sparse at extremes		0 ~5°	0
Duration of Program	.1	0	0	6	0.6	8 0.8 4-6 mos		8 0.8 4-6 mos		9 1-2 yrs	0.9
Diurnal Coverage	.15	0	0	6	0.9	4 0.6 Part Day 2 points		4 0.6 Part Day 2 points		4 0.6 Part Day 2 points	
Launch Time	0	10	0	10	0	10	0	10	0	10	0
Vertical Profile Coverage	.15	5	.75	9	1.35	10 1.5 Full		10 1.5 Full		10 1.5 Full	
Vertical Profile Resolution	.15	3	.45	9	1.35	9 1.35 ~20 points		9 1.35 ~20 points		9 1.35 ~20 points	
Longitude	.05	0	0	8	0.4	10 0.5 Full		10 0.5 Full		10 0.5 Full	
	1.0		1.2		7.8	7.55		7.95		4.85	
Total Value			1		8.	8		8		5	
Incremental Gain Over Present						7		7		4	

LEGEND:

V = Value

VXWF = Value x weighting factor

TABLE 5-XVI

EVALUATION OF HYDROGEN FLUORIDE, HF, HALOE SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.2	0	0	7	1.4	7 1.4 90° sparse at extremes		8 1.6 150° sparse at extremes		0 0 ~5°	
Duration of Program	.1	0	0	6	0.6	8 0.8 4-6 mos		8 0.8 4-6 mos		9 0.9 1-2 yrs	
Diurnal Coverage	.15	0	0	6	0.9	4 0.6 Part Day 2 points		4 0.6 Part Day 2 points		4 0.6 Part Day 2 points	
Launch Time	0	10	0	10	0	10 0		10 0		10 0	
Vertical Profile Coverage	.25	0	0	7	1.75	10 2.5 Full		10 2.5 Full		10 2.5 Full	
Vertical Profile Resolution	.25	0	0	7	1.75	9 2.25 2Km		9 2.25 2Km		9 2.25 2Km	
Longitude	.05	0	0	8	0.4	10 0.5 Full		10 0.5 Full		10 0.5 Full	
	1.0		0		6.8		8.05		8.25		6.75
Total Value		0		7		8		8		7	
Incremental Gain Over Present				7		8		8		7	

LEGEND:
V = Value
VXWF = Value x weighting factor

TABLE 5-XVII

EVALUATION OF NITRIC OXIDE, NO, HALOE SOLAR OCCULTATION

Parameter	WF 0-1	Present Knowledge		Required Capability		Shuttle 30°		Shuttle 56°		Sun-Sync Noon	
		V	VXWF	V	VXWF	V	VXWF	V	VXWF	V	VXWF
Latitude	.25	4	1.0	10	2.5	6 1.5 90° sparse at extremes		9 2.25 150° sparse at extremes		0 0 ∿5°	
Duration of Program	.2	8	1.6	9	1.8	5 1.0 4-6 mos		5 1.0 4-6 mos		9 1.8 1-2 yrs	
Diurnal Coverage	.3	5	1.5	9	2.7	3 0.9 Part Day 2 points		3 0.9 Part Day 2 points		3 0.9 Part Day 2 points	
Launch Time	0	10	0	10	0	10 0		10 0		10 0	
Vertical Profile Coverage	.1	7	0.7	10	1.0	10 1.0 Full		10 1.0 Full		10 1.0 Full	
Vertical Profile Resolution	.1	7	0.7	10	1.0	8 0.8 2Km		8 0.8 2Km		8 0.8 2Km	
Longitude	.05	0	0	8	0.4	10 0.5 Full		10 0.5 Full		10 0.5 Full	
	1.0		5.5		9.4	5.7		6.5		5.0	
Total Value			6		9	6		7		5	
Incremental Gain Over Present					3	<1		1		<1	

LEGEND:
V = Value
VXWF = Value x weighting factor

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relative value on a scale of 0 to 10 (low to high) for the stated performance where 0 indicates no capability and 10 indicates perfect capability. The weighting functions show the value of one parameter relative to the others under study. The product of the value and its corresponding weighting function (VXWF) yields the desired weighted value for each parameter. The sum of the weighted values for each parameter yields the total relative value for each pollutant (see Appendix A for full explanation).

5.1.1 Ozone Related Single Instrument Missions

In Table 5-XVIII the incremental gains have been summarized to show the totals for each instrument/orbit/species combination which could be used in an ozone related mission. The results have been weighted by the weighting factors for the various ozone related pollutant groups. These weights adjust to individual pollutant values to account for the different priority groups into which they were placed in Section 4.1.1 (Table 4-II). The factors assigned to the different ozone priority groups are as follows:

Group 1 - Measurements of properties and species   1.0
          directly associated with UV change

Group 2 - Components of the basic reactions in-   0.9
          volved in the direct production or
          depletion of ozone

Group 3 - Major components of the basic reactions   0.8
          indirectly involved in the production or
          depletion of ozone

Group 4 - Other significant components of the ozone   0.6
          chemistry chains

TABLE 5-XVIII

SUMMARY OF INCREMENTAL GAINS FOR EACH OZONE RELATED
SPECIES/INSTRUMENT/ORBIT COMBINATION

SPECIES	OZONE PRIORITY GROUP	GROUP WEIGHTING FACTOR	INSTRUMENT	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
					30° ORBIT	56° ORBIT	POLAR ORBIT
O_3	1	1.0	LIMS	3	<1	1	2
	1	1.0	SAGE	3	<1	<1	<1
NO	2	0.9	HALOE	3	<1	<1	<1
NO_2	2	0.9	LIMS	4	4	4	4
H_2O	3	0.8	CIMATS	3	<1	<1	<1
	3	0.8	LIMS	3	2	3	4
NH_3	3	0.8	CIMATS	6	6	6	6
HNO_3	3	0.8	LIMS	3	2	3	4
HCl	3	0.8	HALOE	3	2	2	<1
CH_4	3	0.8	CIMATS	6	6	6	3
	3	0.8	HALOE	6	6	6	3
N_2O	3	0.8	CIMATS	3	2	2	<1
CO	3	0.8	CIMATS	6	6	6	3
CO_2	4	0.6	LIMS	<1	<1	<1	<1
HF	4	0.6	HALOE	4	5	5	4

$$\sum = 44\text{-}45^*$$

---

*Uncertainty due to use of values <1. The total equals the sum of the best values for each species.

The incremental gain totals for each instrument/orbit combination which could be used in an ozone related mission are summarized in Table 7-XIX. It is obvious that those combinations showing the highest gains exhibit two prominent characteristics,

(1) the instrument measures a larger number of species, and/or

(2) most of the species measured represent those for which little data now exist; this allows large incremental gains for any successful measurement.

5.1.2 Aerosol Related Single Instrument Missions

In Table 5-XX the incremental gains have been summarized to show the totals for each instrument/orbit/species combination which could be used in an aerosol related mission. The results have been weighted by the weighing factors for the various aerosol related pollutant groups. These weights adjust the individual pollutant values to account for the different priority groups into which they were placed in Section 4.1.2 (Table 4-III). The factors assigned to the different aerosol priority groups are as follows:

Group 1A –	Direct measurements of climatic change and ultraviolet change	1.0
Group 1B –	Major aerosols	1.0
Group 2 –	Major sulfate aerosol precursor gases	1.0
Group 3 –	Major specific aerosols	0.8
Group 4 –	Other specific aerosols	0.6
Group 5 –	Other precursor gases	0.5
Group 6 –	Quasi aerosols (clusters)	0.3

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TABLE 5-XIX

SUMMARY OF INCREMENTAL GAINS FOR EACH OZONE RELATED
INSTRUMENT/ORBIT COMBINATION

INSTRUMENT	SPECIES MEASURED	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
			30° ORBIT	56° ORBIT	POLAR ORBIT
LIMS	CO_2, O_3, H_2O, NO_2 HNO_3	13-14[*]	8-10[*]	11-12[*]	14-15[*]
SAGE	O_3	3	<1	<1	<1
CIMATS (solar occultation)	H_2O, CH_4, N_2O, NH_3, CO	24	20-21[*]	20-21[*]	12-14[*]
HALOE	HF, CH_4 HCl, NO	16	13-14[*]	13-14[*]	7-9[*]

[*]Uncertainty due to use of values of <1

TABLE 5-XX

SUMMARY OF INCREMENTAL GAINS FOR EACH AEROSOL RELATED
SPECIES/INSTRUMENT/ORBIT COMBINATION

SPECIES	OZONE PRIORITY GROUP	GROUP WEIGHTING FACTOR	INSTRUMENT	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
					30° ORBIT	56° ORBIT	POLAR ORBIT
Total aerosols	1	1.0	SAGE	2	<1	<1	<1
H_2O	2	1.0	CIMATS	4	1	1	<1
	2	1.0	LIMS	4	3	4	5
NH_3	2	1.0	CIMATS	7	8	8	7
O_3	5	0.5	LIMS	2	<1	<1	1
	5	0.5	SAGE	2	<1	<1	<1
HNO_3	5	0.5	LIMS	2	2	2	3
HCl	5	0.5	HALOE	2	1	2	<1
HF	5	0.5	HALOE	4	4	4	4

$$\sum = 23^*$$

*The total equals the sum of the best values for each species.

The incremental gain totals for each instrument/orbit combination which could be used in an aerosol related mission are summarized in Table XXI. Inspection of the data shows that the highest gains are produced by those instruments which,

(1) measure a larger number of species, particularly those species in high priority groups, and/or

(2) measure high priority species for which little data now exists; thus allows large incremental gains for any successful measurement.

Thus the CIMATS instrument, which has the potential for measuring the high priority but previously unmeasured ammonia, scores very well as opposed to SAGE which measures relatively well known ozone and total aerosol distributions.

5.2 Evaluation of Multiple Species or Instrument Missions

5.2.1 Ozone Related Missions

Table 5-XXII shows the summary of incremental gains resulting when various combinations of two, three, or four instruments are flown on the same ozone oriented mission. These values are obtained by adding the individual contributions of each species/instrument except in those cases where two instruments measure the same species. In this later case, the value is determined by using the better value for each parameter between the instruments involved.

Inspection of the results reemphasizes some previous intuitive knowledge and also presents some new concepts. In the former category are such results as:

TABLE 5-XXI

SUMMARY OF INCREMENTAL GAINS FOR EACH AEROSOL RELATED INSTRUMENT/ORBIT COMBINATION

INSTRUMENT	SPECIES MEASURED	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
			30° ORBIT	56° ORBIT	POLAR ORBIT
LIMS	H_2O, O_3, HNO_3	8	5-6*	6-7*	9
SAGE	Aerosols, O_3	4	<1	<1	<1
CIMATS (solar occultation)	H_2O, NH_3	11	9	9	7-8*
HALOE	HCl, HF	6	5	6	4-5*

*Uncertainty due to use of values <1

TABLE 5-XXII

SUMMARY OF INCREMENTAL GAINS RESULTING
FROM
VARIOUS INSTRUMENT COMBINATIONS USED IN OZONE ORIENTED MISSIONS

INSTRUMENTS	SPECIES MEASURED	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
			30° ORBIT	56° ORBIT	POLAR ORBIT
Four Instruments					
LIMS, SAGE, CIMATS, HALOE	O_3, NO, NO_2, H_2O, NH_3, HNO_3, HCl, CH_4, N_2O, CO, CO_2, HF	44-45[*]	36-37	38-40	31-33
Three Instruments					
LIMS, CIMATS, HALOE	O_3, NO, NO_2, H_2O, NH_3, HNO_3, HCl, CH_4, N_2O, CO, CO_2, HF	44-45	36-37	38-40	31-33
LIMS, SAGE, CIMATS	O_3, NO_2, H_2O, NH_3, HNO_3, CH_4, N_2O, CO, CO_2	34-35	29-30	31-32	26-28
SAGE, CIMATS, HALOE	O_3, NO, H_2O, NH_3, HCl, CH_4, N_2O, CO, HF	37	28-29	28-29	18-19
LIMS, SAGE, HALOE	O_3, NO, NO_2, H_2O, HNO_3, HCl, CH_4, CO_2, HF	29-30	22-23	24-26	22-23
Two Instruments					
LIMS, CIMATS	O_3, NO_2, H_2O, NH_3, HNO_3, CH_4, N_2O, CO, CO_2	34-35	29-30	31-32	26-28
CIMATS, HALOE	NO, H_2O, NH_3, HCl, CH_4, N_2O, CO, HF	34	27-28	27-28	17-19
SAGE, CIMATS	O_3, H_2O, NH_3, CH_4, N_2O, CO	27	20-21	20-21	13-14
LIMS, HALOE	O_3, NO, NO_2, H_2O, HNO_3, HCl, CH_4, CO_2, HF	29-30	22-23	24-26	22-23
LIMS, SAGE	O_3, NO_2, H_2O, HNO_3, CO_2	13-14	8-10	11-12	14-15
SAGE, HALOE	O_3, NO, HCl, CH_4, HF	19	13-15	13-15	8-9

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[*] Uncertainty due to use of values <1

- the more individual species and/or instruments involved the greater the value

- Solar occultation-type instruments give poor global coverage in polar orbits

- Limb-looking instruments give excellent global coverage in polar orbits

The principal conclusion in the later category is that the highest potential for gain in value lies in the measurement of those species in ozone priority group 3 which play important roles in stratospheric processes but whose characteristics and spatial/temporal distribution are poorly known. Thus those instruments which measure species such as ammonia, methane and carbon monoxide score relatively high. These factors consistently lead to higher results for instrument/orbit combinations involving LIMS, CIMATS and HALOE as opposed to the SAGE instrument which measures only the reasonably well understood ozone.

In terms of orbit selection it is clearly shown in every combination that the 56° Shuttle type orbit is superior to the 30° Shuttle type orbit and the polar orbit.

5.2.2 Aerosol Related Missions

Table XXIII shows the summary of incremental gains resulting when various combinations of two, three or four instruments are flown on the same aerosol oriented mission. As was the case with ozone missions these results show that combinations which measure more species score relatively higher, particularly if the species is high priority and relatively unmeasured.

TABLE XXIII

SUMMARY OF INCREMENTAL GAINS RESULTING
FROM
VARIOUS INSTRUMENT COMBINATIONS USED IN AEROSOL ORIENTED MISSIONS

INSTRUMENTS	SPECIES MEASURED	WEIGHTED REQUIRED GAIN	WEIGHTED INCREMENTAL GAIN		
			30° ORBIT	56° ORBIT	POLAR ORBIT
Four Instruments					
LIMS, SAGE, CIMATS, HALOE	Aerosols, H_2O, NH_3, O_3, HNO_3, HCl, HF	23	18-20*	20-22	20-22
Three Instruments					
LIMS, CIMATS, HALOE	H_2O, NH_3, O_3, HNO_3, HCl, HF	21	18-19	20-21	20-21
LIMS, SAGE, CIMATS	Aerosols, H_2O, NH_3, O_3, HNO_3	17	13-15	15-17	16-17
SAGE, CIMATS, HALOE	Aerosols, H_2O, NH_3, O_3, HCl, HF	21	14-16	15-17	12-14
LIMS, SAGE, HALOE	Aerosols, H_2O, O_3, HNO_3, HCl, HF	16	10-12	12-14	13-15
Two Instruments					
LIMS, CIMATS	H_2O, NH_3, O_3, HNO_3	15	13-14	14-15	16
CIMATS, HALOE	H_2O, NH_3, HCl, HF	17	14	15	11-13
SAGE, CIMATS	Aerosols, H_2O, NH_3, O_3	15	9-11	9-11	8-9
LIMS, HALOE	H_2O, O_3, HNO_3, HCl, HF	14	10-11	12-13	13-14
LIMS, SAGE	Aerosols, H_2O, O_3, HNO_3	10	5-7	6-8	9-10
SAGE, HALOE	Aerosols, O_3, HCl, HF	10	5-7	6-8	5-6

*Uncertainty due to use of values <1

In contrast with the ozone results, orbit selection for combinations of instruments for aerosol missions does not consistently show the 56° orbit to score highest. The polar orbit tends to prevail in combinations containing the limb-emission LIMS instrument while the 56° orbit is superior when it is absent. In no case is the 30° orbit shown to be superior.

APPENDIX A

MISSION EVALUATION METHODOLOGY

A.1 INTRODUCTION

In order to properly determine how well any selected strato-
spheric species measurement mission improves on present knowledge of
the characteristics and spatial/temporal distribution of the species,
a method is presented that evaluates a selected mission in terms of
the present status of stratospheric knowledge of the species of
interest and the required level of knowledge (as expressed by the
scientific user community). The method has also been inverted and
used to select the mission that is most effective.

The selection of an optimum mission involves not only the
evaluation of orbital characteristics but also the selection of those
species to be measured that provide the optimum incremental improvement
from present knowledge to required knowledge. Thus, two factors are
involved:

(1) Prioritization of pollutants based on a combination
of present knowledge and required knowledge.

(2) Selection of the "optimum" mission (orbit plus instru-
ment) based on present measurement knowledge and re-
quired knowledge.

The following sections will be limited to a discussion of the
"optimum" mission selection for a single species. The prioritiza-
tion of species based on requirements was discussed in Section
5.2. Incorporation of these priorities into the evaluation method-
ology will be discussed later.

This evaluation technique can be applied specifically to orbit evaluation, instrument evaluation, or both by selection of the appropriate parameters.

A.2 DEVELOPMENT OF THE METHOD

### A.2.1 Approach to the Ranking and Evaluation

For each stratosphere species of interest one may assign a ranking or value in terms of an arbitrary scale of, say, 0 to 10 based on a comparison of either: (1) the present knowledge of the species distribution, (2) the required knowledge of the species distribution, or (3) the projected measurement capability of a specific mission with the total possible four-dimensional knowledge. For a typical species this may be exemplified as follows:
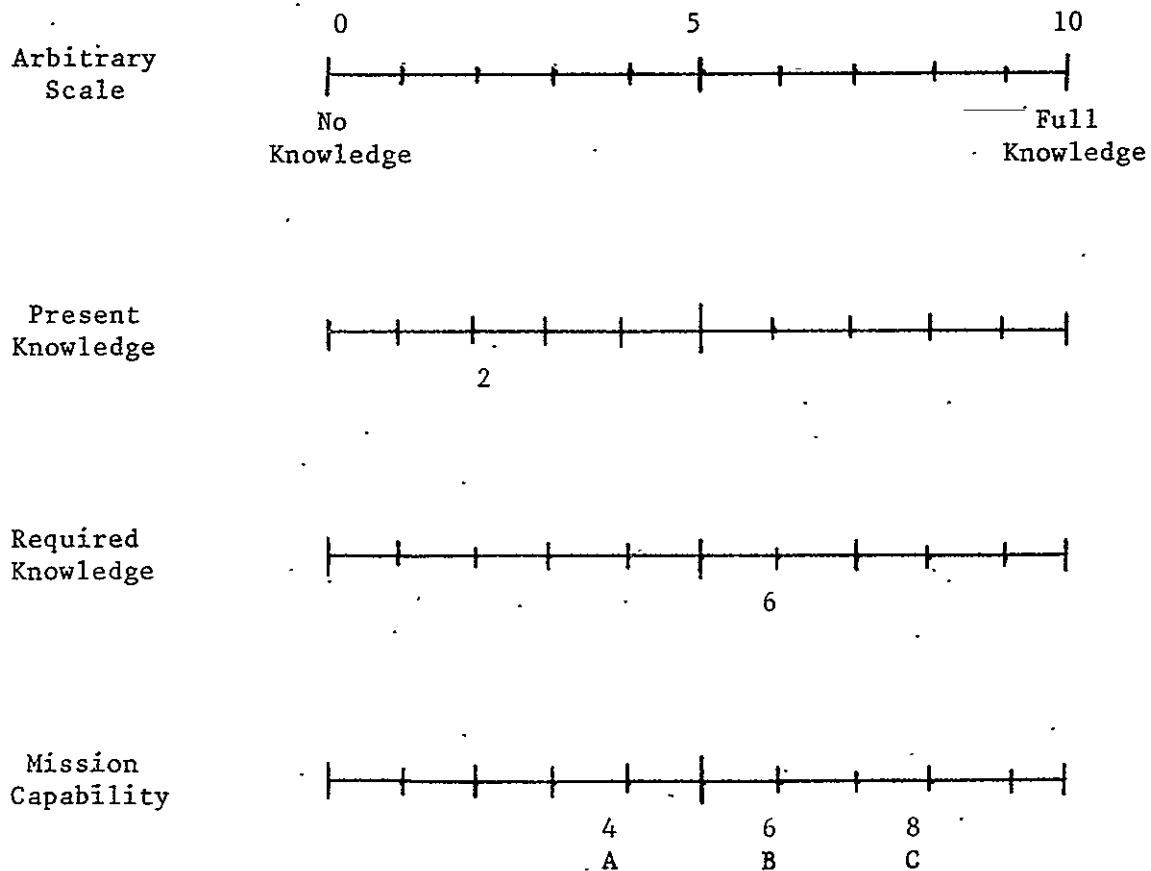
The key to assessing the value of a particular mission lies in comparing the mission capability with the incremental improvement between present knowledge and required knowledge. In the example illustrated above, the present level of knowledge has been given an arbitrary rating of 2 and the required knowledge an arbitrary rating of 6. It is important to note that the required knowledge level is not always set at the maximum. This may be for two reasons. On the one hand, a full capability of 10 may provide the user with much more data than he needs or could ever make use of. On the other hand, the present level of knowledge may be so low that the user would require only a small increase in knowledge to achieve a significant improvement in understanding the chemistry and distribution of the pollutant. Requirements should be set at the level that best equals the capability of the user community to assimilate the data measured.

Thus, in the given example, the critical area for gain lies between the present knowledge and the required knowledge. Therefore, system C is not automatically much better than system B. However, each (B and C) is significantly better than system A.

In order to indicate this in a more powerful way, the ranking scheme may be presented in a slightly different manner:

P — Present
      Knowledge

R — Required
      Knowledge

F — Full Capability
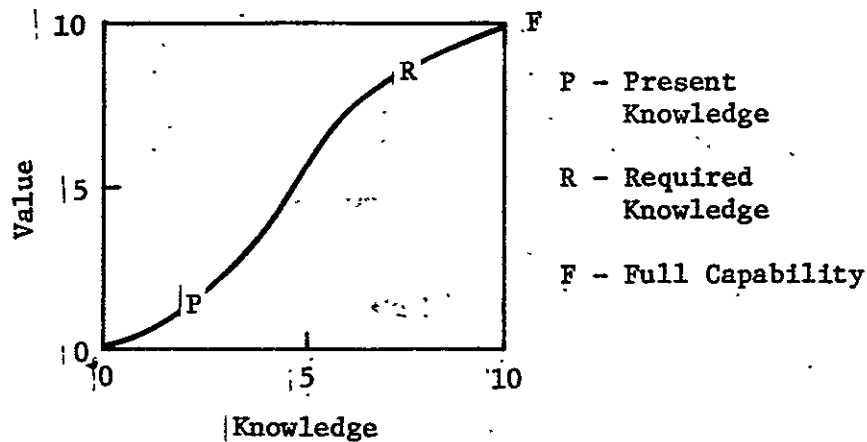
Here we see a sharp rise in value between present and required knowledge
and little gain thereafter. Present knowledge is assigned a value at
or near zero and required knowledge is assigned a value approaching 10
but allowing some small value for additional knowledge up to full.

   In other cases the present knowledge may be such that it commands
a high value in relation to full capability leaving little room for
improvement. Conversely, the current requirements may be such that
they can be fulfilled with only a minimum additional capability.

Only
minimum
improvement
necessary

Here, require-
ments are set
at a low level
of knowledge
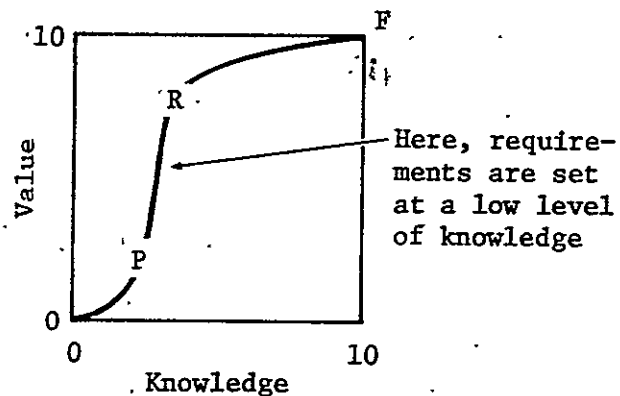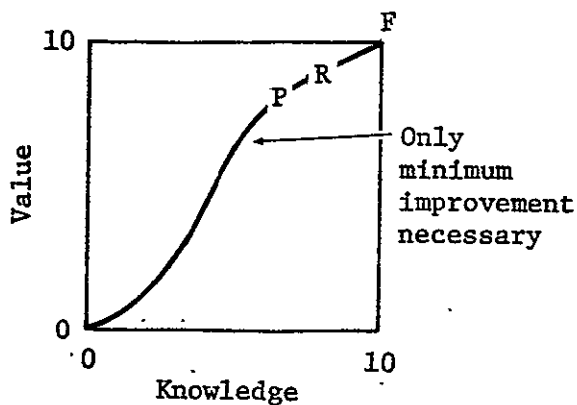
This type of evaluation has been used previously in a variety of system evaluations [108-112]. These reports give the details of the application of the method to both real cases and illustrative examples. The evaluation method makes use of value judgments of experts, either individually or by consensus, to provide information where "hard" data are unavailable. The objective is to make use of as much information as is available to the system. Much of this information is derived from the experience of experts associated with the system being evaluated. It is the objective of the evaluation to extract this information and check for its validity and utility. Critical areas can be identified where further gathering of information would be most effective. The success of the method depends on two critical factors:

- Availability of expert opinions or facts on the subject either directly or through adequate documentation.

- A thorough understanding of the structure and utilization of the evaluation procedure.

A logical sequence of steps in the application of the evaluation method is shown in Figure A-1. The first step is to identify the appropriate evaluation parameters. These parameters when measured will provide the information needed to describe and adequately evaluate the candidate species, instruments, and orbits. The selection of the parameters must be made independent of any particular knowledge of instruments or orbits.
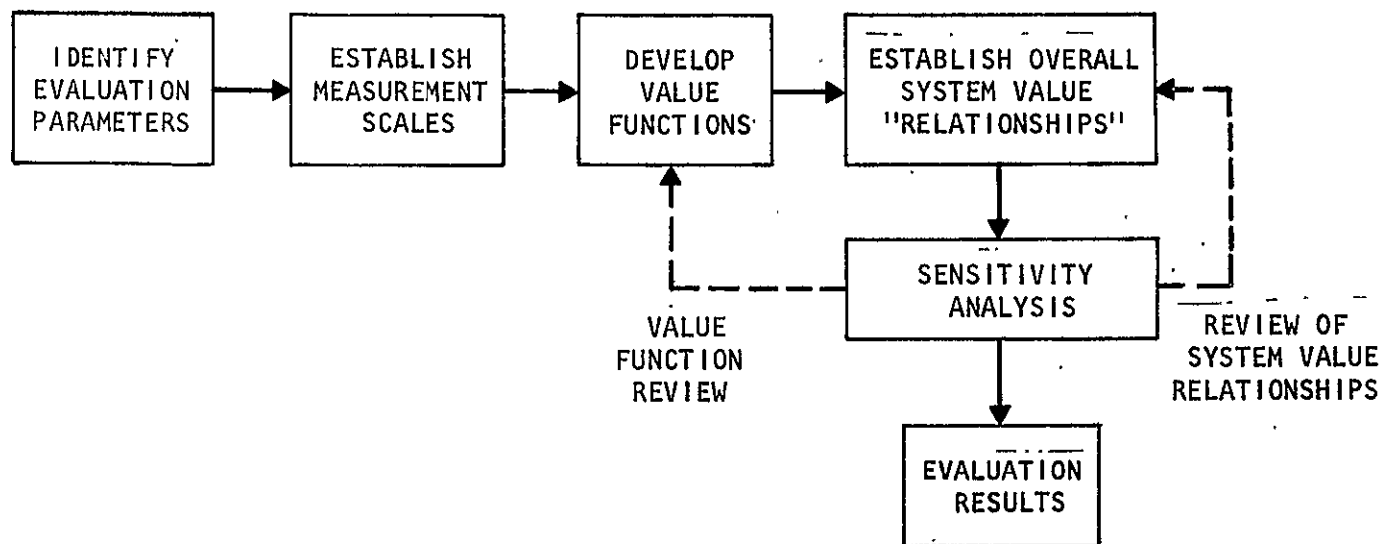
```
┌──────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────────┐
│  IDENTIFY    │     │  ESTABLISH   │     │   DEVELOP    │     │ ESTABLISH OVERALL│
│  EVALUATION  │ ──▶ │ MEASUREMENT  │ ──▶ │    VALUE     │ ──▶ │   SYSTEM VALUE   │◀─ ─┐
│  PARAMETERS  │     │    SCALES    │     │  FUNCTIONS   │     │ "RELATIONSHIPS"  │    │
└──────────────┘     └──────────────┘     └──────────────┘     └──────────────────┘    │
                                                 ▲                        │            │
                                                 ┊                        ▼            │
                                                 ┊              ┌──────────────────┐   │
                                                 └┄ ┄ ┄ ┄ ┄ ┄ ┄│   SENSITIVITY    │┄ ┄┘
                                           VALUE                │    ANALYSIS      │
                                         FUNCTION               └──────────────────┘   REVIEW OF
                                          REVIEW                         │             SYSTEM VALUE
                                                                         ▼             RELATIONSHIPS
                                                               ┌──────────────────┐
                                                               │   EVALUATION     │
                                                               │    RESULTS       │
                                                               └──────────────────┘
```

FIGURE A-1
EVALUATION TECHNIQUE DEVELOPMENT AND VALIDATION

Once the parameters are identified, measurement scales must be established for each parameter. The ranges of the technical parameter measurement values can be based either on established facts (which are generally unavailable) or expert judgments. The analytical formulation of the technique begins with the development of the value functions. The value function and its graphic representation, the value judgment curve, are the basic inputs of the method. The value function relates points on the parameter measurement scale to a value scale that ranges between zero for no value to the user and some arbitrary positive number for maximum value to the user. (Ten was selected as maximum in this study.)

The first step in developing a typical value judgment function is to establish the maximum and minimum points for each of the evaluation parameters. Additional points between the parameter maximum and minimum points are defined and each assigned a value to the user. Identification of all break points is very valuable in this procedure. These points are then plotted on a value judgment scale to indicate the nature of the actual relationship. In most cases the judgment curves should have the following characteristics,

- Smooth variation over the entire range
- Zero slope at the origin
- An asymptotic approach to zero or the maximum for large values of the parameters
- Flexibility so that special cases are easily incorporated

These characteristics are best represented by the family of hyperbolic

tangent curves characterized by the scale factors α and n. Then,

$$V = \tanh(\alpha x^n) \qquad \text{or} \qquad V = 1-\tanh(\alpha x^n)$$

where, V = value to the user; x = parameter value; α determines at

what point a change in parameter value begins to have a significant

effect on the value to the user and n determines the slope of the

change. In order for value to user to increase with increasing

parameter change n must be greater than 1. While the hyperbolic

tangent curve is used in most cases, it should be noted that other

types of value functions can be used. These may in some cases be

step functions or binary functions.

The next phase in the formulation of the technique is to develop

the overall system value relationship. This is accomplished by

establishing the relative importance of each of the parameters

through weighting functions. The initial step in developing these

functions is to designate each parameter as a factor or a term. A

parameter is designated as a factor if it is of such paramount

importance that if the value to the user is zero for that parameter,

the entire system is considered valueless. If a parameter is not of

the same level of criticality as a factor, it is designated a term.

A term is related to the other parameters through an additive relation-

ship.

The second step in establishing the relative importance of the per-

formance parameters is to assign weights to each parameter designated

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a term; where the sum of these weights is equal to unity. Various methods can be used to assign the weights. For example, the Delphi technique developed by the RAND Corporation has been used to reach a consensus within a group of experts as to the weights which should be assigned. Another method is to assign an initial set of weights and evaluate them against candidate species whose characteristics and relative importance are known. Refinement of the weights is then made based on the results. However, there is no substitute for the participation of experts in the field, either actually or by proxy.

The relationship among all parameters, including terms and factors, is then established, taking the general form of the following equation:

$$V = \prod_{j=1}^{n} \left(F_j (x_j) \right) \sum_{i=1}^{m} \left(A_i G_i (x_i) \right)$$

where

$$\sum_{i=1}^{n} A_i = 1$$

V = value

A_i = weight

F_j = value function (factor)

G_i = value function (term)

x_i, x_j = parameter measurement

This equation is termed a value set and can be used to evaluate for example all candidate instruments and/or orbits for a single stratospheric species.

A total system value can be calculated by combining all the individual value sets for the various species into one equation such as,

$$\text{Total System Value} = V_1 V_2 \left(W_3 V_3 + \cdots + W_8 V_8 \right)$$

where

V_1, V_2 are individual value sets which are factors

$V_3 \cdots V_8$ are individual value sets which are terms

$W_3 \cdots W_8$ are term weighting functions where $W_3 + \cdots + W_8 = 1$

A sensitivity analysis can be performed on all value sets and value functions if desired. The analysis should indicate which evaluation parameters are most critical to the system value. In addition this analysis may also indicate if the various weighting functions or value set algorithms should be modified.

This technique is of high utility for decision making. However, it is a tool for use in decision making and not a decision maker itself. The ultimate decisions should be made by the experts in the field who have benefited from the logical presentation of available information by means of this structured technique.

A.2.2 Application of the Method to Stratospheric Species Measurement

The evaluation method discussed in the previous section was used in the development of the evaluation techniques applied to stratospheric species measurement. However, two basic changes were made in its present application:

(1) Incremental values were used in place of smoothly varying value functions

(2) Two-dimensional value functions were used for each measurement parameter

The first change was indicated by the minimal amount of information available about most species of interest. The second change was made because the quality and quantity of the various measurements were considered to be an important part of the value function development. In a sense, these may be considered as weighting factors on each measurement parameter. In the actual application, these were combined into a common parameter called the data status.

The parameters considered to be of sufficient importance to be included in stratospheric species · ˙ ˊ · analysis are:

- Latitude coverage

- Duration of the mission or measurement program

- Diurnal coverage

- Launch date

- Vertical coverage

- Vertical resolution, and

- Longitude coverage

Each of the above parameters must be analyzed and values assigned to the various performance levels from zero to full capability. The measurement scales selected for each parameter are shown in Figures A-2 through A-5.

For each matrix shown, values must be selected for each incremental improvement from no capability for both the parameter and the status of the data up to full capability for both. The general approach is first to determine the level of present knowledge and the required level of knowledge for each species. These levels are then assigned appropriate values from 0 to 10 and the levels beyond and in between these levels are given other appropriate values based upon the present and required knowledge. For example, for the case of latitude coverage for nitric acid vapor, it is known from Section 5.3 and supporting information that nitric acid has been measured in the stratosphere over various latitudes that cover approximately 120°. However, the quantity of data available is very small. Thus the value matrix for nitric acid versus latitude becomes:

DATA	Good				R 10
STATUS	Med				
	Sparse			P	
	None	0			
		None	60	120	180

LATITUDE BAND COVERED

Nitric acid vapor, HNO_3

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Latitude Coverage -

	Good				10
DATA	Med				
STATUS	Sparse				
	None	0			
		None	60°	120°	180°

LATITUDE BAND COVERED*

*Includes nadir coverage plus any additional coverage due to orientation of instrument.

Duration of Measurement Program -

	Good				10
DATA	Med				
STATUS	Sparse				
	None	0			
		None	Short Survey	One Year Plus	Decades

DURATION OF MEASUREMENT PROGRAM

FIGURE A-2
PARAMETERIZATION OF LATITUDE COVERAGE AND PROGRAM DURATION

Diurnal Coverage

	None	Fixed Time	Partial Day	Full Day	Partial Day and Night	Full Diurnal
Good						10
Med						
Sparse						
None	0					

DATA STATUS (vertical) — DIURNAL COVERAGE*

*Based on both orbit and instrument capability.

Launch Date or Beginning of Experiment -

DATA STATUS	270°	180°	90°	None or DNA
Good				10
Med				
Sparse				
None	0			

SEASONAL PHASE DEVIATION*

* 90° – Launch is one season prior to desired season
180° – Launch is two seasons prior to desired season
270° – Launch is three seasons prior to desired season
DNA – Launch time not important therefore does not apply

FIGURE A-3
PARAMETERIZATION OF DIURNAL COVERAGE AND TIME OF LAUNCH

Vertical Coverage -

		None	<10%	50%	100%
DATA	Good				10
	Med				
STATUS	Sparse				
	None	0			

STRATOSPHERIC VERTICAL COVERAGE

Vertical Resolution -

		None	<1	1	10	>40
DATA	Good					10
	Med					
STATUS	Sparse					
	None	0				

NUMBER OF DATA POINTS OBTAINED*

*Note: <1 data point refers to column density through entire atmo-
         sphere which provides only part of a stratospheric data point.

FIGURE A-4
PARAMETERIZATION OF VERTICAL COVERAGE AND VERTICAL RESOLUTION

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:·Longitude Coverage -

Good				˙10
Med				
Sparse				
None	0			

DATA STATUS (left axis label)

Column headers (bottom):
:None 0-90° 90°-180° 180°-360°

|LONGITUDE BAND COVERED*

*It is assumed that all orbits being considered for stratospheric
pollution missions automatically provide good longitudinal coverage.
Therefore mission capability is automatically raised from present
knowledge to full capability.

FIGURE A-5
PARAMETERIZATION OF LONGITUDINAL COVERAGE

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where the P indicates the present knowledge. Since nitric acid vapor

is considered to be one of the very important members of the NO_x

chemistry chain, requirements (R) have been set at full capability.

Values from 0 to 10 are then assigned to each of the matrix areas

yielding:

DATA	Good		. 6	9	R 10
STATUS	Med		4	8	9
	Sparse		2	P 5	7
	None	0			
		None	60	120	180

Nitric acid vapor, HNO_3^-

LATITUDE BAND COVERED

These value matrices were prepared for all species prioritized into

Groups 1 and 2 plus those in Groups 3 and 4 for which satellite-borne

remote sensing instruments either exist or are under development.

The matrices are presented in Volume III of this report.

A.2.3 Weighting Factors

In order to determine the extent (in terms of value) to which

each orbit and/or instrument under consideration raises the present

knowledge of the species distribution up to or beyond the required

knowledge, the capability of the mission for each parameter (i.e.,

latitude coverage, vertical coverage, etc.) must be known. The

values corresponding to the capabilities for each parameter are then

combined into the value set for each species which provides a ... re

of how the entire orbit/instrument improves on present knowledge and how it compares with other orbit/instrument missions. However, as indicated in Section A.2.1, simple combination of such values assumes that all of the parameters are of equal importance. This is definitely not true. For any given species some of the parameters are of much greater interest to the user community than others. Thus weighting factors must be assigned for each measurement parameter. For example, in general the latitudinal distribution of stratospheric species is considered to be more important than the longitudinal distribution. Thus, it is more valuable to measure the latitudinal distribution before the longitudinal distribution if both cannot be measured simultaneously. However, if the latitudinal distribution is already well known then the primary value lies in extending knowledge to include the longitudinal distribution.

For most stratospheric species distributions the desirable progression from "no knowledge" to "full knowledge" would be:

(1) No data

(2) a. Fixed point data exist (one latitude, longitude, altitude, and time.)

b. Fixed point column burden data exist (one latitude, longitude, and time.)

(3) Fixed point vertical profile

(4) Latitude coverage

(5) Seasonal coverage*

(6) Diurnal coverage*

(7) Longitude coverage

(8) Long time coverage (years or decades)

Thus weighting factors must be assigned to each parameter for each species based on present and required knowledge and the logical progression of desired knowledge given above. High weights should be given to those parameters that would yield the best improvement from present to required knowledge and smaller weights to the other parameters.

The various values for each parameter (adjusted by the weighting functions) are combined to yield the total value for the mission under study. Each mission value is then compared with the value of the present knowledge and the required knowledge. The mission that provides the largest improvement from present knowledge to required knowledge should be considered the "optimum" system. If any mission achieves a value beyond the required knowledge level, the mission value should be truncated at the required knowledge level since this is the goal for each pollutant. However, if several missions achieve approximately equal values then this additional benefit should be acknowledged.

In some cases the mission may show only a small improvement over present knowledge or in fact none at all. Thus, the incremental

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* For a few specific species diurnal coverage may be more important than seasonal coverage and possibly latitude coverage.

gain in value over the value of present knowledge would be zero. However, this in no way implies that the entire mission under evaluation has no value at all. At the present state of the art of remote sensing of the stratosphere any successful mission would have value in terms of engineering, technological, and scientific advances. The value derived from the present evaluation only indicates that the mission would not significantly advance our knowledge of the mean stratospheric distribution of the species measured. For this reason, no mission will be given an absolute zero in the actual application of this method. Such cases will be indicated as less than one.

In order to evaluate a multiple pollutant or multiple instrument mission the value of each individual orbit/instrument is added to give the total value. In the case where several instruments measure the same pollutant the highest capability for each parameter is used to determine the contributing value. However, in the case of a multi-species mission, simple addition of the individual species values assumes that all are of equal importance. As was discussed in Section 5.2 and again at the beginning of this section, the species have been prioritized. These priorities must be taken into account when comparing the values of different species. This is accomplished by applying weighting factors. These factors have been assigned to the different species groups as follows:

Group 1a — Direct measurements of climatic   1.0
             change and ultraviolet change

Group 1b — Species directly associated with changes in climate and/or ultra-violet   1.0

Group 2 — Important species associated with two or more chemistry chains   0.9

Group 3 — Components of the basic reactions involved in the direct production or depletion of ozone   0.9

Group 4 — Components of the basic reactions indirectly involved in the production or depletion of ozone   0.8

Group 5 — Other significant components of the chemistry chains   0.6

Group 6 — Specific aerosols   0.6

The rationale for selecting these factors is as follows. On a scale of 0 to 1 a factor of 1 was given to Groups 1a and 1b since no distinction in importance could be identified. Group 2 rates almost as high due to the fact that the species are involved in more than one major chemistry chain. The Group 3 species are considered to be primary from both the NO_x and Cl chemistry chains. All of these species are directly related to the ozone generation and destruction reactions. Thus, the weighting remains high. Group 4 species are considered to be secondary in the sense that they are primarily involved in the production of the primary species listed in Group 3. The Groups 5 and 6 species, although very important in stratospheric chemistry, cannot be considered as important as the species in the previous groups. In the actual evaluation an initial set of weights was postulated. This set was exercised against a small set of

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species for which relative importance was known with some confidence.
From this the final revised set of weights was determined.

The combined values for present and required knowledge for all
pollutants for which value matrices were generated are given in Volume
III of this report. The combined values also include the parameter
weighting functions and the rationale for the selection of each. It
should be mentioned, that for the particular stratospheric species
and missions considered here, all final values are rounded off to the
nearest integer since this is considered to be the maximum preciseness
that can be justified by the accuracy of the input values.

APPENDIX B

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NOTE: For the convenience of the user, the same set of references is presented in Volumes I, II and III of this report. Therefore, in any one volume, all references are not cited in the text.

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