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Report of the NASA Working Group on Tropospheric Program Planning

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PREFACE

The NASA Office of Space and Terrestrial Applications, seeking to strengthen the scientific foundation for its long-range tropospheric research program, formed a Working Group on Tropospheric Program Planning in 1978 with the undersigned as Chairman. The first task of the Working Group was to identify the major scientific questions in tropospheric pollution, to point out high priority scientific areas for current emphasis, and to recommend research tasks which could be achieved in a joint NASA/EPA program. That task was accomplished in 1978. The second task of the Working Group was to develop the scientific rationale and recommend research activities to be conducted by NASA, the execution of which would increase our understanding of the troposphere. This task is now complete.

The results from the Working Group are presented herein. The body of this report presents the scientific rationale and research activities recommended for NASA. Appendix A identifies the major scientific questions in tropospheric pollution, points out high-priority scientific areas for current emphasis, and recommends research tasks which could be achieved in a joint NASA/EPA program. Appendix A was completed in 1978, and some of the material became obsolete in the ensuing two years during which the remainder of the Working Group report was being drafted. This appendix, therefore, has been updated to reflect important recent results. It should be emphasized that appendix A is not intended to be a technical review of the state-of-the-art in tropospheric pollution. Rather, it represents a summary of important unresolved problems in tropospheric chemistry and transport as perceived by the Working Group. Thus, even though new data in this rapidly changing field have become available since 1978, the underlying research problems outlined in appendix A have not changed.

The Working Group is, of course, well aware that other groups over the years have compiled lists of research problems and associated research tasks in atmospheric pollution. To be sure, many scientists are aware of most, if not all, of the questions that have been raised. Nonetheless, the list of research problems and recommendations for research activities contained in this report fulfills a specific need that has not been previously addressed. A useful reference in delineating major scientific questions was the NASA Reference Publication 1022 entitled "Man's Impact on the Troposphere - Lectures in Tropospheric Chemisty," Joel S. Levine and David R. Schryer, editors.

This Working Group report is intended to serve primarily as an advisory document for NASA. Attention is basically confined to those areas in which there would be potential NASA interest, and, in addition, is focused on scientific (as opposed to technical or engineering) questions relating to tropospheric pollution. Many of the research tasks outlined in the report could be carried out under NASA programs. Others could be of interest to EPA and other agencies which conduct tropospheric studies.

Tropospheric pollution is ultimately reflected in changes in climate, weather, visibility, human health, and other effects on ecosystems. Short-lived species, those with residence times on the order of hours to days, are generally implicated in regional effects such as visibility and human health degradation. Long-lived species may ultimately contribute to changes in climate and weather through their interaction with the Earth's radiation balance. Tropospheric pollution resulting from both short- and long-lived species is considered in this report.

The following Working Group members contributed to this report: John H. Seinfeld, California Institute of Technology, Chairman; Frank Allario, Langley Research Center; William R. Bandeen, Goddard Space Flight Center; William L. Chameides, University of Florida (now at Georgia Institute of Technology); Douglas D. Davis, Georgia Institute of Technology; E. David Hinkley, Jet Propulsion Laboratory; Robert G. Lamb, U. S. Environmental Protection Agency; Benjamin Y. H. Liu, University of Minnesota; and Richard W. Stewart, Goddard Space Flight Center.

The Working Group wishes to acknowledge the significant efforts of Freda Nevias Bloch of the NASA Langley Research Center in editing this NASA Reference Publication.

John H. Seinfeld
California Institute of Technology
Chairman

CONTENTS

EXECUTIVE SUMMARY

Based on the acknowledged coupling between atmospheric and biospheric processes, the trace gas chemistry of the troposphere can be identified as a key component of the biogeochemical cycles of elements such as carbon, nitrogen, oxygen, sulfur, and the halogens. Tropospheric chemistry, therefore, impacts on many aspects of environmental quality relevant to human health, agriculture, climate, and weather.

Recognizing the need to utilize remote sensing techniques to further our understanding of key biogeochemical processes operating within the tropospheric system, and given NASA's special role in the development and implementation of these techniques, this report proposes that NASA vigorously expand its current tropospheric research program. The proposed scope of this expanded program would encompass three very general tropospheric research problems:

I. What are the principal processes governing the global carbon/nitrogen/ozone system?

II. What are the principal processes governing the global sulfur/ammonia/trace metal/carbon/aerosol system?

III. What are the relative roles of transport, transformation, and removal processes in governing the behavior of regional- and urban-scale polluted air masses? (This problem is of interest to NASA in responding to requests from EPA and other agencies for the development and application of space technology for monitoring tropospheric processes.)

To make major advances in each of these stated problem areas, it is proposed that NASA place its primary emphasis on the execution of a well-defined field-measurement program, with important supporting tasks being identified as mathematical modeling, laboratory measurements, and new technology development for atmospheric sensors. It is further recommended that the field-measurement program involve both aircraft and space platforms, and that the sampling strategy in each case reflect our growing recognition that the global troposphere be viewed as consisting of an ensemble of composition domains coupled together by transport processes. In this global context, each composition domain is to be defined in terms of characteristic sources and sinks of trace gases, chemical transformation rates, and atmospheric transport.

The proposed program initially calls for in-depth studies, using aircraft platforms, of representative composition domains, both basic photochemical and transport processes characteristic of each domain being identified. The study of these representative domains will then be followed by more globally oriented investigations, especially satellite measurements, that will elucidate the coupling between various domains and define their global distributions. This approach should eventually lead to a truly global understanding of tropospheric processes with sufficient knowledge of the horizontal and vertical inhomogeneities to successfully predict the impact of anthropogenic emissions as well as natural perturbations to the tropospheric system.

The specific research tasks selected for implementation are divided into four basic categories:

1. Field measurements: This program includes a tropospheric aircraft sampling program which will investigate the detailed chemistry and surface sources and sinks of various representative concentration domains. The aircraft program should be followed by a Lower Atmospheric Research Satellite (LARS), which will establish the global distributions of several key tropospheric species. The final design of this program will be determined in part by the findings of the aircraft sampling program. Also discussed is an aerosol sampling program, coordinated with the existing NASA Aerosol Climate Effects (ACE) special study, which will take advantage of present-day satellite and remote sensing technology to elucidate key parameters in the global aerosol distributions.

2. Modeling: This effort will be concentrated on the continued development of global-scale models with predictive capabilities. In addition, the program includes the development of theory applicable to the assimilation of satellite and aircraft data into regional-scale models.

3. Laboratory measurements: These tasks are designed to aid in the measurement and evaluation of atmospheric properties and processes. They include spectroscopic data studies, calibration studies, gas-phase chemical kinetic studies under atmospheric conditions of pressure and temperature, and gas-to-particle investigations.

4. Technology development: These tasks, aimed at establishing and applying new techniques for measuring atmospheric processes, are key elements of the tropospheric research program. Both remote sensor (passive and active) and in situ sensor technologies are featured.

CHAPTER 1 - INTRODUCTION

The state of the troposphere impacts on a number of areas of concern to man and the environment, including health, weather, climate, and agriculture. The troposphere consists of a large number of chemical species, some long-lived, such as oxygen, nitrogen, and carbon dioxide, and some of an extremely transient nature that are rapidly formed and destroyed by chemical reactions. In general, the chemical transformations that occur interrelate the individual biogeochemical cycles of carbon, nitrogen, sulfur, etc. through these transient species. The transient, or trace, species exert a disproportionate leverage on tropospheric chemistry over what might be expected on the basis of their absolute concentrations. They may influence visibility by conversion to light-scattering and absorbing aerosols, climate through their effects on the radiation balance, or the ecosystem through effects such as acid-rain formation. Understanding the distribution, sources, sinks, and variabilities of the minor and trace species in the troposphere is a fundamental goal of the NASA Air Quality Program.

In an attempt to form a scientific basis for a long-term tropospheric research program, NASA convened (in 1978) a Working Group on Tropospheric Program Planning. This group prepared a report entitled "Scientific Research Objectives in Tropospheric Pollution" which is presented as appendix A to this report. This appendix has as its objective the delineation of major scientific questions relating to the troposphere. Associated with the scientific questions are a series of research tasks, the execution of which will increase our understanding of the troposphere. The research tasks include field measurements and model and instrument development. The scientific questions are divided roughly according to global chemical cycles and regional air pollution. Thirty-nine scientific questions were posed, followed by 38 operational research tasks and 12 instrument development tasks. That report serves as the scientific basis for the present recommended program.

The body of this report is devoted to the scientific rationale and recommendations for the NASA Tropospheric Research Program Plan. The overall goal of the research program is to increase our understanding of the chemical phenomena occurring in the troposphere, with particular emphasis on those aspects that impact on environmental quality such as health, agriculture, climate, and weather.

From a program planning point of view, studies in tropospheric chemistry can be divided into two broad categories: (1) Investigations designed to determine the detailed chemical interactions of atmospheric species and (2) investigations designed to define the concentration distributions of atmospheric trace gases and aerosols. In the first case, one of the most productive approaches has involved studies of individual elementary reactions under controlled conditions in a laboratory environment. In the second case, field studies in conjunction with modeling activities have been the principal sources of information.

The scientific questions posed in appendix A were intentionally broadly based without special delineation of those particularly relevant for NASA attention. Drawing on that general survey, the present research plan concentrates on those scientific questions and research tasks which could take advantage of NASA's unique capabilities and contribute to the Agency's objective of developing and applying space technology to studies of the atmosphere. Because of the interrelated nature of many of these scientific questions, it is possible to encompass the entire set within three very general tropospheric research problems:

I. What are the principal processes governing the global carbon/nitrogen/ozone system?

II. What are the principal processes governing the global sulfur/ammonia/trace metal/carbon/aerosol system?

III. What are the relative roles of transport, transformation, and removal processes in governing the behavior of regional- and urban-scale polluted air masses?

These three questions form the organizational basis for the present document. Those research tasks that have been recommended for implementation are divided into four basic categories:

1. Field measurements

2. Modeling

3. Laboratory measurements

4. Technology development

A matrix structure is thus developed consisting of three major scientific questions and four categories of research tasks. (Laboratory studies were not considered in appendix A; such studies are included in the present plan.)

The remainder of this document presents the NASA Tropospheric Research Program Plan recommended by this Working Group. Chapter 2 contains a brief discussion of major tropospheric research needs. The research programs proposed to meet the research needs presented in chapter 2 are detailed in chapter 3. Chapter 4 presents a summary of the major recommendations of the Working Group. Appendix A presents the scientific research objectives in tropospheric pollution, appendix B presents a list of acronyms, abbreviations, and symbols used, and appendix C discusses the measurement of atmospheric state variables required to achieve many of the recommended research objectives.

CHAPTER 2 - MAJOR RESEARCH NEEDS AND TASKS

2.1 INTRODUCTION

In this chapter, the scientific rationale for the proposed NASA Tropospheric Research Program Plan is outlined. Research needs based on the scientific rationale are then summarized. These research needs form the basis for the recommended program plan of chapter 3. The discussion in the present chapter is divided roughly according to three different spatial regions. The largest scale to be considered is the "global" one. On this spatial scale, the detailed coupling between land, sea, and the atmosphere can be examined in terms of the biogeochemical cycles of such key elements as carbon, nitrogen, phosphorous, and sulfur.

Defining subglobal spatial scales is considerably less precise, but historically at least two additional scales have received much attention. The first of these is now commonly referred to as the "regional scale," involving distances of a few hundred kilometers up to 10 000 km. The regional scale corresponds approximately to the area influenced by many types of synoptic weather patterns, i.e., frontal zones, high-pressure systems, and large storm centers. Past regional field sampling and modeling studies have generally been conducted over continents, where trace-gas and aerosol concentration levels have been largely under the control of anthropogenic emissions as modulated by synoptic weather patterns. However, regional-scale studies need not inherently be labeled as pollution oriented. In a global context, regional-scale studies can be defined for any geographical area (100 to 10 000 km) where the dominant sources and sinks of trace-gas and aerosol species can be shown to be reasonably uniform. Thus, a study of the South American Amazon River basin could be properly labeled as a regional-scale study. In like manner, studies of the South Pacific central gyre or the Sargasso Sea could also be classified as regional-scale field studies.

The final spatial scale that will be discussed is the "mesoscale." The mesoscale can be defined in terms of distances of 10 to 100 km. Meteorologically, this is the scale over which land-sea breezes and thunderstorms take place. As in the case of regional-scale studies, mesoscale field sampling, as related to atmospheric chemistry, has traditionally been identified with environmental pollution - specifically urban pollution. Once again, though, mesoscale sampling need not be considered synonymous with urban field studies. The geographical size and the intensity and uniformity of sources should be the major criteria employed in defining mesoscale chemical phenomena.

In the text that follows, sections 2.2 and 2.3 are devoted to the global chemical cycles of carbon/nitrogen/ozone (C-N-O_3) and sulfur/ammonia/carbon/trace metal/aerosol systems, respectively. Pollution effects are considered in section 2.4.

2.2 THE GLOBAL CARBON/NITROGEN/OZONE SYSTEM

2.2.1 Tropospheric Carbon/Nitrogen/Ozone Photochemistry

Tropospheric global photochemistry is fueled by a combination of actinic solar radiation, which leads to the production of highly reactive free radicals, and the release of reduced species from the biosphere, lithosphere, and oceans into the atmosphere. The oxidation of reduced gases by free radicals triggers the complex trace-gas photochemistry of the troposphere, which influences the natural abundance of methane (CH_4), nonmethane hydrocarbons (NMHC), formaldehyde (H_2CO), carbon monoxide (CO), ozone (O_3), active nitrogen (e.g., NO, NO_2, and HNO_3), ammonia (NH_3), sulfur oxides, and many halogen-substituted halocarbons. As a result, tropospheric photochemistry plays a role in controlling key environmental parameters, such as global temperatures, visibility, and the impact of the atmospheric composition upon respiration and other biospheric processes, and is a major mechanism for coupling the chemical cycles of the biosphere and atmosphere.

The reaction that can be considered to initiate the tropospheric photochemical system is the near-UV photolysis of O_3, producing molecular oxygen (O_2) and metastable excited oxygen atoms ($O(^1D)$)

$$\text{(R1)}\quad O_3 + h\nu(\lambda \lesssim 3100\ \text{Å}) \rightarrow O_2 + O(^1D)$$

that react with water vapor to produce the hydroxyl radical (OH)

$$\text{(R2)}\quad O(^1D) + H_2O \rightarrow 2OH$$

This initial source of hydroxyl radicals leads to a long series of key reactions involving OH and other radicals before chain-terminating steps such as

$$\text{(R3)}\quad NO_2 + OH + M \rightarrow HNO_3 + M$$

$$\text{(R4)}\quad HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

and

$$\text{(R5)}\quad CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

followed by heterogeneous removal and

$$\text{(R6)}\quad H_2O_2 + OH \rightarrow H_2O + HO_2$$

remove free radicals from the system. Figure 1 illustrates several of the H_xO_y radical-loss paths.

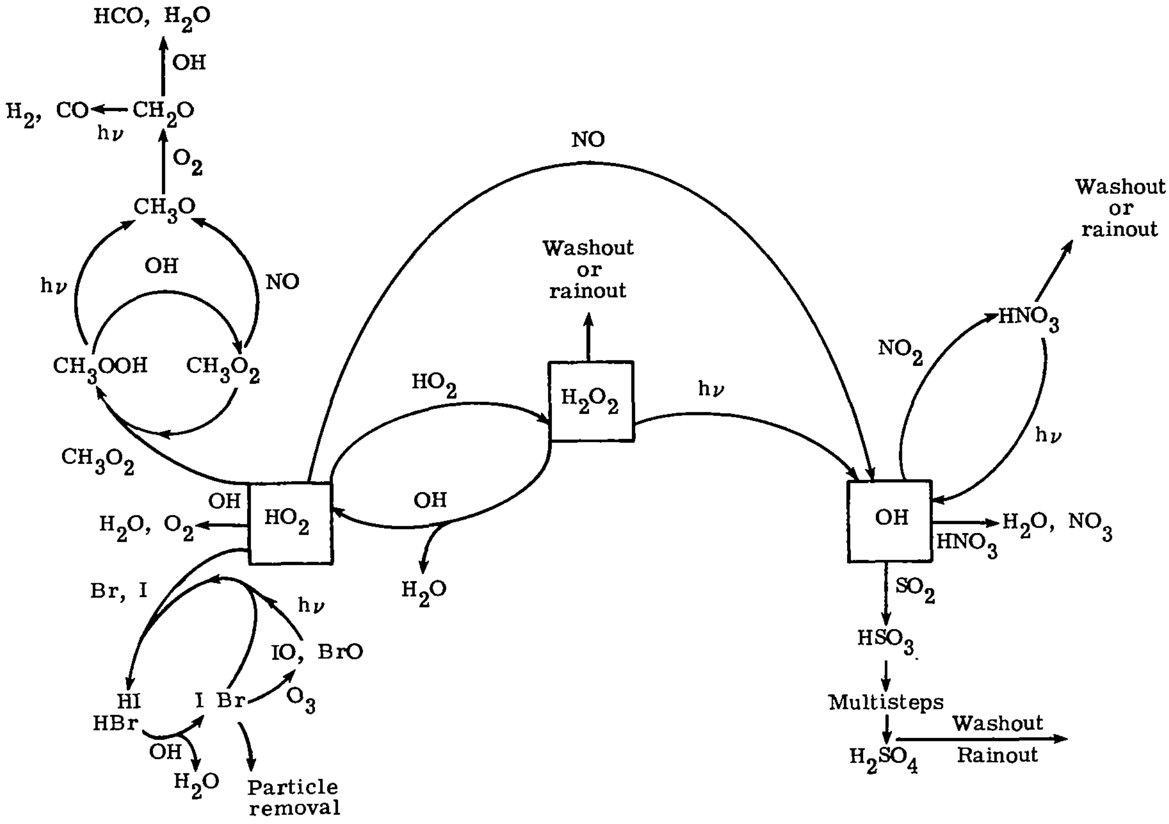


Figure 1.- Illustration of H_xO_y radical-loss paths.

The oxidations of many of the reduced tropospheric gases are initiated by reactions with OH, as indicated in figure 2. A key oxidation is that of methane, produced by fermentation in anaerobic environments such as swamps, tropical rain forests, and rice-paddy fields:

(R7) $CH_4 + OH \rightarrow CH_3 + H_2O$

Reaction (R7) initiates a complicated series of steps known as the methane oxidation chain, which includes the production of H_2CO, CO, and H_2. A schematic representation of a possible tropospheric methane oxidation cycle is illustrated in figure 3. The production of H_2CO, H_2, and CO is followed by OH oxidation:

(R8) $H_2CO + OH \rightarrow H_2O + HCO$

(R9) $H_2 + OH \rightarrow H_2O + H$

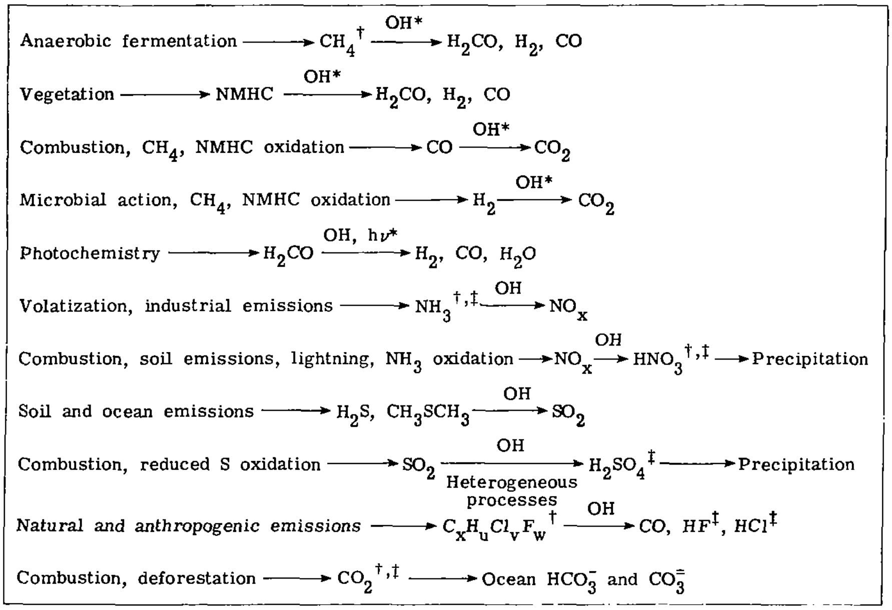
(R10) $CO + OH \rightarrow CO_2 + H$

or, by photolysis,

(R11(a)) $H_2CO + h\nu \rightarrow H + HCO$

(R11(b)) $H_2CO + h\nu \rightarrow H_2 + CO$

The final product of the gas-phase oxidation of methane is CO_2, though CO is an important and relatively long-lived intermediate. Heterogeneous removal of some intermediates in the oxidation chain, such as CH_3OOH, may lower the yield of CO and CO_2 per molecule of CH_4 oxidized. Nonmethane hydrocarbons are also oxidized by OH and may have oxidation chains leading to CO production which are equivalent, in many respects, to the oxidation chain of methane. The importance of nonmethane hydrocarbons in the C-N-O_3 system remains a key uncertainty in our understanding of tropospheric photochemistry.



*Process in which RO_2 radicals are produced.

†Species which absorb terrestrial radiation and affect the atmospheric radiative equilibrium.

‡Species which may affect pH in precipitation and visibility.

Figure 2.- Oxidation of atmospheric reduced gases and their products in troposphere.

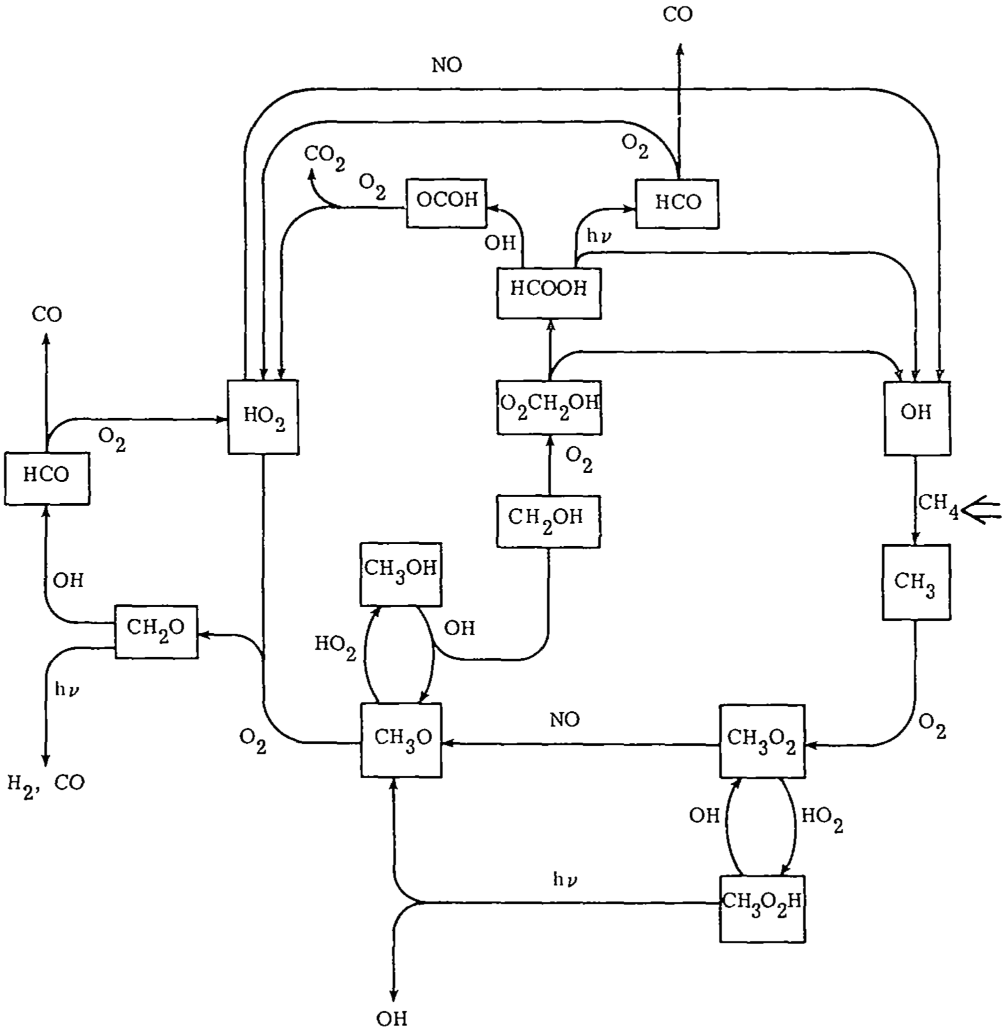


Figure 3.- Possible tropospheric methane oxidation cycle.

Although CO is produced from the photochemical oxidation of hydrocarbons, it appears that anthropogenic production through the burning of fossil fuels and biomass (for agricultural purposes) comprises a significant fraction of the total global CO source. Because calculations indicate that the largest single photochemical sink of tropospheric OH is reaction with CO (reaction (R10)) and because of the central role OH plays in the tropospheric photochemistry, a major goal in the tropospheric program is the quantitative characterization of the importance of anthropogenic sources of CO and their potential for perturbing tropospheric OH photochemistry. Our present understanding of the global tropospheric CO distribution is shown in figure 4. Although the measurements on which this figure is based were taken over the Atlantic, the few available CO measurements from the Pacific tend to confirm its main feature, which is the large interhemispheric difference in CO concentrations. Even though the asymmetric CO distribution in figure 4 appears to imply significant anthropogenic

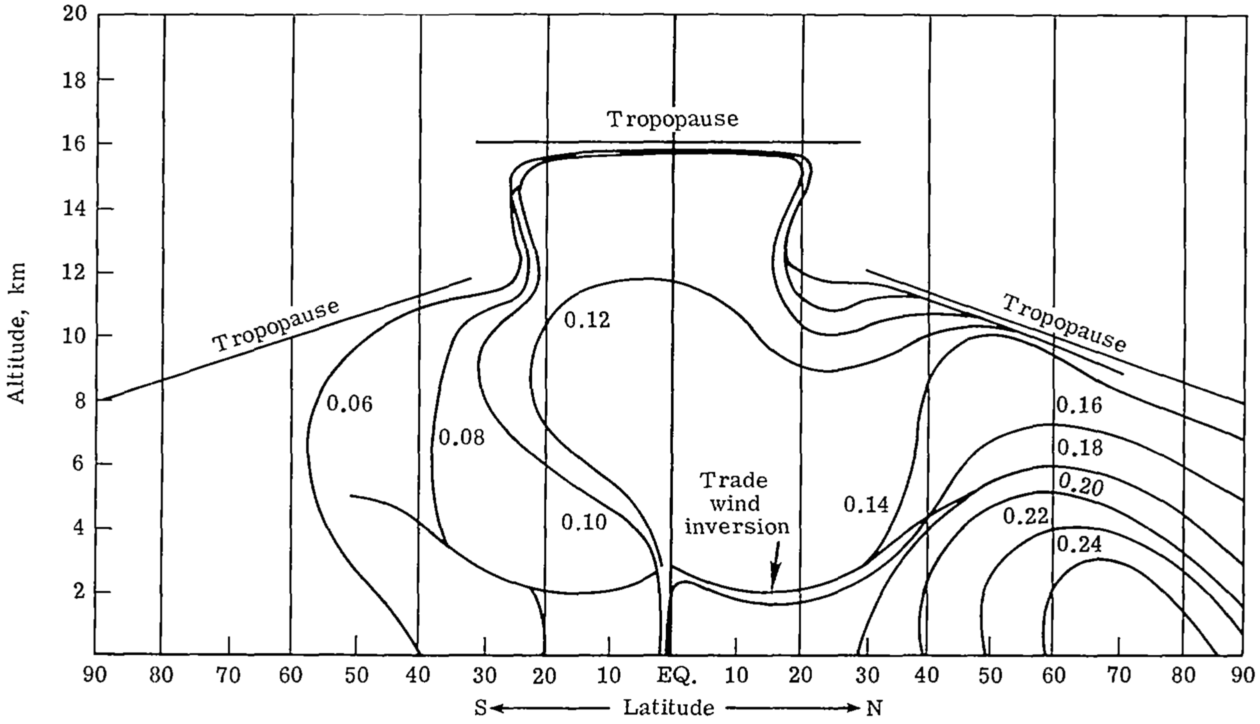


Figure 4.- General distribution of CO (numbers indicate concentrations in ppm) in marine air in the troposphere and lower stratosphere from reference 1. (Seiler, Wolfgang: The Cycle of Atmospheric CO. Tellus, vol. 26, nos. 1-2, 1974, pp. 116-135.)

influence, global CO measurements are needed to refine our understanding of the CO distribution and its influence on tropospheric OH.

A key facet of the methane and nonmethane hydrocarbon oxidation chains is the conversion of OH to peroxy radicals (RO_2). The production of HO_2, for instance, is accomplished via

(R12) $CH_3O + O_2 \rightarrow HO_2 + H_2CO$

which also produces H_2CO. In addition, the production of H atoms by reactions (R9), (R10), and (R11(a)), as well as by

(R13) $HCO + h\nu \rightarrow H + CO$

is immediately followed by a three-body reaction which produces HO_2:

(R14) $H + O_2 + M \rightarrow HO_2 + M$

Similarly, the production of CH_3 by reaction (R7) is followed by

(R15) $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

thereby producing CH_3O_2. It is likely that the oxidation of higher hydrocarbons leads to the production of peroxy radicals containing two or more methyl groups, as well as the production of HO_2 and CH_3O_2.

Peroxy radicals produced as a result of hydrocarbon oxidation can lead to the local photochemical production and destruction of tropospheric ozone. In the presence of NO_x (NO and NO_2), peroxy radicals can catalytically produce ozone via

(R16) $RO_2 + NO \rightarrow RO + NO_2$

(R17) $NO_2 + h\nu \rightarrow NO + O$

(R18) $O + O_2 + M \rightarrow O_3 + M$

Since one $O(^1D)$ atom can produce two OH radicals, sequences such as reactions (R1), (R2), (R10), (R14), (R17), and (R18) lead to a net source of ozone. (Reaction (R16) is also important in that it regenerates OH from HO_2, allowing further oxidation of hydrocarbons, CO, and other gases.) On the other hand,

$HO_2 + O_3 \rightarrow 2O_2 + OH$

in combination with reactions (R1) and (R2) represent photochemical sinks for tropospheric ozone.

Iodine compounds may also act to remove tropospheric ozone via catalytic reaction sequences. Atmospheric CH_3I, produced via oceanic and also possibly industrial processes, is photolyzed to produce I atoms:

(R19) $CH_3I + h\nu \rightarrow CH_3 + I$

Iodine (I) may then react with O_3 and various radical species to produce several inorganic I compounds, such as IO, HI, HOI, and $IONO_2$, before heterogeneous processes remove iodine from the atmosphere. Figure 5 illustrates various reactions of the iodine system. Depending on the rates of some key reactions, the relative partitioning of the various iodine species, and the abundance of tropospheric iodine, catalytic cycles such as

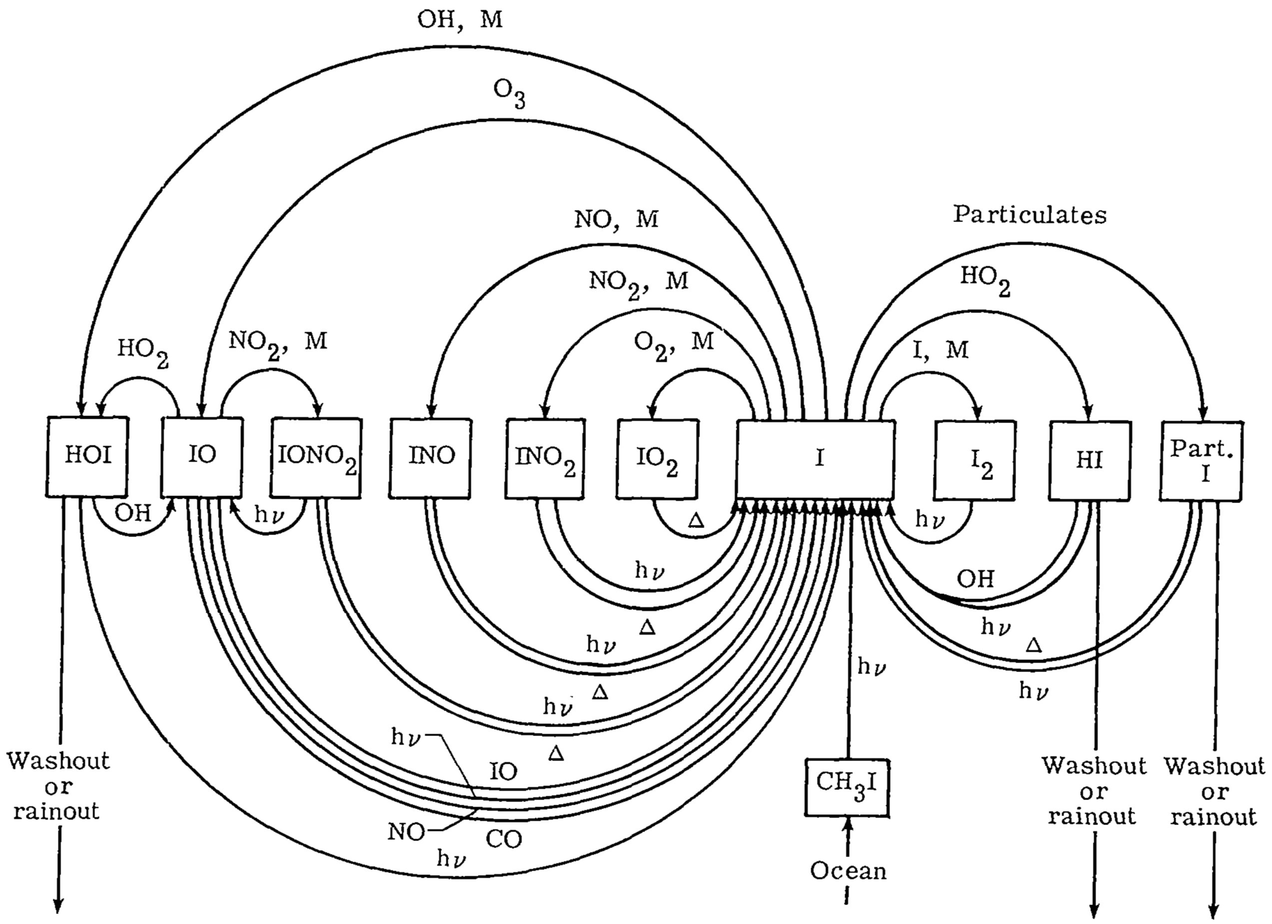


Figure 5.- A possible chemical scheme for iodine (I) in the tropospheric marine boundary layer.

(R20) $I + O_3 \rightarrow IO + O_2$

(R21) $IO + IO \rightarrow 2I + O_2$

or reaction (R20) followed by

(R22) $IO + HO_2 \rightarrow HOI + O_2$

(R23) $HOI + h\nu \rightarrow OH + I$

may need to be considered in tropospheric reaction mechanisms, especially in marine environments. The possibility that iodine, previously a relatively ignored component of the atmospheric photochemical system, may lead to a significant O_3 sink further emphasizes the large uncertainties in our understanding of tropospheric photochemistry. The implementation of the NASA Tropospheric Research Program Plan will no doubt bring new revelations to the science of atmospheric chemistry, and the program should remain sufficiently flexible to adjust to and act upon these new insights.

Figure 6 schematically depicts the photochemical and transport processes responsible for the production and loss of tropospheric ozone. Whether photochemistry supplies a net source or sink of ozone in the troposphere depends on the rate at which hydrocarbons are oxidized and on the concentration of NO relative to O_3. The relative roles of photochemistry, injection of stratospheric ozone, and loss at the surface of the Earth in controlling tropospheric ozone, as well as the impact of increased anthropogenic emissions of CO and NO_x upon tropospheric ozone levels, are presently subject to intense scientific debate and are key issues in the NASA Tropospheric Research Program Plan. Important needs in this regard are the acquisition of a global data base for tropospheric ozone to indicate quantitatively its spatial and temporal vari-

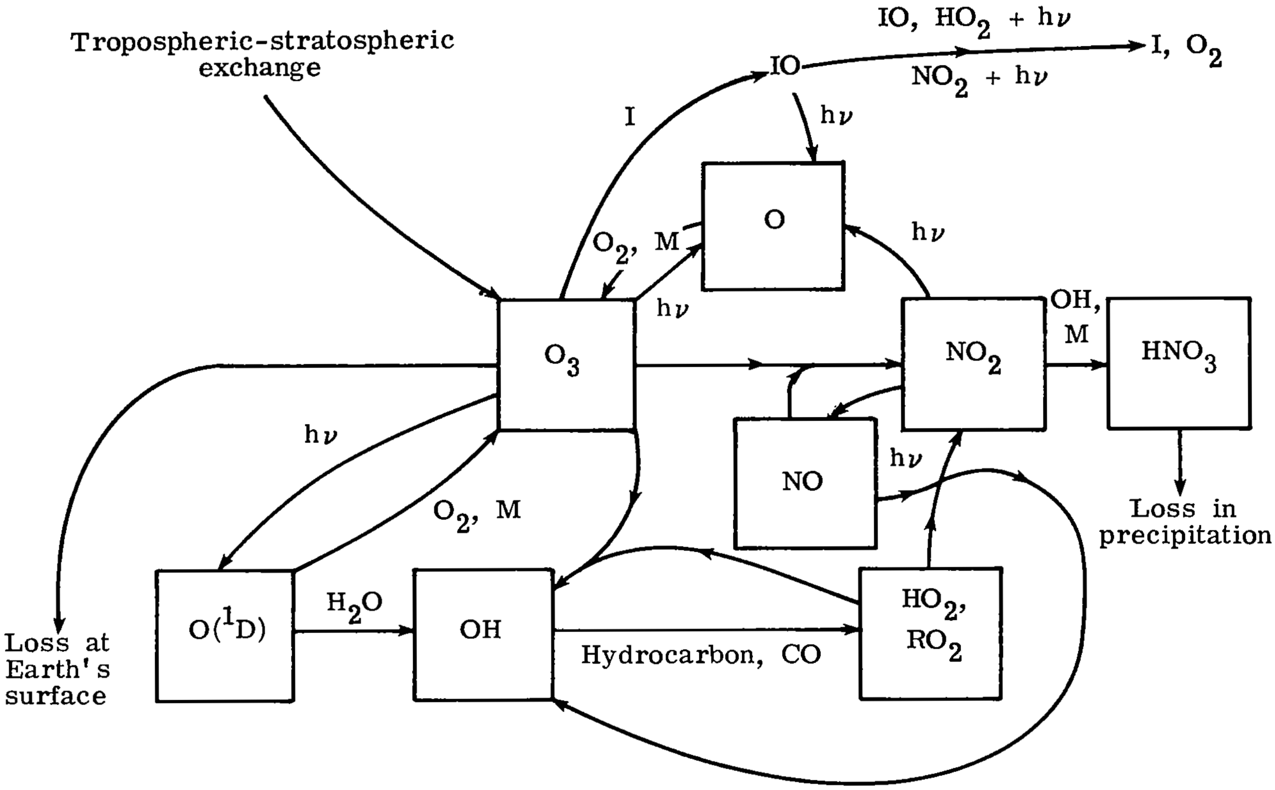


Figure 6.- Schematic diagram of the major sources and sinks of tropospheric ozone.

ability, an understanding of the role of photochemistry in establishing ozone concentrations, and more complete information on the rates and mechanisms of ozone transport through the tropopause and at the surface of the Earth.

Active-nitrogen compounds play a central role in the tropospheric photochemistry. As indicated previously, NO_x may lead to the photochemical production of tropospheric ozone and may act to recycle OH through reaction (R16). Atmospheric active-nitrogen compounds are initially produced in the form of NO or NO_2 by lightning, soil emissions, and ocean processes. Anthropogenic combustion emissions of NO_x may be an important source of atmospheric active nitrogen. It is not known if NH_3 oxidation, initiated by

$$\text{(R24)}\quad NH_3 + OH \rightarrow NH_2 + H_2O$$

significantly affects atmospheric NO_x. The major sink for active nitrogen involves formation of nitric acid

$$\text{(R3)}\quad NO_2 + OH + M \rightarrow HNO_3 + M$$

followed by heterogeneous removal in precipitation. Observations indicate that the dissolution of HNO_3 in cloud water droplets is often a major source of H^+ ions in rainwater and thus a contributor to acid rain.

The relative abundances of NO and NO_2 are approximately determined by the rapid cycle of

$$\text{(R25)}\quad NO + O_3 \rightarrow NO_2 + O_2$$

followed by reactions (R17) and (R18). If these reactions occur at equal rates, the photostationary state predicts that

$$\frac{[NO]}{[NO_2]} = \frac{J_{17}}{[O_3]\, k_{25}}$$

where [ ] denotes the concentration of the appropriate constituent and J_{17} and k_{25} are the rate constants for reactions (R17) and (R25), respectively. Local photochemical ozone production may be indicated by the extent to which this photostationary state relation does not hold because of reactions such as reaction (R16) that convert NO to NO_2 without consuming a molecule of ozone. Despite the importance of active N in the C-N-O_3 system, the global distribution of NO and NO_2 and the processes that control their abundances remain a major source of uncertainty.

2.2.2 Global Carbon/Nitrogen/Ozone System Summary

As outlined in the previous section, the carbon/nitrogen/ozone species are coupled by a complex series of photochemical reactions involving free radicals. Figure 7 summarizes the various interactions that occur in the overall photochemistry by indicating the chemical lifetime for each species to react or photolyze. An important observation from this figure is the large number of coupling time constants that are calculated to be less than 1 or 2 days. Thus,

Reactant

Reactant	hν	$O(^1D)$	$O(^3P)$	O_3	O_2	H	OH	HO_2	H_2O_2	H_2O	CH_4	CH_3	CH_3O_2	CH_3O_2H	CH_3OH	CH_2O	CO	NO	NO_2	NO_3	HNO_2	HNO_3
hν																						
$O(^1D)$					1(-14) (a)					1(-13)												
$O(^3P)$					2(-10)																	
O_3	.3						30 (b)	20 (b)										5 (b)				
O_2																						
H					1(-11)																	
OH								7(-4)	1(-3)		3(-5)			2(-3)			1(-5)					
HO_2							7(-2)	6(-3)					7(-2)					1(-2)				
H_2O_2	3						2															
H_2O	1(-13)																					
CH_4							300 (b)															
CH_3					2(-12)																	
CH_3O_2	1 (c)						2 (b)	2(-2) (d)										2(-2) (d)				
CH_3O_2H	2 (c)						2 (b)															
CH_3OH							2 (b)															
CH_2O	7(-2)						.15															
CO							12															
NO				1(-3)			.2	3(-3)					2(-3)									
NO_2	2(-3)			.5			.2	.2														
NO_3	2(-4)																	5(-3)	5 (b)			
HNO_2	2(-2)						.3															
HNO_3	12						20 (b)															

[a] Lifetime based on N_2 and O_2 concentrations present in the lower troposphere.

[b] Lifetime based on diurnally averaged radical concentrations.

[c] Estimated J values with a possible uncertainty of a factor of 5.

[d] Lifetime based on estimated rate constant. Possible uncertainty in lifetime is a factor of 3.

Figure 7.- Daytime coupling constants for several carbon, oxygen, and nitrogen species for 25°N latitude and the marine boundary layer. Numbers in each box refer to chemical lifetime in days of species on the left to react with species above box; negative numbers in parentheses represent negative powers of 10.

spatial and temporal variations in such key variables as solar flux, water vapor, ozone, and nitrogen oxide levels can result in significant changes in the levels of numerous other species in the system. It must be concluded, therefore, that to have a reasonably complete chemical understanding of why specific concentration levels of photochemical species are observed in the atmosphere, one must be prepared to look simultaneously at a very large fraction of the total system. Furthermore, since many of the chemical lifetimes are equivalent to or shorter than the characteristic tropospheric transport times of 30 to 60 days, global-scale observations of many key species will be needed to map their distributions accurately.

Appendix A contains, in table 18, an extensive list of scientific questions related to the global carbon/nitrogen/ozone system. All these specific questions can be encompassed within the single general query: What are the principal processes governing the global carbon/nitrogen/ozone system? Several research tasks will be proposed to answer this question.

2.3 THE GLOBAL SULFUR/AMMONIA/CARBON/TRACE METAL/AEROSOL SYSTEM

2.3.1 Tropospheric Sulfur

One of the central questions about this system is how gaseous sulfur released from the biosphere or from anthropogenic sources is ultimately converted to its final chemical form (aerosol) and subsequently returned to the biosphere. Extensive documentation exists in the literature that suggests the importance of both homogeneous and heterogeneous mechanisms. In no case, however, have quantitative field experiments been carried out that show the absolute or even relative importance of these two different generalized mechanisms. In this section, a general outline of the coupling between gaseous sulfur species, ammonia, carbon, trace metals, and atmospheric aerosol is presented. As suggested above, this outline will be subdivided into a discussion of homogeneous and heterogeneous mechanisms.

2.3.1.1 Homogeneous sulfur oxidation mechanisms.- For the reduced forms of sulfur such as H_2S, CH_3SCH_3, and CH_3SH, the major homogeneous reaction process leading to the formation of S^{+4} is that of reaction with atmospheric OH. Although the initially formed radical fragment (i.e., HS or CH_2SCH_3) must undergo several additional elementary reactions before conversion to SO_2, the rates of these processes are predicted to be fast compared with the initial reaction with OH. Of equal importance, however, is the fact that the chemical lifetime of SO_2 is almost certainly longer than that of the reduced sulfur species.

Before discussing the oxidation of SO_2 to sulfate, comments on two additional gaseous sulfur species, COS and CS_2, are necessary. At this time, it is not clear whether all COS is formed from CS_2 or whether part of the atmospheric burden is derived directly from primary sources - natural or anthropogenic. Gas kinetic data and field data, however, tend to support the idea that COS does have a long tropospheric residence time and, in fact, it is quite likely that a major sink for this compound is transport to the stratosphere where both photolysis and reaction with atomic oxygen result in its conversion to SO_2. CS_2 has been shown to have both biospheric and anthropogenic sources and appears to have a moderately long chemical lifetime dictated primarily by its reaction with atomic oxygen. The SO and CS radicals resulting from this reaction would subsequently undergo reaction with O_3 to produce SO_2 and COS molecules. As discussed previously, COS is probably degraded only after mixing into the stratosphere.

One of the critical links between gaseous sulfur species and aerosol sulfur involves the mechanism by which SO_2 is converted to H_2SO_4 or other S^{+6} oxidation forms. Under natural tropospheric conditions, one can readily reduce the important initiating homogeneous reactions possible to three:

(R26) $HO_2 + SO_2 \rightarrow SO_3 + OH$

(R27) $RO_2 + SO_2 \rightarrow SO_3 + RO$

(R28) $OH + SO_2 \xrightarrow{M} HSO_3$

In the case of reactions (R26) and (R27), the resulting SO_3 species has been shown to readily react with H_2O to form a complex which subsequently rearranges to form H_2SO_4:

(R29) $SO_3 + H_2O \rightarrow H_2O \cdot SO_3$

(R30) $H_2O \cdot SO_3 \xrightarrow{M} H_2SO_4$

Reaction (R28), unlike reactions (R26) and (R27), does not appear to result in a sulfur radical species that immediately converts into H_2SO_4. Since existing gas kinetic-rate data combined with field measurements suggest that reaction (R28) could be the most significant process of reactions (R26) to (R28), it is important to explain the details of the fate of the HSO_3 radical.

Laboratory and field research needs in the area of homogeneous sulfur chemistry are extensive. The most pressing needs in the laboratory are those of obtaining better rate-constant values for reactions (R26) to (R28) (in each case at atmospheric pressures of O_2 and H_2O) and of determining the fate of the HSO_3 radical. Field-data needs cover a broad spectrum ranging from flux and concentration measurements of H_2S, CH_3SH, CH_3SCH_3, $(CH_3)_2SO$, CS_2, and SO_2 over an extensive range of latitude as well as over highly varied continental and ocean surface types. Sulfur-aerosol concentration measurements as a function of size are needed under the same conditions as for the aforementioned sulfur species. In order to assess the importance of homogeneous reaction processes in controlling the distribution of H_2S, CH_3SH, $(CH_3)_2S$, $(CH_3)_2SO$, SO_2, and H_2SO_4-aerosol, concentrations of the radical species OH, HO_2, and RO_2 should be measured simultaneously with those of the sulfur species.

2.3.1.2 Heterogeneous sulfur oxidation mechanisms.- The most important heterogeneous pathway for oxidation of SO_2 on a global scale is presently believed to involve diffusion of gas-phase sulfur into liquid cloud droplets, wherein the liquid-phase oxidation of sulfur occurs. Thus, although the overall process can be viewed as heterogeneous, the actual chemical reaction itself occurs entirely in the liquid phase and is thus homogeneous. This being the case, one might expect reasonably reliable rate data to be available from liquid-phase kinetic studies. Unfortunately, experiments carried out using rainwater appear to give results quite different from those involving distilled water. Minute amounts of organics and inorganics can have a significant impact on the measured liquid-phase rate constants. Even so, there now seems to be growing evidence that only a limited number of trace metals or combinations of trace metals have an appreciable catalytic effect on sulfur oxidation by dissolved O_2. It is generally agreed that sulfur oxidation by O_2 in the liquid phase in the absence of a catalyst is far too slow to account for observed oxidation rates. Finally, whereas some metals do appear to have catalytic activity that increases the SO_2 oxidation rate by orders of magnitude over the rate when they are absent, the levels of these metals in natural-background tropospheric areas appear to be too low to be significant in oxidizing S^{+4} to S^{+6}.

Dissolved ozone and hydrogen peroxide in cloud droplets have been actively explored as a means of explaining liquid-phase sulfur oxidation. Although the ozone-sulfur oxidation rate appears to be at least two to three orders of magnitude faster than that of the O_2 system, the rate of the O_3-S system (like O_2) is sensitive to the pH of the liquid medium. For example, in shifting from a pH of 7 to a pH of 4, the rate of sulfur oxidation via the O_3 mechanism decreases by approximately 10^5. This then raises the important question of neutralization of acidic cloud droplets, and the principal species that must be considered here is ammonia.

A third important liquid-phase SO_2 oxidation mechanism is that involving hydrogen peroxide. This reaction can be of major importance due to three factors: (1) The high solubility of H_2O_2 in cloud droplets, (2) the moderately high H_2O_2 levels expected in clean, sunlit tropospheric air, and (3) the fact that the rate for this reaction is not inhibited as pH decreases. (In fact, the rate increases with decreasing pH.) For these reasons, the liquid-phase heterogeneous hydrogen-peroxide reaction scheme could be of equal importance as the gas-phase oxidation of SO_2. It should be noted, however, that since the level of H_2O_2 is strongly controlled by the intensity of fast photochemistry, both this mechanism and the gas-phase homogeneous mechanism will be important under similar climatological conditions. This again underscores the fact that the ozone liquid-phase cloud-droplet mechanism may be the dominant one in many parts of the global atmosphere at specific times of the year.

A final point to be stressed concerns the role of NH_3 in sulfur aerosol formation. As discussed previously, NH_3 can play a direct role in controlling the rate of the O_3 cloud-droplet SO_2 oxidation mechanism because of the strong dependence of its rate on pH. Ammonia would seem to have a smaller impact on the rate of the liquid-phase H_2O_2 oxidation mechanism and would appear to have virtually no impact on the rate of homogeneous gas-phase SO_2 conversion (i.e., involving OH, HO_2, or RO_2). In all cases, though, NH_3 is the dominant species responsible for neutralizing acidic sulfur species (i.e., H_2SO_4, H_2SO_5, $H_2S_2O_8$, and $(NH_4)HSO_4$), suggesting that if the global sulfur budget were to increase at a faster rate than the global NH_3 budget, there could result a systematic increase in global rain acidity. This phenomenon, in fact, has already been observed in highly industrialized regions of the world.

Two general classes of materials have been suggested as having potentially important catalytic activity for the oxidation of SO_2 on particle surfaces: (1) Trace metals or metal oxides and (2) elementary carbon in the form of soot particles. With regard to the natural troposphere, however, it is now generally agreed that the somewhat elevated reactivity of trace-metal or metal-oxide particulate material probably does not compensate for the low concentration levels of this type of aerosol in terms of SO_2 oxidation. There is somewhat greater uncertainty as to the relative importance of carbon particles in SO_2 oxidation. Although there is evidence that carbon particles can be important in sulfur oxidation in urban areas, their low concentration in the natural troposphere would seem to preclude a significant global role. However, new data on carbon particle formation from wood burning (natural or controlled) could alter the above point of view during the next few years.

As in the case of homogeneous gas-phase SO_2 chemistry, an improved understanding of the importance of heterogeneous sulfur oxidation mechanisms requires both field and laboratory studies. Of major importance in new field-data needs is measurement of the concentration levels and fluxes of NH_3, H_2O_2, O_3, $(NH_4)_2SO_4$ aerosol, $(NH_4)HSO_4$ aerosol, and H_2SO_4 aerosol. The levels of carbon particles and trace metals in aerosol species require examination but at a somewhat lower priority. Field data should be collected over an extensive latitude range and over widely differing continental and ocean surface-area types.

Laboratory needs should focus on the role of trace organics and catalysts on the O_3-sulfur and H_2O_2-sulfur liquid-phase oxidation mechanisms, the ultimate goal in each case being the identification of the mechanism and the measurement of reliable absolute rate constants for these reactions. Studies are needed to determine whether the rate-constant data generated in batch liquid reactors are, in fact, applicable to cloud-droplet-size liquid spheres.

2.3.2 Tropospheric Ammonia

In recent years, considerable research has been devoted to atmospheric nitrogen species, the nitrogen cycle, and the impact of anthropogenic activities in altering nitrogen-species concentrations in the troposphere and stratosphere. To date, most of the research in nitrogen species has focused on nitrous oxide (N_2O) and the nitrogen oxides (NO and NO_2). Ammonia (NH_3), however, is the most abundant nitrogen species after N_2 and N_2O, with a highly variable mixing ratio ranging from 1 to 20 ppb.

On a worldwide basis, the major fraction of atmospheric ammonia is produced by bacteriological action on biological waste. The primary anthropogenic source of ammonia is combustion, especially combustion of coal. In addition, ammonia can be emitted in automobile exhausts and produced as a result of agricultural operations.

Reaction with the hydroxyl radical is thought to be the major gas-phase reaction of ammonia in the troposphere:

$$NH_3 + OH\cdot \rightarrow H_2O + NH_2\cdot$$

The rate constant for this reaction has been recently measured; however, the fate of the NH_2 radical thus formed is essentially unknown.

Ammonia is thought to play a major role in aqueous aerosol formation. Preliminary epidemiological results suggest that ammonium-containing particles may have adverse health effects. Data indicate that ammonium salts - NH_4NO_3, NH_4HSO_4, and $(NH_4)_2SO_4$ - account for most of the nitrate and sulfate particulates present in airborne aerosols in the South Coast Air Basin of California. Reactions of NH_3 with HNO_3 and H_2SO_4 are thought to be major gas-to-particle conversion processes; that is,

$$NH_{3(g)} + HNO_{3(g)} \rightarrow NH_4NO_{3(s)}$$

$$2NH_{3(g)} + H_2SO_{4(g)} \rightarrow (NH_4)_2SO_{4(s)}$$

NH_4NO_3 aerosols can be formed in the atmosphere by direct reaction between NH_3 and HNO_3, by direct reaction between NH_3 and O_3, or by NH_3 oxidation on soot particles. Although appreciable amounts of nitric acid are formed in photochemically polluted atmospheres, the high vapor pressure of HNO_3 (about 45 torr at 25^oC (1 torr = 133.3 Pa)) precludes the formation of nitric-acid aerosol. Therefore, nitrate-aerosol formation may be limited by ambient ammonia levels rather than by the levels of nitrogen oxides. Determination of the role of ammonia upon nitrate-aerosol formation requires measurement of ambient NH_3 levels. Most of the destruction of NH_3 occurs in the troposphere, with about one-half being removed heterogeneously and one-half homogeneously, presumably by reaction with OH. The estimated time constant for each of these processes is about 1 month. In addition to aerosol formation, NH_3 is removed by precipitation scavenging and absorption at the surface of the Earth.

It has been suggested that the oxidation of ammonia as a result of photolysis and reaction with OH may represent an important, hitherto neglected source of nitric oxide (NO) in both the troposphere and stratosphere. Recently, it has been suggested that the oxidation of NH_3 in the combustion of coal or in oxidizing catalytic converters may be a source of N_2O. A potentially important anthropogenic source of NH_3 is the volatilization of ammonium contained in nitrogen fertilizers applied to agricultural soils. Moreover, since NH_3 has an absorption band at 10.53 µm within the "atmospheric window," it may affect climate, particularly if the anthropogenic production of NH_3 continues to increase.

To date there have been no long-term, systematic measurements of tropospheric ammonia. The few measurements that have been reported (e.g., in situ sampling and IHR measurements) indicate that NH_3 exhibits strong spatial and temporal variations. The few available surface NH_3 measurements exhibit a large variation in mixing ratio (from 1 to 20 ppb). The first objective of a tropospheric NH_3 measurement program should be to measure the diurnal and seasonal variations of the tropospheric NH_3 profile. The second objective should be to measure the diurnal and seasonal variations over different types of terrain (e.g., swamps, forests, various types of grasslands, open oceans, along the coast, and over urban areas). The role of NH_3 in tropospheric photochemistry cannot accurately be assessed until the vertical distribution of tropospheric NH_3 and its daily, seasonal, and latitudinal variability are determined.

2.4 TROPOSPHERIC POLLUTION

Atmospheric chemical components can be characterized by their mean residence time, which is determined by chemical transformation and removal rates. The lifetimes of atmospheric trace constituents emitted as a result of man's activities range from a few seconds for tire debris from an automobile to many years for fluorocarbons and CO_2. The common gaseous pollutants emitted into the lower troposphere, such as SO_2 and NO_x, reside in the troposphere for time periods on the order of a few days. Figure 8 depicts the spatial and temporal scales relevant for tropospheric air pollutants. The "Mesoscale," "Regional scale," and "Global scale" were described in the introduction to this chapter. The "Microscale" represents a spatial scale of 1 km or less. There are only a few primary pollutants for which mean residence time is within the microscale. Heavy particles from sources such as automobile-tire erosion fall into this category.

There are several important man-made pollutants for which residence time is restricted to a few days or a week and transport distance is within a few thousand kilometers. These include the gaseous and particulate sulfur compounds, oxides of nitrogen, nitric acid, and ozone.

The urban troposphere can be characterized as those regions of the troposphere wherein large quantities of concentrated man-made pollutant emissions exceed natural emissions by several orders of magnitude, leading to pollutant concentration levels that exceed natural levels by comparable orders of magnitude. Because of the spatial scale typically associated with such regions, the applicable meteorological phenomena are those of the microscale and mesoscale. Although there are no chemical reactions peculiar to the urban atmosphere, the relative importance of the various reactions may shift substantially from that in the global troposphere as a result of the orders-of-magnitude higher concentrations. For example, oxidation reactions involving higher molecular weight hydrocarbons assume paramount importance in the urban atmosphere.

Chemically, the regional troposphere within the planetary boundary layer differs from the polluted urban atmosphere in that the contributions from major source types such as urban automobile emissions and power-plant plumes have sufficient time to mix and interact chemically. Such multiple-source chemical interaction is most distinct during stagnating anticyclones, when there is cir-

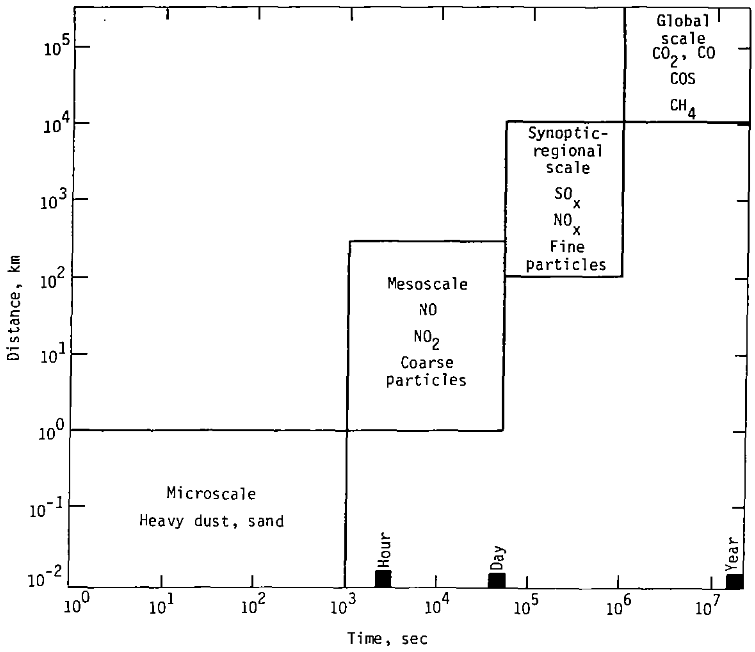


Figure 8.- Spatial and temporal scales revelant to tropospheric air pollutants.

culation within a high-pressure system but without overall ventilation of a given region. In the Eastern United States, for example, such stagnating anticyclones have resulted in the development of large-scale hazy air masses containing high levels of sulfate, ozone, and other secondary pollutants.

Much of the current concern in transport and chemistry of tropospheric air pollutants is due to the more recent recognition of "long-range transport," that is, air-pollution transport beyond the boundaries of air-quality-control regions, States, or, for that matter, countries. In Europe, the long-range transport of sulfur and nitrogen compounds has resulted in an appreciable acidification of rain in Scandinavia. Similar evidence of acidification of lakes in upper New York and Canada is now available.

The perturbation of the atmospheric radiative properties by large-scale regional hazes has also been receiving increased attention. The vertical optical depth of such regional hazes is generally such that about one-half of the incident solar radiation is scattered within the haze. Most of the light reaches the ground but about 10 percent of the scattered light is reflected back toward space, thus reducing the radiation reaching the surface. The corresponding increase in the surface albedo can be detected by satellites in the visual band. (See fig. 9.) Such satellite photographs of large regional-scale haziness have in fact produced the most convincing evidence of long-range aerosol transport from industrial sources. The perturbation of the atmospheric radiative balance has also received attention.

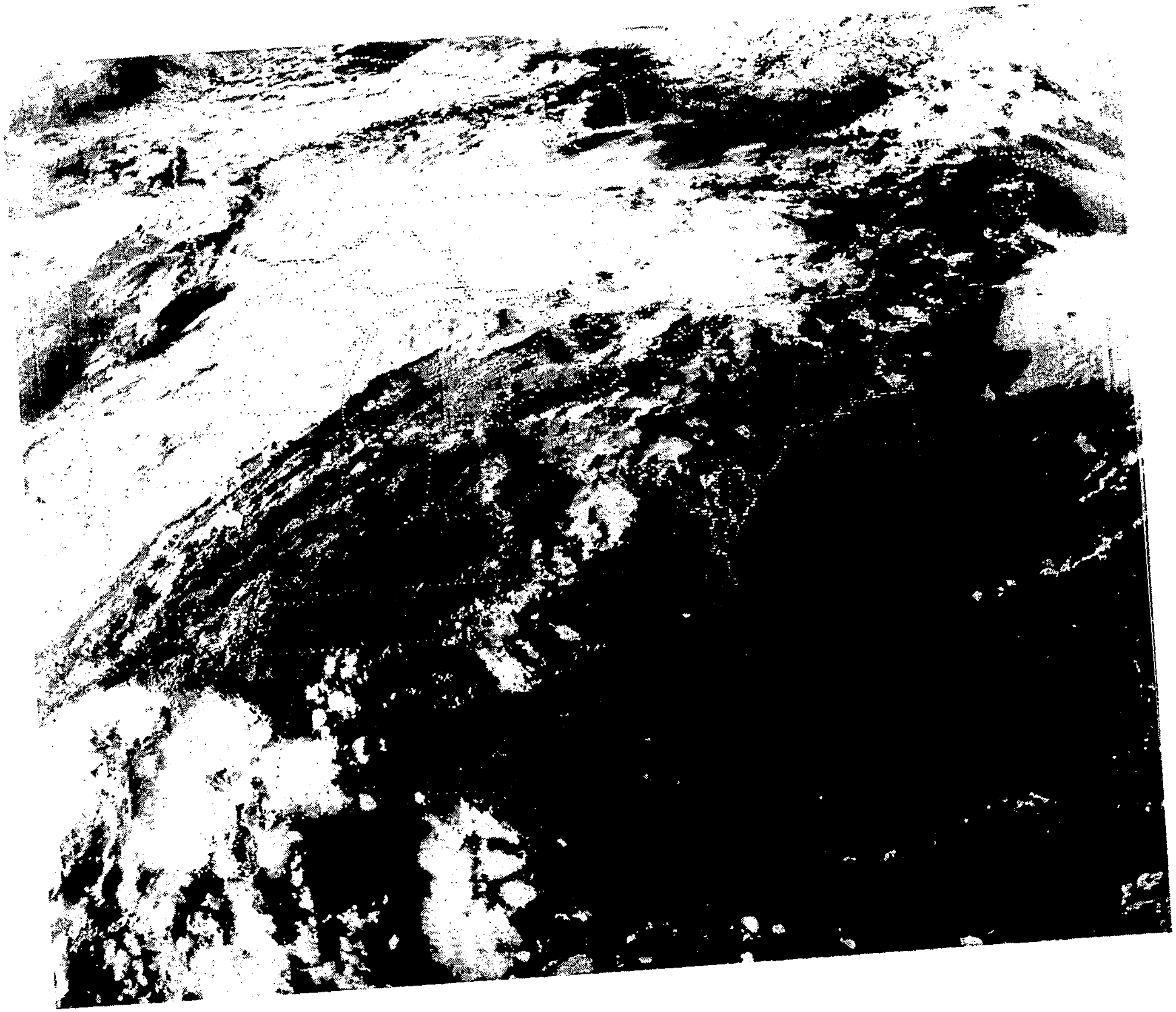


Figure 9.- A hazy airmass covered large areas of the East coast on July 22, 1978, as seen from the geostationary satellite image.

The key research problem associated with the urban troposphere is to develop a quantitative understanding of the chemical and physical processes that govern the transport and transformation of pollutants. A quantitative understanding of these roles may then lead to mathematical models for relating primary emissions of gases and particles to airborne concentration levels of both primary and secondary gases and particles. The U.S. Environmental Protection Agency (EPA) has devoted a major effort toward explaining the chemistry and physics of urban atmospheres and toward developing emission/air-quality models. This effort has involved extensive field-measurement programs as well as theoretical studies. The vast majority of the measurement programs conducted by EPA and by State and local agencies have been based on ground-based point measurements. There is a continuing need for data on the vertical and horizontal distributions of pollutant concentrations.

In its primary role as a developer of space-derived technology, NASA is assisting EPA in urban and regional atmospheric research through the development and field application of airborne remote-sensing systems under an existing Memorandum of Understanding between the two agencies. Attention is confined, therefore, to this aspect of research on the urban atmosphere in the present recommended research plan.

Relative to the regional troposphere, the major scientific question can be posed as: What are the relative roles of transport, transformation, and removal processes in governing the behavior of regional- and urban-scale polluted air masses?

2.5 MAJOR RESEARCH NEEDS IN THE TROPOSPHERE

In this chapter, the scientific basis for several general questions relating to the troposphere has been briefly discussed. Additional discussion is contained in the Scientific Research Objectives in Tropospheric Pollution in appendix A. In response to the detailed list of 39 scientific questions posed by the Working Group, 38 operational and 12 instrument-development tasks were identified. The 39 specific questions posed by the Working Group were found to be encompassed by the three very general tropospheric research problems of this chapter:

I. What are the principal processes governing the global carbon/nitrogen/ozone system?

II. What are the principal processes governing the global sulfur/ammonia/trace metal/carbon/aerosol system?

III. What are the relative roles of transport, transformation, and removal processes in governing the behavior of regional- and urban-scale polluted air masses?

Table 1 indicates how the research tasks identified by the Working Group correspond to the three major questions and the four research categories of modeling, laboratory measurements, field programs, and technology development. The tables referred to in the first column are those in appendix A and the task numbers shown indicate the number of the task in the appropriate table.

TABLE 1.- SUMMARY OF RESEARCH TASKS

[Tables referred to in parentheses are in appendix A]

Research categories	Research task number corresponding to major question -		
	I	II	III
Modeling (table 19)	1, [a]27, [a]33	[a]27, [a]33	[a]27, [a]33
Laboratory measurements	---	(b)	(b)
Field programs (table 19)	2, 4, 11, 12, [c]13, 15, 16, 18, 23, 24, 25, 31, 38	7, 12, [c]13, 20, 21, 26, 31, 38	29, 31, 32
Technology development (table 20)	1, 2, 4, 8, 9, 12	3, 5, 6, 7, 10, 11, 12	1, 2, 3, 4, 6, 7, 8, 9, 12

[a] Use, interpretation, and assimilation of remote sensing data into tropospheric models.

[b] Optical properties of aerosols.

[c] Satellite monitoring of global land types and resources.

In the next chapter the research tasks identified by the Working Group are formulated into a series of coherent programs of modeling, laboratory measurements, field programs, and technology development.

CHAPTER 3 - PROPOSED RESEARCH PROGRAMS

3.1 INTRODUCTION

In this chapter, the programs proposed to meet the major research needs of chapter 2 are outlined. Four classes of programs are proposed:

(1) Field measurements

(2) Modeling

(3) Laboratory measurements

(4) Technology development

Each of the major problems posed in chapter 2 has components that suggest theoretical and experimental research studies. The experimental studies are divided according to those conducted in the field and in the laboratory. In view of the role of NASA as a developer of space-derived technology and as a catalyst for the adoption of this technology by operational U.S. agencies and agencies of other countries, emphasis is also given to a number of technology development tasks. This aspect is important because of the need for the continued development of advanced technology to achieve a global monitoring capability for the natural and perturbed troposphere. The technology development, in turn, requires a laboratory and field program, supported by models, in order to determine the parameters needed for a measuring instrument.

Among the four classes of programs, field-measurement programs and technology-development programs are the areas of primary emphasis in the research plan because of the unique role of NASA in orbital remote sensing and instrument development. The field-measurement programs proposed consist primarily of orbital remote sensing and airborne monitoring. Airborne and, to some extent, ground-based measurements are being proposed as high-priority programs early in the NASA tropospheric program since the in situ data to be obtained will be essential for improving our understanding of tropospheric processes, a necessary step for development of optimum measurement techniques.

Two specific modeling tasks are herein delineated:

1. Continued development of chemical-transport models of the global troposphere

2. Development of methods for the use, interpretation, and assimilation of remote sensing data into tropospheric models for both the global troposphere and for regional air pollution

NASA has played a central role in the development of mathematical models of the global troposphere, and continued refinement of such models is essential for the proper interpretation of tropospheric measurements. Because of the need to interface remote sensing data with the prediction of models (both for the global troposphere and regional air pollution), the development of techniques for such integration is an important task. (Because of the role of EPA in developing models for synoptic-regional-scale and urban-scale air pollution, this aspect is not proposed for NASA involvement.)

A variety of laboratory studies are needed to support the major components of field programs and technology development. The laboratory programs proposed are divided according to supporting tasks and fundamental kinetic measurements. Supporting tasks are studies of the interaction of electromagnetic radiation with matter, calibration, and characterization of the properties of atmospheric constituents. Fundamental kinetic measurements include the measurement of rate constants under tropospheric conditions and measurements aimed at explaining the process of gas-to-particle conversion. It is anticipated that NASA programs in this area will be primarily concerned with those that are in direct support of the field-measurement, modeling, or instrument-development programs.

Technology development has been a cornerstone of NASA's mission. In this chapter, available remote and in situ instruments (those developed both with and without NASA support) applicable to tropospheric research and current NASA programs in technology development are summarized. Then several proposed programs are outlined for technology development in support of tropospheric research.

3.2 FIELD-MEASUREMENT MISSIONS - INTRODUCTION

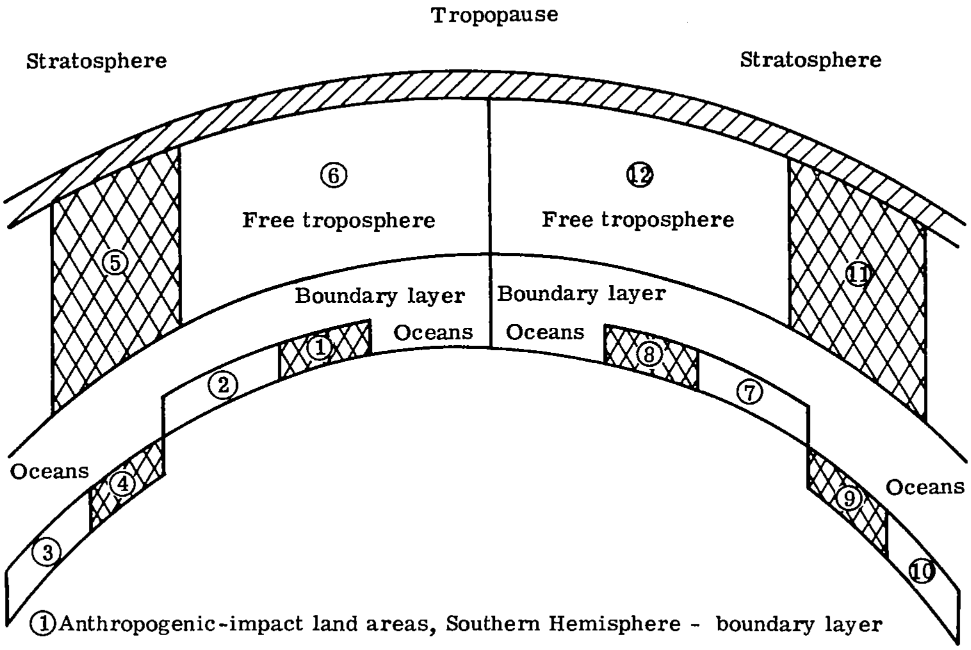
As discussed in chapter 2, two scientific goals toward which NASA's program should attempt to make major gains during the coming two decades are that of establishing the global atmospheric distributions and budgets of those elements believed to be of key importance in global biogeochemical cycles and that of determining the cause-and-effect relationships between these observed distributions and the dominant controlling factors such as atmospheric chemical transformations, biospheric and atmospheric source and sink strengths, and atmospheric transport. Since an extraordinary amount of field sampling at a considerable cost will be required to satisfy the above goals, the decision on what type or types of sampling platforms to use in each case is obviously a critical one. Establishing the detailed relationships between concentration levels and source and sink strengths, as well as chemical-transformation rates, will best be accomplished using a combination of aircraft, ground-base, and ship sampling platforms coupled with limited satellite observations. The first goal (global distributions), on the other hand, conceptually could be most effectively reached via satellite and/or Space Shuttle sampling platforms. Unfortunately, the basic limitations of these platform types (i.e., physical space, payload weight, and availability of electric power) now and in the immediate future make this option initially appear to be impractical. This is particularly true if one takes the position that around 100 different chemical species are present in the clean troposphere and many of these will need to be monitored with high resolution. Taking a more realistic point of view, though, this situation obviously represents an extreme case since, even with our present limited knowledge of tropospheric chemistry, one-half to two-thirds of this total number of 100 species could probably be rejected as being of only minor importance. The real difficulty then is trying to select a critical subset of 10 to 15 species for which chemical coupling and source and sink relationships with other tropospheric trace gases and aerosols are understood well enough that the measured global-distribution profiles will permit a reliable assessment of the global distributions of numerous other major as well as minor tropospheric trace gases.

In conjunction with the task of identifying a critical subset of tropospheric species for satellite viewing, there is also the very difficult problem mentioned earlier of establishing the spatial resolution that will be required of these new measurements. In the horizontal direction, for example, resolution on the order of tens of kilometers will be needed for some species, whereas resolution of several thousand kilometers will probably be adequate for others. In the vertical direction, the resolution limits will be much smaller, ranging from 1 km to as much as 15 km. In general, our present ability to predict the vertical and horizontal resolution requirements for monitoring a tropospheric trace gas via a satellite platform ranges somewhere between poor to fair. (The obvious exception to this statement involves the very long-lived species such as N_2O, CF_4, $CFCl_3$, CF_2Cl_2, and CO_2.)

Based on the above discussions, it is concluded that if a cost-effective tropospheric-research orbital platform is to be developed by NASA, a considerable amount of "front-end" information will be required. It is the recommendation of this research planning document that the most efficient means of obtaining this advance information will be through the initiation of a well-conceived global tropospheric aircraft sampling program. Unlike the blanket sampling coverage expected from a satellite platform, such an aircraft program would encompass a "select" global sampling strategy. Thus, the objective will be that of carrying out detailed atmospheric field studies on a global scale, but involving a carefully selected set of "representative" global regions.

Since the proper identification of these "representative" regions will dictate, to a large degree, the success of the proposed tropospheric aircraft sampling program, the authors have attempted here to provide a modest review of this subject. Central to this approach for measuring global trace-gas distributions is the idea that the global troposphere can be defined in terms of an ensemble of "unique atmospheric composition domains." The basis upon which one domain is terminated and a new one initiated is dictated by the existence of multichemical concentration gradients in a specific region of the troposphere. These gradients, in turn, are taken to be a reflection of the chemical influences exerted by four key tropospheric factors: (1) Atmospheric transport, (2) chemical transformation rates, (3) the distributions of sources and sinks for tropospheric gases, and (4) the distributions of sources and sinks for tropospheric aerosols.

From this approach, it becomes possible to develop several different "domain" models having varying degrees of spatial resolution. In general, the more extensively the four control factors are permitted to influence the chemical composition of the troposphere, the higher the resolution of the model. The simplest of these models, representing the lowest possible resolution of the global troposphere, is shown in figure 10. In this case, a total of 12 unique composition domains have been defined. Most field data now reported in the literature are classified in a manner similar to this low-resolution profile. The low-resolution model is based on the inclusion of two atmospheric transport characteristics (i.e., interhemispheric mixing and boundary-layer/free-tropospheric mixing) and three very low resolution natural trace gas source



①Anthropogenic-impact land areas, Southern Hemisphere - boundary layer
②Remote natural land areas, Southern Hemisphere - boundary layer
③Remote natural oceanic areas, Southern Hemisphere - boundary layer
④Anthropogenic-impact oceanic areas, Southern Hemisphere - boundary layer
⑤Anthropogenic-impact areas, Southern Hemisphere - free troposphere
⑥Remote natural areas, Southern Hemisphere - free troposphere
⑦Remote natural land areas, Northern Hemisphere - boundary layer
⑧Anthropogenic-impact land areas, Northern Hemisphere - boundary layer
⑨Anthropogenic-impact oceanic areas, Northern Hemisphere - boundary layer
⑩ Remote natural oceanic areas, Northern Hemisphere - boundary layer
⑪ Anthropogenic-impact areas, Northern Hemisphere - free troposphere
⑫ Remote natural areas, Northern Hemisphere - free troposphere

Figure 10.- A low-resolution scheme for defining global tropospheric distributions.

regions (labeled in fig. 10 as "Remote natural land areas," "Remote natural oceanic areas," and "Free troposphere"). Finally, it has been recognized that anthropogenic emissions can also have an impact on the concentration levels of tropospheric gases. Thus, a total of 6 different source types was combined with two transport characteristics, resulting in 12 independent composition domains. In this simple model, no consideration was given to the possible influence of either chemical transformations or tropospheric sink processes.

The proposed medium-resolution model with a total of 37 composition domains is too complex to illustrate in graphic form as in figure 10. Instead, the key elements of this scheme are presented in the form of a flow diagram (see fig. 11), the lowest resolution elements typically being positioned near the top of the figure.

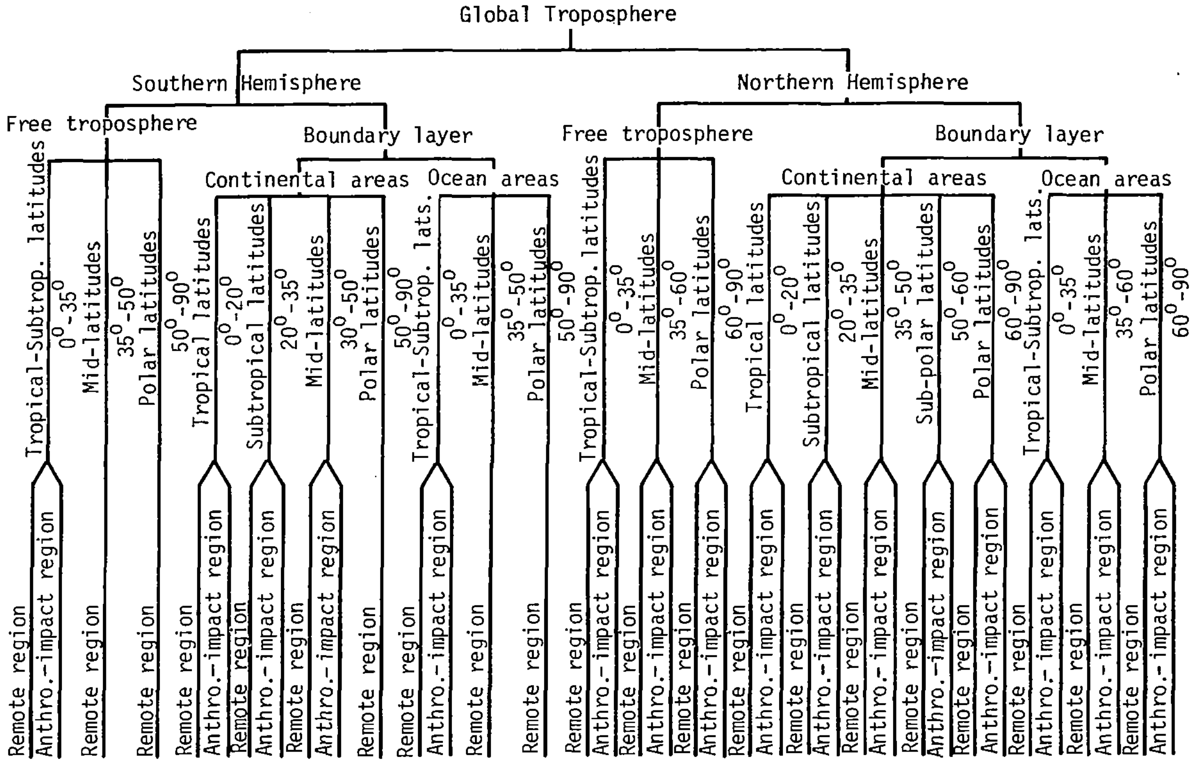
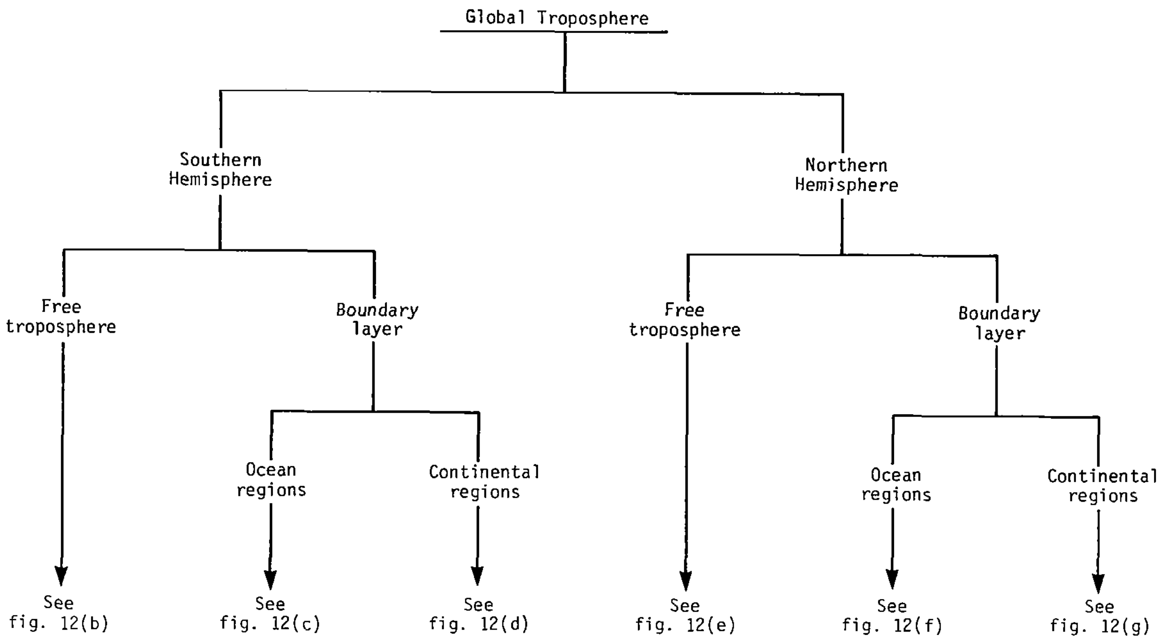


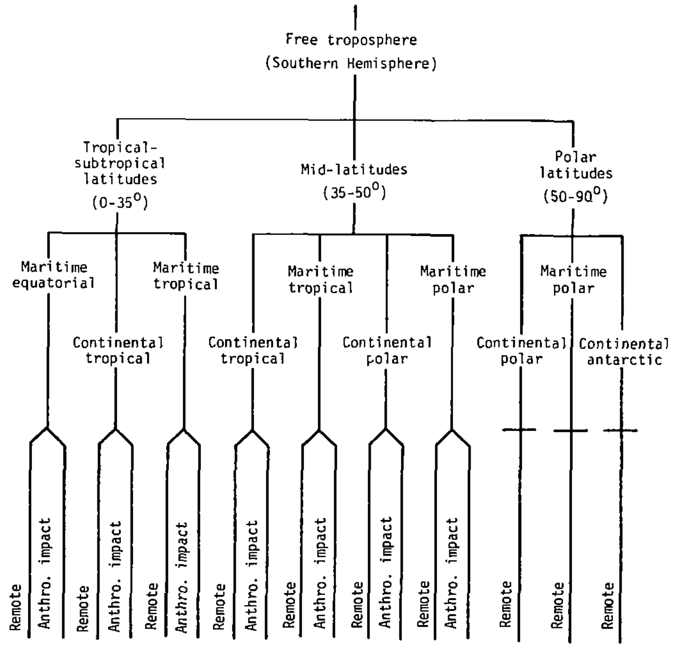
Figure 11.- A medium-resolution tropospheric distribution scheme.

In this scheme, as well as in the high-resolution one (fig. 12), the temporal averaging period was taken to be one calendar year. Under these conditions, concentration gradients resulting from diurnal and/or seasonal variations are significantly dampened. Even so, the medium-resolution distribution scheme does provide two important new elements not present in the simple model: (1) Geographical specification for source regions and (2) a geographical framework for considering the effects of chemical transformations and atmospheric sinks. In the latter case, the strong latitudinal dependence of the solar flux and the OH concentration, both of which have a pronounced effect on chemical-transformation rates, have been estimated in terms of four latitudinal zones: 0° to 20°, 20° to 35°, 35° to 60°, and 60° to 90°. These same four zones have also been used to provide some geographical specification for wet and dry removal processes.

Figure 12 shows the high-resolution global distribution model. The number of independent composition domains in this presentation has now increased to 132. Most of this increase reflects the much higher density of sources which

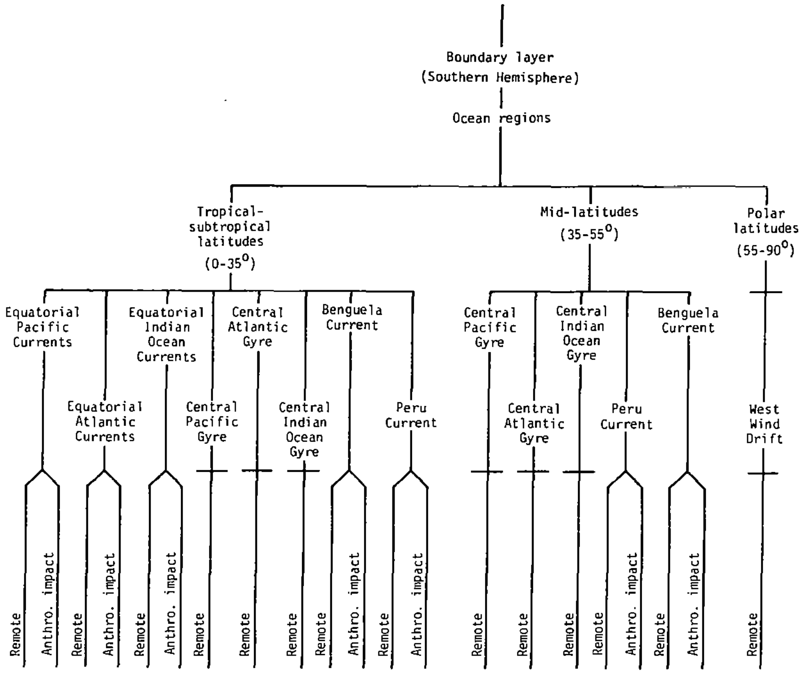


(a) Entire scheme.

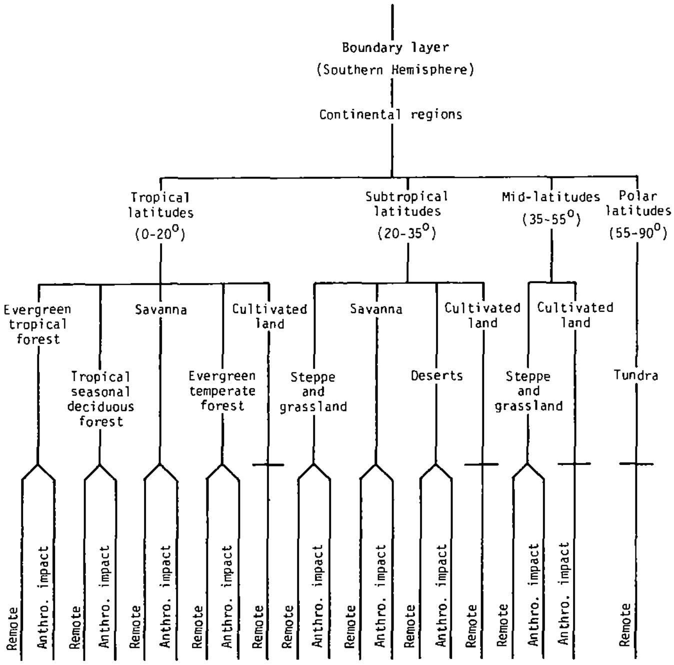


(b) Free troposphere, Southern Hemisphere.

Figure 12.- A high-resolution tropospheric distribution scheme.

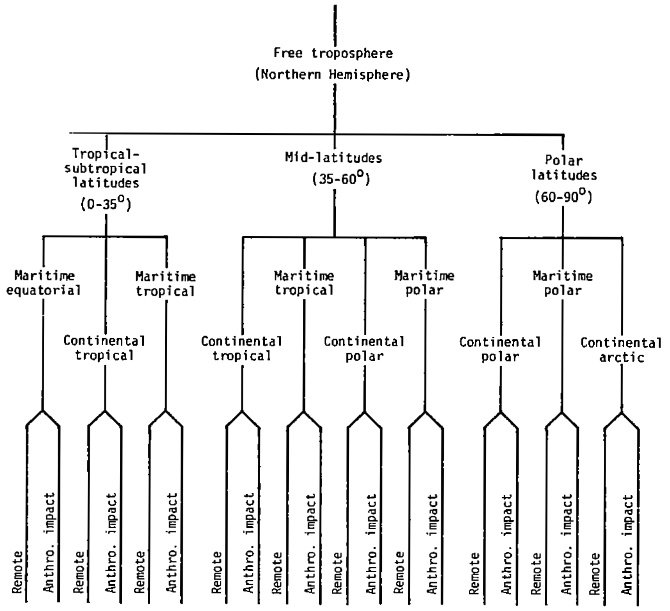


(c) Ocean regions, Southern Hemisphere.

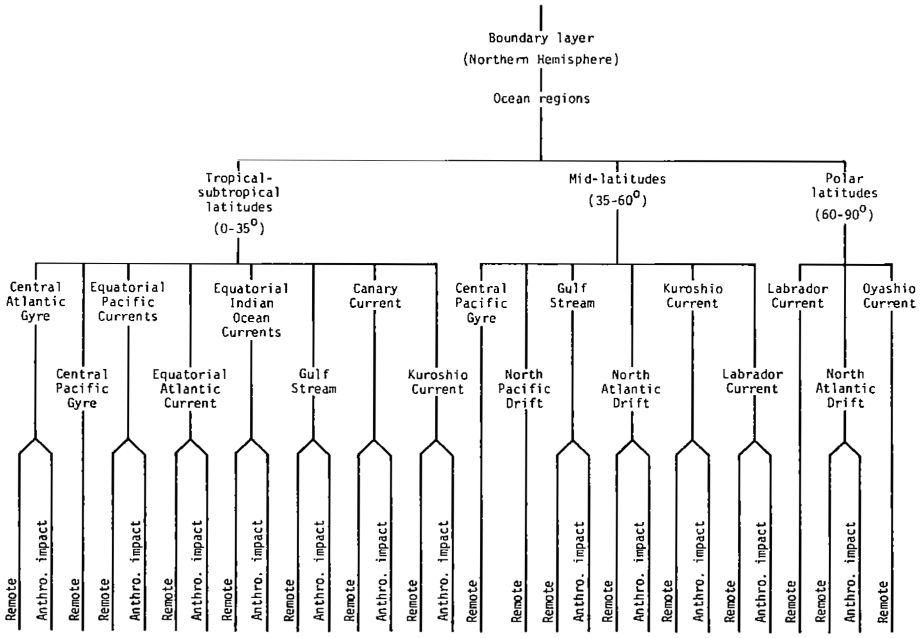


(d) Continental regions, Southern Hemisphere.

Figure 12.- Continued.

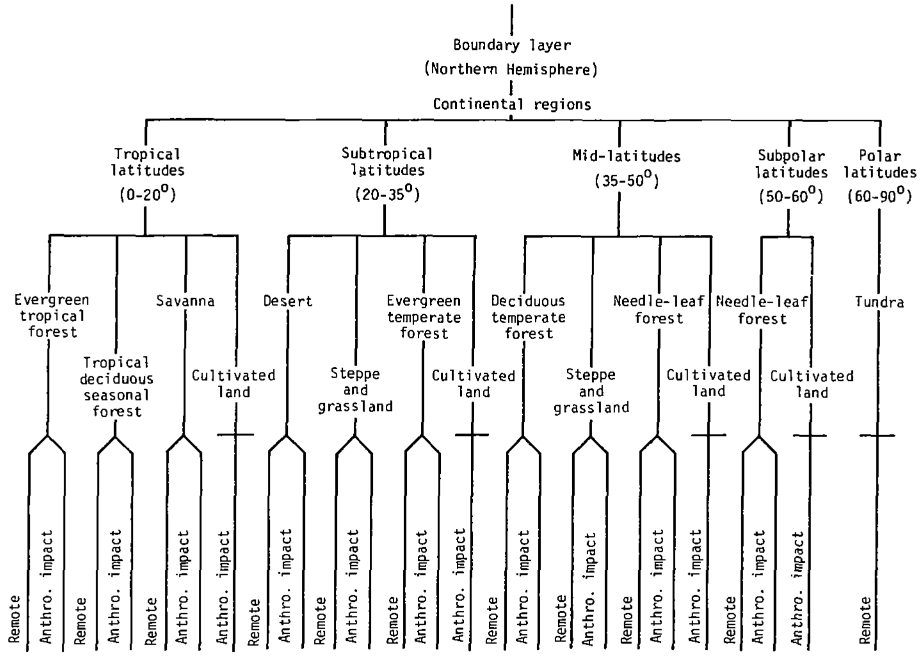


(e) Free troposphere, Northern Hemisphere.



(f) Ocean regions, Northern Hemisphere.

Figure 12.- Continued.



(g) Continental regions, Northern Hemisphere.

Figure 12.- Concluded.

have been used for both continental and marine boundary-layer regions. Each continental zone, for example, has been subdivided into source domains which reflect major natural vegetation types growing in that area. (See fig. 13.) Although field data are now lacking to fully support this extensive breakdown of natural source domains, the justification for this approach is based on the hypothesis that major differences in the plant communities of two regions will result in major differences in the release and uptake rates of numerous tropospheric trace gases. If correct, it follows that there will be observed differences both in the absolute concentration levels of these same gases and in the overall chemical composition of the atmosphere within each domain type. The strong correlation between vegetation types and annual precipitation patterns also permits the use of the former to label composition domains according to the possible impact of atmospheric washout and rainout in each region.

Another source type considered is shown in figure 12 as "Cultivated land." The argument given here is that, with the application of large amounts of fertilizer in modern farming technology, trace-gas releases from cultivated land are likely to be substantially different from those from natural vegetation in the same area.

As a final adjustment to the continental breakdown of composition domains, the potential role of anthropogenic sources in various latitudinal zones has been indicated. In this case, global population density and per capita energy-

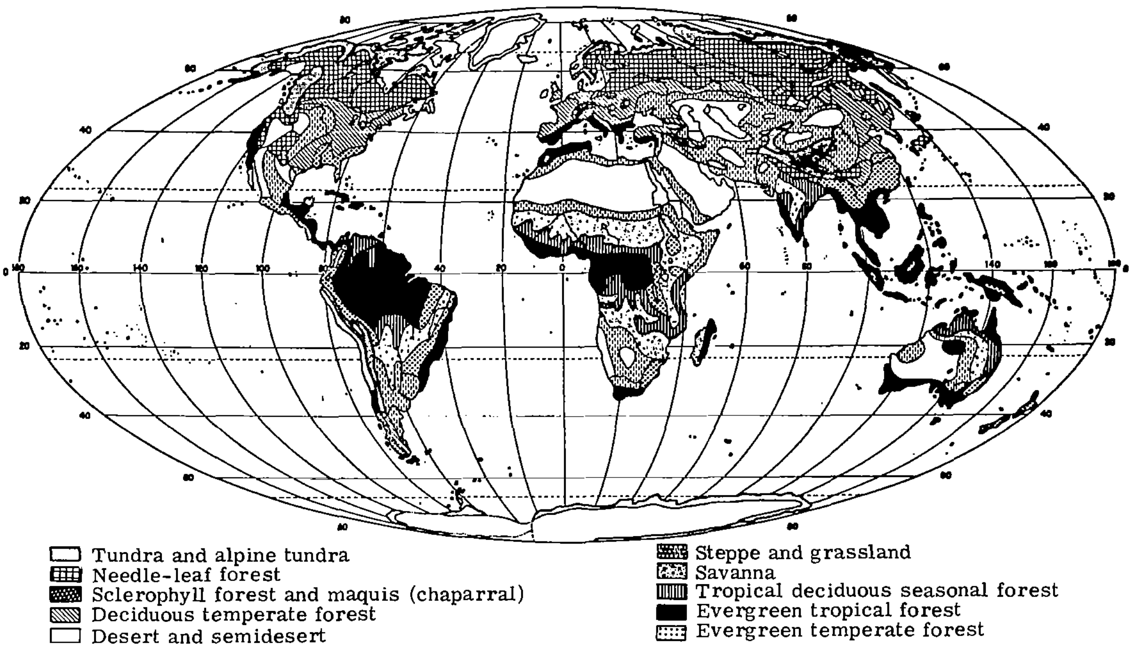


Figure 13.- Principal plant formation types of the Earth from reference 2 (Tricart, J.; and Cailleux, A.: Introduction to Climatic Geomorphology. St. Martin's Press, c.1973.)

consumption charts (figs. 14 and 15) in combination with general atmospheric-circulation patterns were used as a guide.

The approach taken in defining a higher density of sources for the marine environment was necessarily more indirect than that used for continental areas. In this case, we have specified the major ocean surface currents and the central gyres of each ocean as domain boundary limits. The justification for this approach has been illustrated in figures 16 and 17. From these figures it can be seen that a reasonably good correlation can be made between many of the physical features of the ocean and biomass productivity. In general, the highest nutrient levels in the ocean are found in upwelling regions and in ocean surface currents leading away from these upwelling regions. The lowest nutrient levels are typically found in central ocean gyres. Since the number density of phytoplankton and zooplankton (these species being the major source of ocean biomass) strongly parallels nutrient levels, the use of ocean currents and gyres as labels for different composition domains was taken to be a reasonable first approximation. Again, as in the case of continental vegetation, the working hypothesis was that major changes in biological types and number density have a significant impact on the rate of release and uptake of trace atmospheric gases.

The last adjustment incorporated into the high-resolution scheme shown in figure 12 involved a reevaluation of the density of domains in the free troposphere. This number was increased from 10 to 37, reflecting the role that long-

Figure 14.- Global population density as of 1971. Tallest peaks are for Japan, having a population density of 283 per square kilometer; lowest plateau is for Greenland, where density is nearly zero. Figure is from reference 3 (Freedman, Ronald; and Berelson, Bernard: The Human Population. Sci. American, vol. 231, no. 3, Sept. 1974, pp. 31-39. Copyright ©1974 by Scientific American, Inc. All rights reserved.)

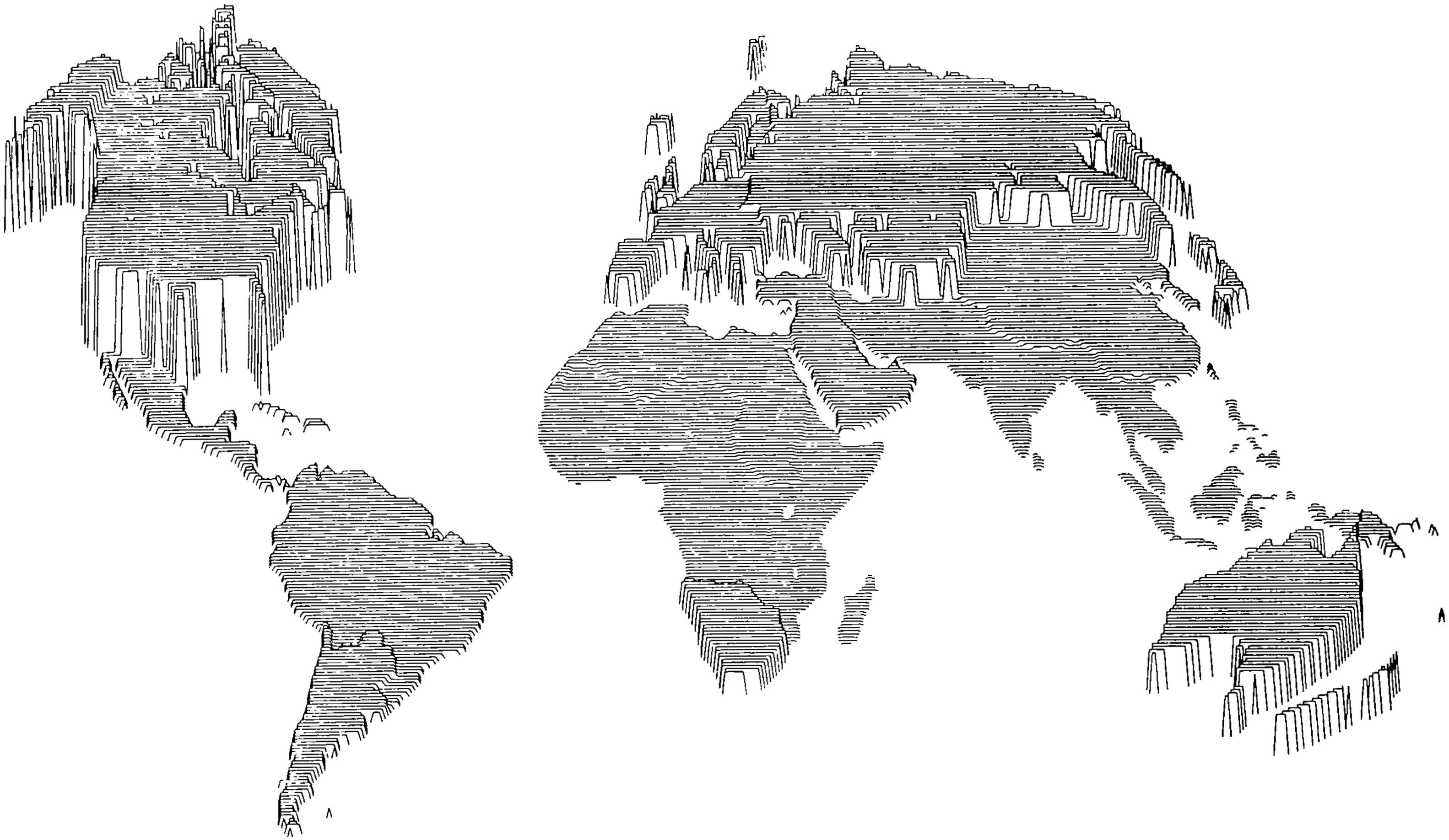


Figure 15.- Global energy consumption as of 1968. Units of energy are equivalent kilograms of coal burned per capita. Highest plateau is the U.S.A., with a figure of 10,331; lowest is western Africa with 51. Figure is from reference 3 (Freedman, Ronald; and Berelson, Bernard: The Human Population. Sci. American, vol. 231, no. 3, Sept. 1974, pp. 31-39. Copyright ©1974 by Scientific American, Inc. All rights reserved.)

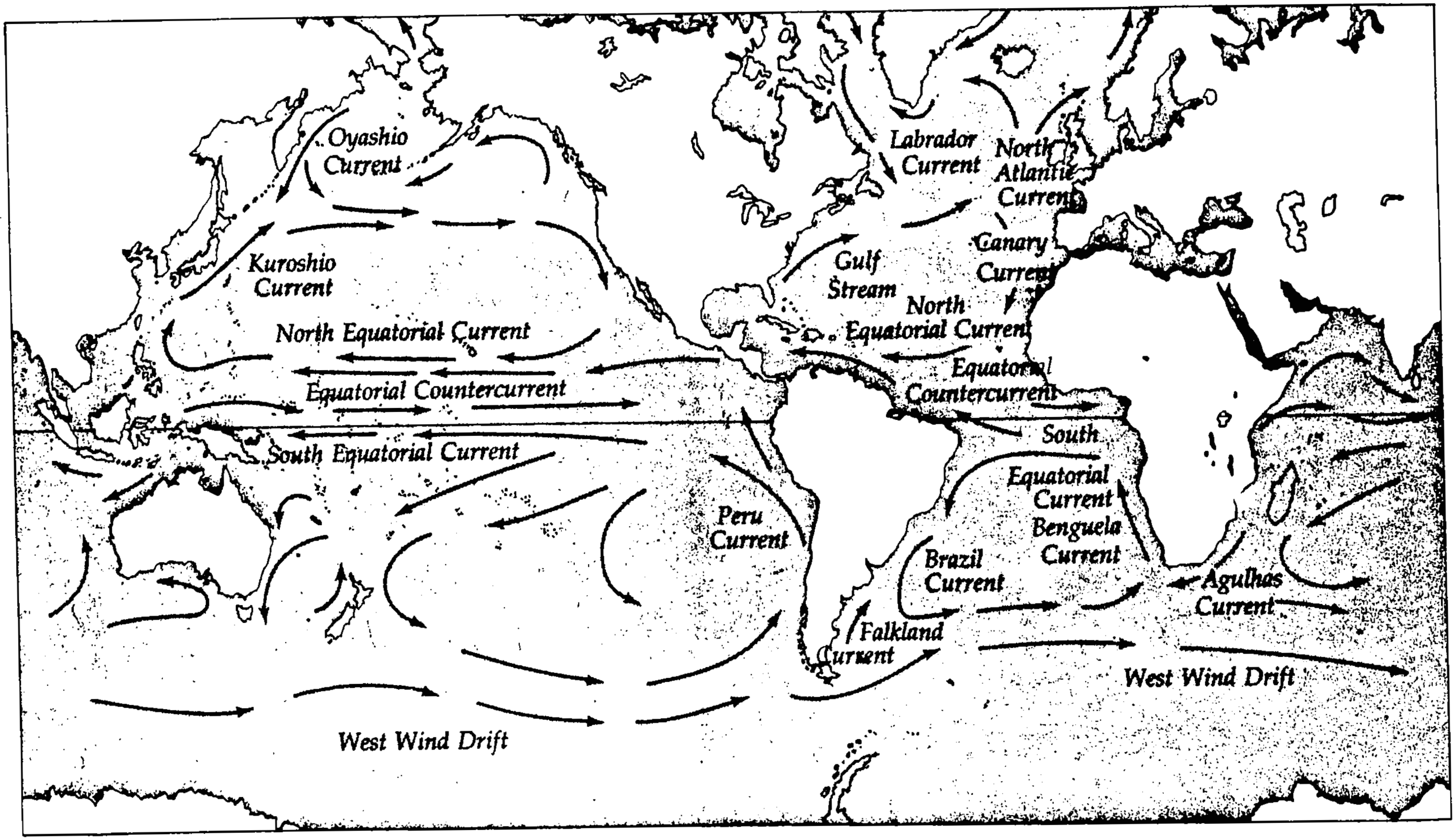


Figure 16.- Major surface ocean currents.

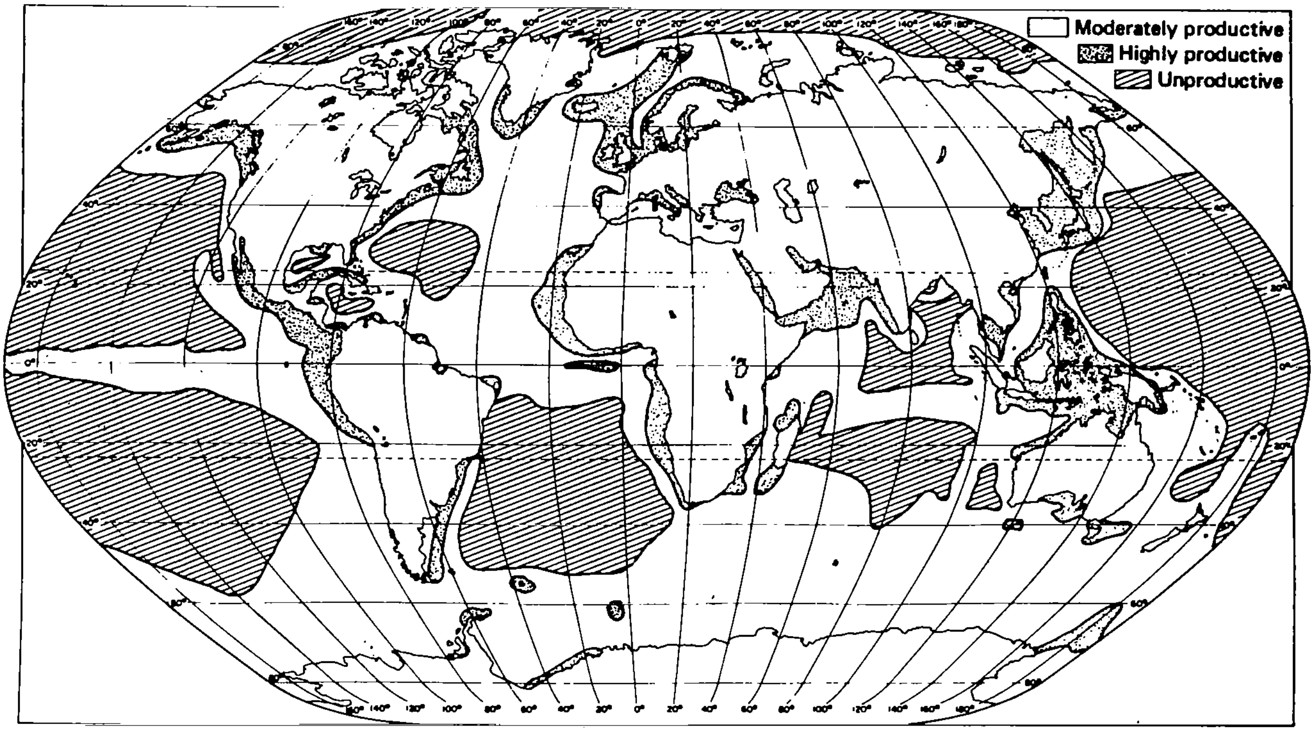


Figure 17.- Biomass productivity in coastal regions and the open oceans from reference 4. (Koblentz-Mishke, Olga J.; Volkovinsky, Vadim V.; and Kabanova, Julia G.: Plankton Primary Production of the World Ocean. Scientific Exploration of the South Pacific - Proceedings of a Symposium, Warren S. Wooster, ed., Natl. Acad. Sci., 1970, pp. 183-193.)

range transport may play in controlling trace-gas and aerosol distributions. In figure 12 the new composition domains resulting from this reevaluation of the transport characteristics of the free troposphere have been labeled in terms of air mass types, which, in turn, are identified in terms of their geographical source of origin.

In summary, if the results from the high-resolution model are accepted as being generally well founded (based on reasonable assumptions), the implications for future global tropospheric sampling programs are twofold:

(1) The troposphere is indeed very complex with regard to the global distributions of numerous trace gases which collectively define the bulk of the chemistry of the troposphere; thus, satellite monitoring of many of these gases is considered to be essential.

(2) Although the number of regions in the troposphere that might be labeled as having a unique chemical composition is very large (i.e., 132 and possibly much higher), there is at the same time considerable redundance in domain types when the global troposphere is viewed in a fully partitioned format. This observation, when taken in combination with the fact that not all composition

domains are predicted to be of equal importance and therefore in need of equal sampling time, leads to the conclusion that a "select" global aircraft sampling program is both scientifically and logistically feasible.

As related to NASA's long-term tropospheric goals, the justification for an aircraft sampling program is based on the fact that it will provide definitive chemical information on the troposphere which will be invaluable to the successful planning and deployment of a tropospheric-research satellite monitoring system and, as a proven mobile sampling platform, it will provide the single most important source of ground-truth measurements for comparisons with satellite observations.

3.3 FIELD-MEASUREMENT MISSIONS - THE PROGRAM

3.3.1 Tropospheric Aircraft Sampling Program

In section 3.2, the basic guidelines for improving our scientific understanding of the troposphere via field-measurement programs were defined. In particular, arguments were presented which strongly suggested that the most effective means of establishing the global distributions of numerous tropospheric trace gases and aerosols would be through the use of satellite research platforms. At the same time, the point was made that the successful development of such a satellite system could depend critically on the availability of new chemical information on the troposphere. Thus, it was proposed that a select global tropospheric aircraft sampling program be initiated, the results from which could provide this necessary front-end information. In the text that follows, the authors have attempted to examine some of the more practical aspects of defining this global sampling program and thus have extensively used the information presented earlier in section 3.2 (i.e., figs. 12 to 17).

One of the important factors that dictates the spatial resolution required in making measurements of a specific chemical species on a global scale is its atmospheric residence time. (See table 2.) In general, the longer the residence time, the lower the spatial resolution required for the measurement. In the case of $CFCl_3$, CF_2Cl_2, and N_2O, the respective residence times in the troposphere are sufficiently long (i.e., >20 years) that a single, well-placed ground station in the Northern and Southern Hemispheres would suffice for purposes of establishing the distributions of these species.[1] It would also suffice for establishing long-term secular trends in the concentration levels of these same species.

When the residence time of a chemical species is reduced from ≥ 20 years to a time of 1 to several years, the spatial resolution required for field measurements approaches that suggested by the low-resolution model given in figure 10. For species with still shorter residence time (several days to 1 year), the existence of local-regional sources and sinks in combination with the variable

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[1] This statement should not be interpreted to mean that one could understand the source flux strengths of these molecules globally from two monitoring stations. The latter problem would require far more extensive measurement.

TABLE 2.- APPROXIMATE RESIDENCE TIMES FOR SEVERAL ATMOSPHERIC TRACE GASES

Residence time (a)	Carbon species	H_xO_y species	Nitrogen species	Iodine species	Bromine species	Chlorine species	Sulfur species
Very short-lived species (<1 sec to 1 day)	CH_3 CH_3O_2 CH_3O CH_2O C_2H_4 C_3H_6 C_4 to C_{20} hydrocarbons	$O(^3P)$ $O(^1D)$ OH HO_2 H	NO NO_2 NO_3 N_2O_5 HNO_2	I IO $IONO_2$ HI INO INO_2 HOI	Br BrO $BrONO_2$ HBr	Cl ClO $ClONO_2$	$(CH_3)_2S$ CH_3SH $(CH_3)_2SO$ H_2S
Short-lived species (1 day to 2 weeks)	CH_3OOH CH_3OH C_2H_6 C_3H_8 C_6H_6	H_2O_2	[b]NH_3 RNO_3 [b]HNO_3 R=CH_3, C_2H_5, etc.	CH_3I	[b]HOBr	[b]HCl [b]HOCl C_2HCl_3	SO_2
Moderate-lived species (2 weeks to 1 yr)	CO C_2H_2	[c]O_3			CH_3Br	CH_3Cl $CHCl_3$ C_2Cl_4	CS_2 [d]COS
Long-lived species (1 to several years)	CH_4	H_2				CH_3CCl_3	
Very long-lived species (≳ 20 yr)	CF_4		N_2O			$C_2F_3Cl_3$ CCl_4 CF_2Cl_2 $CFCl_3$ $C_2F_4Cl_2$	SF_6

[a] Estimated residence times for a latitude of 30° where average OH concentration was taken to be $1.5 \times 10^6/cm^3$.

[b] Lifetime of these species may be controlled by washout-rainout rather than gas-kinetic or photochemical reactions.

[c] Although the time required for O_3 to be photodecomposed is ≲1 day, 95% or more of the resulting atomic oxygen recombines with molecular oxygen instantaneously to reform O_3; thus, lifetime of O_3 is more like 10-30 days.

[d] Considerable uncertainty in the rate coefficients for reaction of this species with OH; lifetime assignment of this compound must be considered somewhat speculative at this time.

levels of H_xO_y radicals dictates the need for an even higher level of spatial resolution in a field-measurements program. In this case, the medium resolution shown in figure 11 may be required. For rapidly reacting species (residence times of less than 1 minute to 2 days), local sources, sinks, and chemical-transformation rates are expected to create large variations in the observed concentration levels of these compounds. Thus, the minimum field-sampling resolution required would be that shown in figure 12.

In order to illustrate the usefulness of the residence-time concept, we have examined a specific chemical system in terms of the spatial resolution which might be required of any global field-sampling experiment. This preliminary analysis is therefore considered equally valid for either aircraft or satellite sampling platforms. The chemical subsystem selected is one that defines much of the fast photochemical cycle in the troposphere, namely that involving carbon, nitrogen, ozone, and H_xO_y species. For completeness, table 2 summarizes the estimated residence times for all major NO_x, carbon, and H_xO_y species. These residence times, in conjunction with the medium- and high-resolution spatial models in figures 11 and 12 have been used to generate the results given in table 3. These results suggest that for the clean troposphere this class of species would dictate a horizontal sampling resolution ranging from 200 to 6000 km. In general, land areas require somewhat higher sampling resolution than the oceans. If the airspace over major industrial countries

TABLE 3.- SPATIAL RESOLUTION REQUIREMENTS FOR AIRCRAFT MEASUREMENTS

OF CARBON, NITROGEN, OZONE, AND H_xO_y RELATED SPECIES

Species	Vertical resolution, km, for -						Horizontal resolution, km, for -											
	Ocean areas			Land areas			Ocean areas						Land areas					
							Latitude			Longitude			Latitude			Longitude		
	High	Low	Av. (a)	High	Low	Av. (a)	High	Low	Av. (a)	High	Low	Av. (a)	High	Low	Av. (a)	High	Low	Av. (a)
$O(^1D)$	0.5	3	1.5	0.5	3	1.5	200	600	300	200	2000	1000	200	600	400	200	2000	400
$O(^3P)$	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
H	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
OH	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
HO_2	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
CH_3	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
CH_3O_2	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO_2	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO_3	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
HNO_2	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
CH_2O	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
H_2O_2	1.5	5	2.5	1.5	5	2.5	500	1000	700	500	2000	1000	500	1000	700	500	2000	1000
CH_3O_2H	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
CH_3OH	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
HNO_3	2	5	3	2	5	3	500	2000	1000	500	2000	1000	500	1000	700	500	1000	700
O_3	0.5	2	1.0	0.5	2	1.0	300	1000	600	300	1000	600	300	600	500	300	600	500
CO	3	6	5	3	6	5	500	2000	1500	1000	2000	1500	500	1500	1000	500	1500	1000
CH_4	5	10	7	5	10	7	3000	6000	3000	3000	6000	3000	1500	3000	2000	1500	3000	1500
H_2O	0.5	2	1.0	1.5	2	1.0	300	1000	500	300	1000	600	300	600	500	300	600	500

[a] Average value in this case is not the arithmetic average of the high and low values, but rather represents a statistically weighted average.

was to be sampled, much higher sampling resolution would necessarily be required in these land areas than over the oceans. It is also noteworthy that for many species (e.g., transients) higher resolution will be required for latitudinal changes than for longitudinal changes. The latter trend reflects the strong dependence of several fast-photochemical species on the absolute levels of solar flux and H_2O, both of which have strong latitudinal dependences. For the vertical coordinate, the sampling resolution required ranges of 0.5 to 10.0 km. No significant differences are indicated for land areas versus the ocean areas.

Although the sampling strategy is discussed previously in terms of atmospheric trace-gas species, a field-measurement strategy for aerosols can be developed using a similar approach. Also, the aerosol field-measurement strategy should be developed in conjunction with the Aerosol Climate Effects (ACE) special study currently being conducted as part of the NASA Climate Program. The objectives of the ACE special study are to help assess the impact of atmospheric aerosols on climate and to use the special circumstances of a volcanic injection of stratospheric aerosols to test our ability to understand and model climate change. Coordination with the ACE special study could result in cooperative missions between the two programs, mutual use of instruments and sampling platforms, and joint theoretical and laboratory studies.

As discussed in section 3.2, a second major prerequisite that must be satisfied before initiating any major global aircraft sampling program is that of defining a set of "representative" regions of the troposphere that, upon being sampled, will provide the largest possible scientific return for flight hours invested. Again, as a preliminary planning exercise, we have taken the information presented in section 3.2 and developed two possible global sampling scenarios. In each case, the representative regions listed have been labeled in the notation presented in figure 12. These results are summarized in table 4. From table 4(a) it can be seen that the so-called "restricted" format encompasses a total of 27 independent regions, whereas the "expanded" format (table 4(b)) is defined in terms of 43 distinct regions. In both cases, however, an element of redundancy appears in the form of specifying both northern and southern hemispheric sampling for similar domain types. Thus, a more critical analysis of each of these sampling scenarios could possibly result in a further reduction in the total number of regions to be sampled by 30 to 40 percent.

As a final planning exercise for future aircraft sampling programs, the information from the sampling formats presented in table 4 has been combined with other operational/logistic considerations for purposes of evaluating the timetable required for completing several different types of aircraft sampling programs. Other major program variables considered in this analysis were the number of research aircraft participating, one versus two, and the number of seasons of the year during which each "representative" region would be sampled, again one versus two. In each of the field programs presented below, it has further been assumed that the average time required to sample an individual composition domain would be approximately 2 weeks (6 or 7 flights) and that no more than 8 weeks of continuous field sampling would be scheduled in a given year:

Program	No. of aircraft	No. of seasons	Time for completion, yr
Restricted format			
I-A-1	1	1	6.5
I-A-2	1	2	13.0
I-B-1	2	1	3.3
I-B-2	2	2	6.5
Expanded format			
II-A-1	1	1	11.5
II-A-2	1	2	23.0
II-B-1	2	1	6.3
II-B-2	2	2	11.5

TABLE 4.- POSSIBLE SAMPLING SCENARIOS FOR A "SELECT" TROPOSPHERIC AIRCRAFT SAMPLING PROGRAM

(a) "Restricted" sampling format

Representative regions to be sampled for -		
Free troposphere	Boundary layer, ocean	Boundary layer, continental
Southern Hemisphere		
0° to 35° Maritime tropical Continental tropical 35° to 60° Maritime tropical Maritime polar	0° to 35° Central Atlantic Gyre Central Pacific Gyre Equatorial Pacific Current 35° to 55° Peru Current	0° to 20° Evergreen tropical forest Tropical seasonal deciduous forest Savanna 20° to 35° Steppe and grasslands
Northern Hemisphere		
0° to 35° Maritime tropical Continental tropical 35° to 60° Maritime tropical Maritime polar	0° to 35° Central Atlantic Gyre Central Pacific Gyre Gulf Stream Kuroshio Current 35° to 60° North Pacific Drift North Atlantic Drift	0° to 20° Tropical seasonal deciduous forest Savanna 20° to 35° Desert Steppe and grasslands 35° to 50° Needle-leaf forest

TABLE 4.- CONCLUDED

(b) "Expanded" sampling format

Representative regions to be sampled for -		
Free troposphere	Boundary layer, ocean	Boundary layer, continental
Southern Hemisphere		
0° to 35°	0° to 35°	0° to 20°
Maritime tropical	Central Atlantic Gyre	Evergreen tropical forest
Continental tropical	Central Pacific Gyre	Tropical seasonal deciduous forest
	Equatorial Pacific Current	
35° to 60°		Savanna
	Peru Current	
Maritime tropical		Cultivated land
Continental tropical	35° to 55°	Desert
Maritime polar	Central Indian Ocean Gyre	
		20° to 35°
	Central Pacific Gyre	
60° to 90°		Steppe and grasslands
Maritime polar	55° to 90°	
	West Wind Drift	
Northern Hemisphere		
0° to 35°	0° to 35°	0° to 20°
Maritime tropical	Central Atlantic Gyre	Tropical seasonal deciduous forest
Continental tropical	Central Pacific Gyre	
		Savanna
	Equatorial Pacific Current	
35° to 60°		Cultivated land
	Gulf Stream	
Maritime tropical		
	Kuroshio Current	20° to 35°
Continental tropical		
	Equatorial Indian Ocean Current	Desert
Maritime polar		
		Steppe and grasslands
60° to 90°	35° to 60°	Evergreen temperate forest
Maritime polar	North Pacific Drift	
		35° to 50°
Continental polar	North Atlantic Drift	
		Needle-leaf forest
	Central Pacific Gyre	
		60° to 90°
		Tundra

From this array of sampling schemes, it can be seen that the timetable for completing the various possible programs ranges from 3.3 to 23.0 years. Of these possibilities, program I-B-2 is one that appears to be practical both in terms of execution time and funding dollars, and one that also has a high potential for a major scientific payoff. Requiring 6.5 years[2] to complete, this program involves the use of two research aircraft to take samples in 27 "representative" tropospheric regions in the Northern and Southern Hemispheres for two different seasons of the year.

3.3.2 Lower Atmospheric Research Satellite (LARS)

The large spatial and temporal heterogeneities of tropospheric source and sink regions as well as the variability in state parameters make it imperative that a comprehensive global study of the C-N-O_3 and S-NH_3-aerosol systems include the application of remote sensing technology on one or more orbital platforms. Although aircraft measurements can be quite important for characterizing various concentration domains, measurements from space are likely to be the best method to accurately map the global distribution of many species whose abundance is affected by both transport and photochemistry. Space measurements are probably also best to determine whether a concentration variation in a given location is due to Eulerian or Lagrangian effects.

Thus, a goal of the NASA Tropospheric Research Program Plan is the eventual implementation of a Lower Atmospheric Research Satellite (LARS). By chronologically following the tropospheric aircraft sampling program, it is believed that many of the mission and design specifications for atmospheric chemistry experiments on LARS can be formulated on the basis of the findings of the aircraft studies. The long-term global coverage that could be obtained by LARS will complement the data obtained by the aircraft program, which will be more detailed and precise but also more spatially and temporally limited than LARS. Thus, the long range orbital and intermediate range aircraft programs suggested here are complementary in nature and, with the appropriate development and planning of both missions, it is probable that many of the key scientific questions discussed in appendix A of this publication will be answered and that several new and important problems will be identified. Appropriate atmospheric chemistry missions for LARS could include: (1) The detailed global mapping of species distributions and major source and sink regions; (2) a better understanding of the global importance of anthropogenic sources of key trace species; (3) the development and verification of detailed global and regional models of tropospheric trace-gas composition and air quality with capabilities to predict the impact of various anthropogenic emissions; (4) a comprehensive record of the present global tropospheric trace-gas composition, which may ultimately be used in identifying long-term secular or cyclic variations in parameters relevant to regional and global air quality; and (5) a determination via a technology transfer program in which instruments should be implemented for continuous, long-term monitoring of air quality and the effectiveness of pollution control strategies.

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[2] Eight years would probably be a more realistic time period since some extra time would probably be needed after 2 or 3 years of field sampling for more extensive data analyses.

These potential chemical missions for LARS could be conducted in conjunction with other potential missions to study atmospheric structure, dynamics, and climate and to develop operational meteorological sounding techniques.

Because of the highly coupled nature of tropospheric photochemistry, simultaneous measurements from LARS of as many species as realistically possible should be a major objective. Thus, implementation of this mission will depend on a vigorous program to develop remote sensing technology as well as an intense field-measurements effort using ground-based instruments and aircraft measurements. This program will be complemented by modeling calculations to determine which configuration of species measurements from a space platform would be most valuable and the concentrations likely to be observed in the troposphere. Although the ultimate goal of the orbital program for the troposphere is the implementation of a comprehensive, multiple-species measurement program from space (i.e., aboard LARS), smaller data-gathering missions using remote sensors either from space, from ground-based stations, or from aircraft should be included in the tropospheric program. By demonstrating the feasibility of various remote sensing instruments and addressing one or two key scientific questions, these smaller missions will be quite valuable in eventually leading up to the comprehensive LARS mission. For example, projects such as the Measurement of Air Pollution from Satellites (MAPS) experiment, which will measure tropospheric CO from the Space Shuttle, and the ground-based remote measurement of atmospheric NH_3 are in accord with the overall goals and directions of this NASA Tropospheric Research Program Plan. The appropriateness and value of other remote sensing missions preliminary to LARS will have to be judged on a case-by-case basis.

A tentative list of key atmospheric species and the required limits of detectability are listed in table 5. (A final determination of the most important species and their concentrations will have to await the findings of the tropospheric aircraft sampling program and other remote sensing missions.) The tentative list of species that would be desirable to measure from space includes O_3, active N (NO, NO_2, and HNO_3), CO, CH_4, H_2CO, nonmethane hydrocarbons (NMHC), H_xO_y (OH, HO_2, H_2O_2, and H_2O), NH_3, SO_2, and reduced S species (H_2S, CH_3SCH_3, CS_2, and COS). The optical properties of aerosols and atmospheric state variables should also be measured. (See appendix C for a discussion on the measurement of atmospheric state variables.) Spot measurements from aircraft and balloons of the chemical composition of aerosols under a satellite flight track should also be important components of the mission.

To a large extent, the final specifications for any atmospheric chemistry satellite measurements will have to await the findings of the aircraft sampling program and the further development of remote sensing technology. For instance, data from the aircraft program may indicate that because of the validity of various photostationary-state relationships it is necessary to measure only a subset of the active-N and H_xO_y species to determine the local abundances of all the species of interest within these families. Similarly, a determination of which NMHC and reduced-S compounds should optimally be measured from LARS to adequately characterize the chemical system will have to await the results obtained from preceding missions, especially the aircraft program. The preliminary list of species for measurement on the LARS mission includes a measurement from space of CH_4. The long residence time of CH_4 causes the abundance to be

TABLE 5.- PRELIMINARY MEASUREMENT REQUIREMENTS IN TROPOSPHERIC CHEMISTRY

A. Resolution:

Vertical: A minimum of two measurements, one within the boundary layer and the other in the mid-troposphere.

Horizontal: Averaging over approximately 200-km-diameter circles.

B. Species:

Species	Limits of detectability		Precision, percent
	Ideal	Acceptable	
O_3	5 ppb	10 ppb	20
CO	10 ppb	50 ppb	20
CH_4	1 ppm	1.5 ppm	5
NMHC* (C_2 to C_{12})	1 ppt	10 ppt	20
H_2CO	.01 ppb	.10 ppb	20
NO†	1 ppt	10 ppt	20
NO_2†	1 ppt	10 ppt	20
HNO_3†	5 ppt	100 ppt	20
OH†	10^5 cm^{-3}	5×10^5 cm^{-3}	10
HO_2†	10^7 cm^{-3}	10^8 cm^{-3}	20
H_2O_2†	.1 ppb	1.0 ppb	20
H_2O†	10 ppm	100 ppm	20
NH_3	.01 ppb	.10 ppb	20
SO_2‡	10 ppt	50 ppt	20
H_2S‡	1 ppt	5 ppt	20
CH_3SCH_3‡	1 ppt	5 ppt	20
CS_2‡	1 ppt	5 ppt	20
COS	10 ppt	50 ppt	20

*Determination of which NMHC are to be measured will be based upon results of preceding missions.

†It may be possible to measure a selected subset of the active-N and H_xO_y species and infer the abundances of all the species of these families, depending upon results of preceding missions.

‡Measurement of reduced S compounds will depend upon results of preceding missions.

C. State variables: Include temperature (±5 K), pressure or number density (±10%), cloud cover and cloud height, and the frequency and distribution of lightning. (See appendix C.)

D. Aerosol measurements: Optical properties from space, and aircraft and balloon spot measurements, under the flight tract, of chemical composition and size distribution of aerosols.

relatively uniform. Fixed-base measurements are thus often adequate for measurements of CH_4 concentrations. However, the CH_4 measurement from space is suggested for LARS as a potential means of identifying any intense CH_4 sources that may exist, but which are presently unknown.

Though not specifically listed in section 3.3.1 or in table 5, a key component of both the tropospheric aircraft sampling program and LARS missions should be a diagnostic and predictive modeling capability to analyze and simulate the data gathered. Because of the complexity of the photochemical system of the troposphere, a truly complete understanding of the data requires detailed numerical calculations; on the other hand, since no measurement program can entirely define the chemical and physical state of the troposphere, numerical models must be relied upon to provide data for parameters that are not directly measured. Thus, it is envisioned that modeling efforts will be included in both the aircraft sampling program and LARS missions to complement the experimental packages. It is recommended that a central data-handling and computing facility available to all investigators, both experimental and theoretical, be adopted for these missions to facilitate the flow of data and the essential interaction required.

3.4 MODELING

3.4.1 Global-Scale Modeling

The objectives of global-scale modeling are to explain the detailed features of the chemical interactions in the troposphere and to support the development of observing systems applicable to tropospheric pollution. Models provide insight into the relationships between trace-species concentrations and the chemical, physical, and biological processes that determine those concentrations. The capability of models to explore the effects of a wide range of feasible parameter values such as chemical-reaction rate constants permits an assessment of our degree of understanding of natural tropospheric processes and points out those problem areas most in need of further study. Models allow the estimation of the spatial and temporal scales of importance in both natural and anthropogenic-influenced tropospheric processes, thus contributing to the development of sensor requirements for observing systems. Finally, human activities that might play a major role in perturbing the chemical budgets of the troposphere can be studied through various modeling scenarios, and the future consequences of both industrial emissions and proposed control strategies may be estimated.

NASA has played a central role in the development of mathematical models of the global troposphere, and continued refinement of such models is essential for the proper interpretation of tropospheric measurements. In the current NASA program, global tropospheric modeling activities include one- and two-dimensional photochemical modeling, a mean-tropospheric photochemical box model, and a three-dimensional chemical/dynamical model to study the global distribution of CO and CH_4. Present chemical-transport models should be used to guide and to set priorities for the selection of airborne missions in the NASA implementation strategy for the global-scale and synoptic-regional-scale studies of the troposphere. The field measurements, in turn, will be important in refining current concepts in the chemical-transport models through verification of the dominant mechanisms and chains active in the troposphere. In this iteration of field measurements and mathematical modeling, the foundation will be established for development of predictive models of the global-scale and synoptic-regional-scale troposphere. Ultimately, well-developed predictive models will serve as the basis for selection of scientific investigations for a series of lower atmospheric research satellite missions.

The global-scale models being developed and applied in the tropospheric research program are primarily designed to explain the features of the various chemical budgets. Typically these models contain a detailed description of tropospheric photochemistry, adopt an eddy diffusion approach to transport, and specify meteorological parameters (such as temperature and relative humidity) and physical source functions required by the model. The output of such models is the spatial and temporal distributions of the concentrations of selected tropospheric species and the estimates of the global photochemical sources and sinks of key chemicals.

Because of the large number of species involved in the chemical budgets, fully three-dimensional models are not yet computationally practical. Therefore, it is unlikely that full operational utility of a general circulation model (GCM) containing a detailed chemical component will be realized within the 5-yr purview of this plan. Thus, one- and two-dimensional models are likely to continue to be relied on.

Most effort to date in the Air Quality Program on global modeling has been placed on the development and use of box and one-dimensional models. Box models represent the simplest approach to global modeling and are capable of describing the gross features of tropospheric chemical structure. These models have generally been successful in representing average background levels of tropospheric species, at least for those few species for which such a level may be inferred from observations. Because of its simplicity, a box model is particularly useful for carrying out a wide range of sensitivity studies and for investigating the response of the troposphere to assumed perturbations.

Such models cannot, of course, represent any of the spatial structure observed for tropospheric species. The next step in the model hierarchy is the one-dimensional model, which may be either a zonally and meridionally averaged vertical model or a zonally and vertically averaged latitude-dependent model. Several results have been obtained with one-dimensional vertical models, which are particularly suited to studying the effects of stratospheric and surface fluxes on tropospheric composition. These models are similar in concept and structure to the radiative-convective models used in climate studies. It may be anticipated that many of the techniques presently employed in radiative-convective models will be incorporated in the vertical tropospheric models permitting study of the coupling between chemical perturbations and their climatic consequences to a degree not yet realized.

Latitude-dependent models are also currently being used. Such models are particularly suited to studying the variation of tropospheric chemical structure resulting from the latitudinal variation of physical sources and sinks and variation of meteorological inputs such as temperature and relative humidity. These models are similar in concept and structure to the energy-balance climate models used in climate research. It may again be anticipated that the techniques presently used in energy-balance climate models will be incorporated in latitude-dependent chemical models, leading to a more detailed understanding of the role of chemical perturbations in climate.

The two-dimensional diagnostic model which includes latitudinal and vertical variations has also proved useful. In this model, empirical data are used to specify the distributions of long-lived species, such as O_3, CO, and CH_4; the concentrations of short-lived species, such as free radicals, are calculated using assumptions of photochemical equilibrium. Although these models do not include transport and are not therefore predictive, they provide detailed information concerning the global distribution of free radicals, such as OH, and state-of-the-art estimates of global photochemical source and sink strengths of key chemicals, such as CO and CH_3CCl_3.

The present generation of models being used in the Air Quality Program is generally capable of representing qualitatively the average concentration of trace species such as ozone, hydroxyl radical, nitric acid, and odd nitrogen ($NO + NO_2$). In judging the accuracy of model predictions, it is important to keep in mind that the results depend on several poorly known factors, such as the ozone flux from the stratosphere, several physical source strengths, and a large number of chemical rate constants of various reliabilities. Nonetheless, present models are proving useful in addressing a number of important tropospheric problems, among which are the relative roles of transport and photochemistry in establishing the tropospheric ozone distribution, the role of NMHC in the carbon monoxide budget, the role of odd nitrogen in other elemental tropospheric budgets, and the perturbations to tropospheric chemical budgets resulting from human activities.

It is anticipated that future developments in the Air Quality Program on global modeling will proceed along two lines. First, an increasing degree of sophistication will be incorporated into the treatment of physical and biological processes in current models. Second, present models will be extended to higher dimensionality and the spatial and temporal variability of the troposphere will be investigated in increasing detail.

An example of the first type of development is the description of the sources of biologically produced gases as functions of the meteorological parameters (e.g., temperature, relative humidity, soil moisture, and precipitation) on which they might depend. The coupling of aeronomic and meteorological processes within a single model would then permit a description of feedback loops within perturbation models. This coupling is lacking in the present model generation.

The second type of development encompasses the construction of models which include the large horizontal heterogeneity of the tropospheric photochemical system. As discussed previously, measurements imply that the troposphere may be described by a series of concentration regions or domains coupled together by transport processes. Each domain is characterized by a common set of chemical source and sink strengths, terrain, vegetation, and meteorological parameters, and includes polluted as well as remote regions. It is likely that future global photochemical models of the troposphere will attempt to construct compartmentalized models which treat the various concentration domains as dictated by observations. Even though these models may initially be diagnostic in nature and will not treat transport (like the diagnostic two-dimensional model), ultimately semiempirical relationships will have to be developed to parameterize transport. These compartmentalized models, by avoiding the process of averaging over the large longitudinal chemical variability of the troposphere, will be truly global in nature and will have sufficient detail to incorporate data gathered in aircraft and satellite measurement missions.

The relationship of the proposed program to other modeling programs is as follows:

(1) The NASA Climate Plan: NASA climate modeling is primarily directed towards study of the energy and water budgets of the Earth and of the physical properties of aerosols. Modeling of the chemical budgets of the Earth in the Air Quality Program provides a natural complement to the climate-modeling effort since it is through perturbations to the chemical budgets that man may influence climate in the first place. The NASA Climate Plan places major emphasis on the development of general circulation models (GCM's) for climate study. As noted earlier, modeling within the program is concerned with finding the best techniques for incorporating the chemical continuity equations into global circulation-type models. Advances in climate modeling should thus prove of direct benefit to this aspect of the Air Quality Program.

Secondary, but still important, emphasis in the NASA Climate Plan is given to the development of statistical dynamical models (SDM's). The close relationship between two types of SDM's (radiative-convective and energy-balance climate models) and models in use in the Air Quality Program was described earlier. The concomitant development of these modeling efforts should result in a merging of techniques that will permit substantial advances in our understanding of the natural tropospheric chemical system and the perturbations to which it may be subject.

(2) The National Oceanic and Atmospheric Administration (NOAA) Climate Plan: NOAA climate modeling gives major emphasis to study of the CO_2 budget with other efforts directed towards modeling the radiative effects of trace gases. Carbon dioxide, as a chemically inert species, has not received attention in the Air Quality Program on modeling. It is conceivable, however, that if long-term perturbations to other chemical species are to be considered, then incorporation of a CO_2 budget in such a model will prove desirable. This permits projection of future values of climatic variables, such as temperature, to which chemical perturbations might be sensitive.

As noted previously, modeling the radiative effects of trace species is likely to be a component of future air-quality research, and NOAA efforts in this area should be followed.

(3) National Center for Atmospheric Research (NCAR) and University programs: Some aspects of the modeling program being carried out at NCAR and several universities are closely related to the air-quality modeling effort. The problems of the tropospheric ozone budget, carbon monoxide sources and sinks,

and the effects of NO_x have been addressed by these groups. It is thus essential that close familiarity with the results and direction of NCAR and university efforts be maintained.

3.4.2 Assimilation of Remote Sensing Data Into Regional Air Pollution Models

The development of mathematical models for the behavior of air pollutants on regional scales has been a subject of increased interest in the last several years. Because of the extensive commitment of the EPA to the development and application of such models, NASA does not plan to support activities in this phase of regional air pollution. A number of measurement programs, several based on remote sensing, are proposed to further our understanding of the chemical and physical processes in regional air pollution. The measurements made in such programs must then be assimilated into and compared with model predictions to gain the desired understanding. The general problem of the assimilation of remotely sensed and in situ data into regional air pollution models has not received substantial attention. Therefore, because of its central importance to the analysis of data from the measurement programs, the development of theory applicable to the assimilation of data into regional-scale models should represent the principal NASA thrust in the area of regional air pollution modeling.

Regional air pollution models are virtually always based on segmenting the region into an array of cells for the purpose of numerically solving the differential equations governing the spatial-temporal distribution of the species concentrations. Since the smallest spatial resolution attainable is that corresponding to the grid cell size, the concentrations predicted by such models represent values averaged over the volume of each cell. The characteristic spatial scale of the measurements, whether remote or in situ, never corresponds with that of the concentrations predicted by the models. Therefore, it is necessary to reconcile the data and predictions with respect to spatial scale before the data can be assimilated into or compared with model predictions. Similar problems may arise with respect to temporal discrepancies between the scales of data and predictions. Frequently, the temporal resolution of model predictions can be made as fine as desired, although this may lead to excessive computational requirements.

Let $c_i(x,y,z,t)$ denote the true, instantaneous concentration of species i at location (x,y,z) and time t. A stationary, in situ sensor at point (x,y,z) will measure this concentration, perhaps corrupted by experimental error ε_i. Thus, the reported concentration is

$$c_{i,s}(x,y,z,t) = c_i(x,y,z,t) + \varepsilon_{i,s}$$

A remote sensor will generally measure the average concentration of species i in a region of x,y,z-space which can be denoted by Ω. If Ω can be located according to its centroid (x_c,y_c,z_c), then the measured average concentration within the region Ω can be denoted by

$$c_{i,r}(x_c,y_c,z_c,t) = \frac{1}{|\Omega|}\iiint_{\Omega} c_i(x,y,z,t)\ dx\ dy\ dz + \varepsilon_{i,r}$$

A regional air pollution model predicts a concentration $c_{i,m}(x_d,y_d,z_d,t)$, the average concentration over a grid cell with dimensions $(\Delta x,\Delta y,\Delta z)$ centered at (x_d,y_d,z_d). The problem of assimilating data and predictions reduces to reconciling $c_{i,s}$ and $c_{i,r}$ with $c_{i,m}$. This problem is complicated by the fact that, because of unavoidable inaccuracies in both model formulation and input parameters, the relationship between the predicted concentration $c_{i,m}(x_d,y_d,z_d,t)$ and the average of the true concentration over the region of size $(\Delta x,\Delta y,\Delta z)$ is unknown. In addition, models predict the mean concentration, whereas c_i is the instantaneous concentration.

In summary, to enable the effective evaluation of remote sensing data by means of mathematical models, a theoretical program aimed at assessing the sensitivity of both predictions and data to spatial resolution should be undertaken. It is anticipated that the program will involve the use of one of the available regional models that offers the capability of three-dimensional spatial resolution and detailed treatment of atmospheric chemical processes.

3.5 LABORATORY MEASUREMENTS

Laboratory measurements play a significant role in the NASA Tropospheric Research Program Plan in three major areas: (1) Supporting the development of new remote and in situ trace-gas and aerosol instrumentation; (2) supporting the further development of existing atmospheric sensors, particularly as related to improving existing calibration techniques; and (3) determining rate constants for atmospheric elementary reactions as part of an overall effort to improve our understanding of multistep atmospheric processes.

3.5.1 Laboratory Measurements Required for New Instrument Development

Perhaps the single most important type of laboratory measurement that will be required for the development of future remote and in situ atmospheric monitoring instrumentation will be that involving spectroscopic investigations. The spectral regions of interest will cover the microwave, far infrared, mid infrared, near infrared, visible, and ultraviolet. Of specific interest will be the following types of measurements:

(1) Line positions: These are needed to identify the molecular species and establish a degree of specificity. The line-position accuracy should be about 100 MHz (0.003 cm^{-1}) in the microwave regions, 10 MHz (0.0003 cm^{-1}) in the infrared, and approximately 3000 MHz (0.1 cm^{-1}) in the ultraviolet.

(2) Line strengths: These are needed to establish system sensitivity and for calibration. The line strengths should be measured to an accuracy of 5 percent or greater over a range of appropriate temperatures.

(3) Line widths: These are directly related to ultimate sensitivity and are useful for obtaining vertical profile information because of the pressure dependence. The pressure broadening coefficients should be measured to allow estimates to be made of sensitivity and the potential for vertical profiling.

(4) Quenching cross sections: These are important for ultraviolet-fluorescence measurement techniques. These measurements should be performed at a range of temperatures and pressures because of the strong impact of these parameters on the fluorescent signal.

3.5.2 Laboratory Measurements Required To Support Existing Atmospheric Instrumentation

A fundamental question which is raised concerning all ongoing atmospheric monitoring devices is that of their accuracy. Questions of accuracy, in turn, quickly revert back to questions about calibration techniques, and the answers to these questions typically are based on a broad spectrum of laboratory measurements. Presented in this section are several of the more important types of measurements now being used in the calibration of both remote and in situ instrumentation. Also discussed are the future needs of each instrument type. For purposes of clarity, this discussion has been divided into two subsections entitled "In situ sensors" and "Remote sensors."

3.5.2.1 In situ sensors.- Two general approaches have traditionally been used in the calibration of in situ instruments: (1) Fundamental studies of the technique under the controlled conditions of a laboratory environment and (2) interlaboratory comparison studies involving similar instruments from different laboratories or, preferably, other instruments based on totally different operating principles. Calibration studies of the first type have been further subdivided into investigations of basic processes related to establishing calibration standards (e.g., absorption cross sections, quantum yields, quenching cross sections, gas-phase liquid chromatography (GLC) retention times, mass-spectrometer ionization efficiencies, and gas kinetic rate constants) and investigations of fundamental processes designed to define the magnitude of chemical interferences.

Although the calibration of in situ field instrumentation should inherently be more direct (and hence more reliable) than for remote instrumental techniques, in situ devices are still subject to many types of errors. Within the last 3 to 4 years, for example, it has been convincingly demonstrated that even though several different instruments may be put through an interlaboratory comparison that results in similar measured values, significantly different answers frequently are generated under field sampling conditions. Variable temperatures, high humidities, dust, and unknown interfering chemical compounds occurring naturally in the atmosphere (or those produced by the sampling platform) frequently combine to produce systematic errors of unknown magnitude under field conditions. Thus, it is recommended that NASA give a high priority not only to calibration studies of types (1) and (2), but also strongly support field intercomparison investigations. In particular it is recommended that any large field sampling program have designed into it a well-conceived calibration program.

3.5.2.2 Remote sensors.- The measurement of atmospheric trace constituents imposes severe accuracy and precision constraints on experimental test and evaluation instrumentation and procedures for remote sensing instruments. This is due to the small signal changes (typically 1 part in 10^4 to 10^6) introduced by the absorption characteristics of the gases of interest, the variability of spectrally interfering gases (i.e., H_2O and O_3), and the variability of background "scene" effects caused by variations in the emissivity or reflectivity of the Earth.

Current techniques for calibrating remote sensors are limited to laboratory measurements of the radiometric response of laboratory radiation sources (i.e., 300 K to 1100 K), with analytical extrapolation of the radiometric data to temperatures corresponding to natural sources of radiation (i.e., Earth/atmosphere systems and the Sun). These calibration measurements are static in nature and do not properly assess the dynamic response of the sensor to variability in the ground emissivity or reflectivity. Responses to spectral signatures of gases to be measured by differential absorption are limited to short path lengths with corrections required for the presence of cell windows. For relatively stable gases, atmospheric conditions are simulated by using elevated pressures for the gases to be measured and dry nitrogen to simulate an atmospheric air mixture. Uncertainties in foreign and self-gas broadening coefficients provide a degree of radiometric inaccuracy in the sensor response. For unstable gases requiring chemically reacting flow chambers, tropospheric conditions of pressure and temperature cannot be simulated to any degree of confidence and could lead to a high degree of calibration inaccuracy.

Current techniques for calibrating remote sensors depend upon limited calibration information and a high degree of analysis to extrapolate from the laboratory measurements to the expected atmospheric conditions of concentration, temperature, pressure, and radiometric input to the sensor. Instrument performance and accuracy of the data-reduction process are severely limited by the assumptions and uncertainties in the analytical procedures. Correlative measurements with in situ sensors or other remote sensing instruments are required for intercomparison of data. This requires scheduling with a network of sensors and expenditure of correlative testing funds. Inaccuracies of correlative measurements often do not identify the source of inaccuracy in the remote sensor because of either a lack of precision in the remote sensor itself or a lack of precision and accuracy in both the in situ and remote sensing instruments.

In order to improve the calibration of remote sensors, a dual calibration strategy should be developed to improve laboratory calibration data for remote sensors and to improve both the precision and accuracy of in situ instruments used in correlative-data studies. Recommendations for a calibration strategy for remote sensors include the following:

1. Develop a calibration facility for remote sensors with standardized calibration radiation sources; absorption cells with concentration mixture, pressure and thermal control; and chamber monitoring instrumentation with formatting, processing, recording, and display functions. This facility should satisfy calibration requirements to obtain absolute radiant-intensity calibrations and simulation of radiance variability due to ground emissivity and reflectivity changes to determine realistic dynamic response of remote sensors.

2. Develop an accurate, updated atlas of spectroscopic parameters for tropospheric gases (i.e., line strengths, line positions, and broadening coefficients) to improve the analytical studies required for remote sensing calibrations.

3. Develop gas cell chamber capability to simulate conditions in the natural troposphere for the purposes of determining the effects of interfering gases and variations in temperature and pressure.

4. Develop ground-based long-path solar or long-path horizontal measurements with spectral scanning and high-spectral-resolution sensors to determine the existence of atmospheric transmission windows. Systematic data from these measurements should provide the data base for updating the atlas of spectroscopic parameters.

3.5.3 Laboratory Measurements Related to Studies of Fundamental Atmospheric Processes

3.5.3.1 Homogeneous gas phase.- At the present time, at least two major homogeneous-gas-phase tropospheric chemical problems can be identified as being in need of further laboratory study. The first of these involves the elucidation of the methane and higher molecular weight hydrocarbon degradation cycle; the second is concerned with the need for new rate-constant measurements of several key tropospheric elementary processes under atmospheric conditions of pressure and composition. As to the first problem, it is recognized that although the degradation cycles of both nonmethane hydrocarbons (NMHC) and methane may be of equal importance to our understanding of tropospheric chemistry, only minimal support for kinetic studies of NMHC species will be required from the NASA tropospheric program, since EPA is providing significant support for studies of these species. Instead, the major emphasis should be placed on methane studies. The NH_3 degradation cycle is also poorly understood, but the lack of importance of this cycle to either the NO_x or the NH_3 tropospheric budgets does not seem to justify assigning it a high priority at this time.

In the text that follows, current laboratory research needs related to the methane degradation cycle as well as the requirements for studying several pivotal elementary reactions under atmospheric conditions of pressure and composition, are discussed. Also briefly mentioned are the laboratory needs of at least one potential new area of tropospheric chemistry.

Methane degradation chemistry: As outlined in section 2.2 of this document, methane represents the single largest biospheric source of hydrocarbons. As an infrared-sensitive molecule and a major source of atmospheric CO, H_2CO, and other possible tropospheric molecules (i.e., CH_3OH, CH_3OOH, and HCO_2H), its importance to tropospheric chemistry is quite significant. Of particular interest is the role that this species is believed to play in modulating the levels of the free-radical species HO_2 and OH. Mechanisms for the degradation of CH_4, producing CO as the final product, can be written to represent either a net sink or a net source of HO_x radicals. At present, only 4 steps of possibly a 10- to 15-step mechanism are reasonably well understood in terms of their kinetics, i.e.,

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2$$

$$H_2CO + h\nu \rightarrow CO + H_2$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

Among the many possible degradation steps which need further investigation are the following:

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$$

$$CH_3O_2H + OH \bullet CH_3O_2 + H_2O$$

$$CH_3O_2H + OH \rightarrow CH_2O_2H + H_2O$$

$$CH_3O_2H + h\nu \rightarrow CH_3O + OH$$

$$CH_3O + OH \rightarrow H_2CO + H_2O$$

$$CH_3O + O_2 \rightarrow H_2CO + HO_2$$

$$CH_3O + HO_2 \rightarrow CH_3OH + O_2$$

Since a complete understanding of the methane cycle will be a prerequisite to a complete understanding of tropospheric photochemistry, a high priority should be placed on further studies of this system.

High-pressure/atmospheric-composition studies: An examination of the gas-kinetic literature reveals that a substantial number of those absolute rate constants k reported for atmospheric reactions have been measured only under conditions of low pressure. An even larger number of rate constants have been measured under conditions not representative of natural tropospheric-composition conditions, especially concerning the levels of O_2 and H_2O. More recently, kinetic studies on the CO-OH system and on the reactions of HO_2 have indicated that O_2 and H_2O can, in some instances, have a significant influence on the measured k values. In the case of the CO-OH system, several studies using high pressures of He and Ar resulted in rate constants that showed no evidence of a pressure dependence. Initial experiments with high pressures of N_2, on the other hand, showed an enhancement of the rate constant for this reaction of a factor of almost two. More detailed studies with ultraclean N_2 (minus any traces of O_2) did not show a pressure effect. These same investigations also have indicated that as little as 1 torr of O_2 (1.0 torr = 133.3 Pa) in the presence of high pressures of N_2 or other gases can have a significant impact on the measured rate constant for the CO-OH system. It is now believed that O_2 affects the stability of an initially formed HOCO complex, resulting in most of that complex decaying into CO_2 and HO_2 directly. Based on these observations, it seems unlikely that the above system is unique. In fact, any gas-phase elementary reaction that involves complex formation and that also may involve molecular oxygen interacting with one or more departing reaction fragments should be reexamined in terms of possible secondary kinetic effects.

The influence of water vapor on previously measured rate constants has again only recently been the subject of kinetic investigations. In this case, the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

was examined over a wide range of H_2O pressures. The results showed that the apparent rate constant was enhanced by up to a factor of three when the H_2O level was varied from 0 to 20 torr. This enhancement was attributed to the formation of an $HO_2 \cdot H_2O$ complex, which was reported to react nearly two orders of magnitude faster with a second HO_2 molecule than with a noncomplexed HO_2 species. If this hypothesis is indeed correct, it seems reasonable that other HO_2 reactions may be influenced by the absolute water level present in the atmosphere. It also raises the question of whether the rate constants for certain OH reactions could be influenced by atmospheric H_2O.

At this time, the evidence supporting the importance of H_2O-complexed free-radical species is still very limited. Even so, the implications of these data are sufficiently great to justify a very systematic examination of all free-radical species that might have a high probability of complexing with H_2O. Among the more likely candidates are HO, HO_2, HSO_3, and HSO_5.

Potentially important new chemistry: As an example of potentially important new processes, consider the tropospheric chemistry of iodine. The source could be CH_3I or possibly other organic and inorganic iodine species from the ocean. The fact that iodine compounds are both highly photosensitive and thermally unstable suggests that iodine may undergo major recycling between the oceans and the atmosphere. Recent modeling calculations further suggest that the marine iodine photochemical cycle may have a significant impact on NO_x-O_3-HO_x photochemistry. The reliability of these calculations, however, is strongly dependent on several key rate constants, all of which are in need of extensive investigation. The troposphere may hold many such chemical surprises, and new chemical schemes should be studied when models or measurements suggest that they are important.

3.5.3.2 Gas-to-particle conversion.- A fundamental problem in virtually all aspects of atmospheric science is understanding the processes by which airborne particles form and evolve. Atmospheric particles, or aerosols, may be emitted into the atmosphere directly from sources (both natural and anthropogenic) or may be formed in situ by the nucleation of vapor molecules. Once emitted or formed, the particles may grow through coagulation with other particles or through scavenging of vapor molecules. The rate of coagulation is controlled by the sizes of the two particles and the properties of the particles and of the medium. The efficiency of scavenging of vapor molecules by preexisting particles is governed by the particle's size, by the chemical nature of the particles and molecules through their effect on the transport properties of the molecules in air, and on the chemical reactions which occur when the molecule encounters the particle. From the point of view of assessing the climatic and human-health effects of atmospheric aerosols, it is important to be able to measure and predict their size and chemical-composition distribution. The size and composition of atmospheric aerosols is strongly dependent on their mode of formation and growth.

The competitive processes involved in gas-to-particle conversion are depicted in figure 18. Vapor molecules, or monomers, may collide to produce a dimer which may then collide with another vapor molecule to produce a trimer, the process leading eventually to a stable molecular cluster and the entire process being referred to as nucleation. All throughout the process in which molecular clusters are being formed, monomers and molecular clusters may be scavenged by other particles, both by molecular clusters and by much larger particles. Prediction of the rate of gas-to-particle conversion requires that one be able to simulate the detailed kinetic processes depicted in figure 18. Unfortunately, many of the thermodynamic and kinetic parameters required for such simulation are not known for typical atmospheric aerosols. Laboratory programs are needed to obtain such parameters.

An atmospheric particle can be considered to be a multicomponent, multiphase system. Knowledge of the thermodynamic properties of the particles is important in predicting equilibrium size and composition under varying atmospheric conditions. Even when particle composition is known, predicting the thermodynamic properties is difficult because the particles are multicomponent, nonideal solutions or nonideal solid-fluid mixtures. Knowledge of thermodynamic properties is also important in predicting kinetic behavior such as rates of coagulation, growth, and evaporation.

The rate of collision of two inert spherical particles resulting from processes such as Brownian motion or turbulent diffusion can be predicted precisely. Coagulation rates for nonspherical particles or for those having nonnegligible interparticle forces are determined with less accuracy. Once collision occurs, sticking coefficients are frequently assumed to be unity for lack of better information. Particle composition and the associated thermodynamic properties thus influence coagulation rates.

New stable particle formation occurs when growing molecular clusters reach a critical size at which the cluster is thermodynamically stable. As noted previously, the molecular clusters must continually compete with each other and with preexisting particles for the available vapor molecules (monomer). Class-

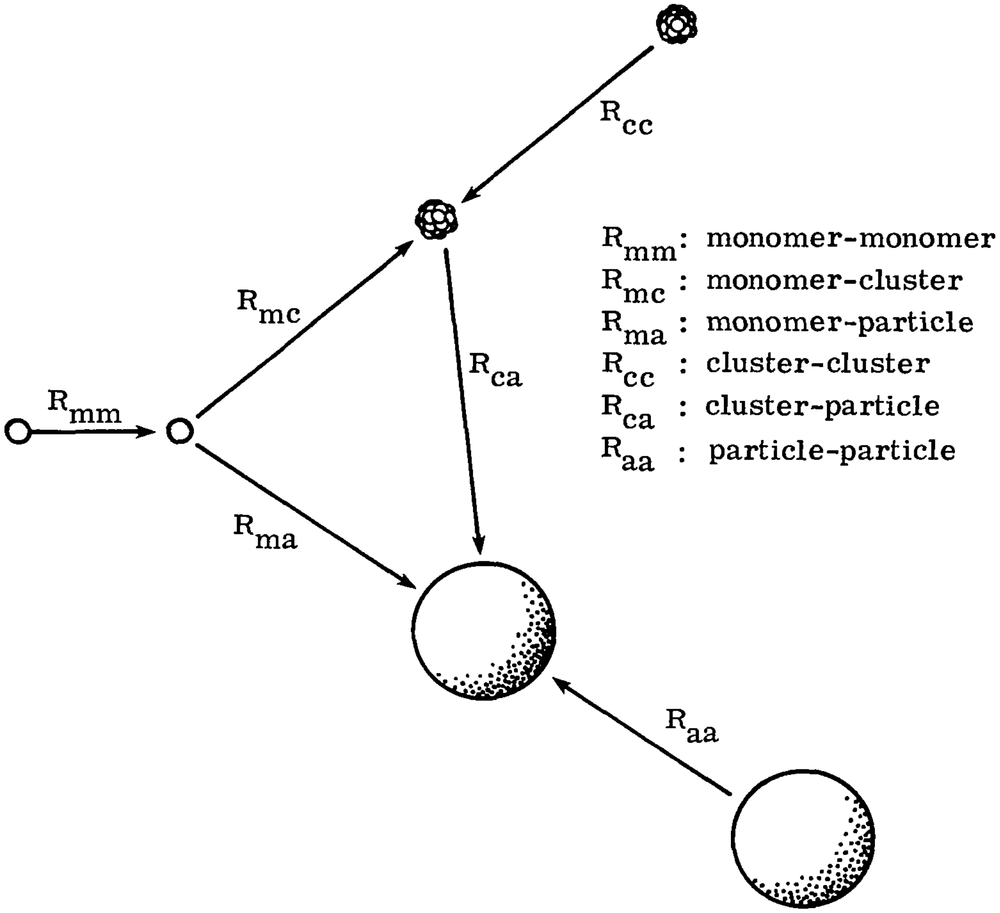

Figure 18.- Competitive processes involved in gas-to-particle conversion.

ical homogeneous-nucleation theory predicts the rate of formation of stable molecular clusters when cluster-cluster coagulation can be neglected and when no preexisting particles are present.

The nucleation rate, the number of stable particles formed per centimeter cubed per second from the supersaturated vapor, is related to the average number density of clusters c_n which, in turn, is related to the free energy ΔG_n necessary to form the particle from the vapor phase,

$$c_n \sim \exp(-\Delta G_n/kT) \tag{1}$$

where k is Boltzmann's constant and T is absolute temperature. The detailed form of ΔG_n and thus of the cluster numbers c_n is controversial.

For very large clusters, ΔG_n will consist mainly of a surface term $4\pi r^2\gamma$, where r is the droplet radius and γ is the surface tension. Thus,

$$c_n \approx \exp(-An^{\zeta}) \tag{2}$$

where A is a constant, n is the number of particles, and $\zeta = 2/3$ in three dimensions such that $An^{\zeta} = 4\pi r^2\gamma/kT$. Several questions remain unanswered:

(1) How large must the particles be in order to satisfy the approximations inherent in equation (2)?

(2) How important is the cluster-cluster interaction neglected in equation (2)?

(3) How important is the monomer scavenging by preexisting particles neglected in equation (2)?

Assessment of these questions suggests carefully designed laboratory experiments in which single- and multicomponent nucleation is carried out both in the absence and presence of preexisting nuclei. Measurement of particle-size distributions down to cluster sizes is a desirable but extremely difficult task. At the same time, thermodynamic properties, such as vapor pressures, densities, and surface tensions, should be measured for mixtures typical of atmospheric particles.

3.6 TECHNOLOGY DEVELOPMENT

3.6.1 Remote Sensors

In this section, a summary of the current status of remote sensing technology in the NASA Air Quality Program is presented. This summary was compiled by identifying remote sensing systems sponsored by the Air Quality Program within the Office of Space and Terrestrial Applications. A major goal of the program is to develop remote sensors from space, aircraft, balloon, and ground-based platforms to address major scientific questions related to chemical and transport properties of the troposphere. This involves development of remote sensors to measure the vertical distributions and total vertical concentrations of molecular species, aerosols, and related meteorological parameters. Development of remote sensing systems generally involves a laboratory calibration and testing phase, technology demonstration from ground-based and airborne platforms, and, ultimately, participation in scientific investigations from space, airborne, or ground-based platforms. In the current state of development of remote sensors, several active and passive systems have matured to the stage where they are being used in or proposed for field-measurement programs from airborne and ground-based platforms to measure gaseous species (e.g., CO, O_3, SO_2, H_2O, NH_3, and NO_2), tropospheric aerosols, mixing-layer heights, and optical-extinction coefficients. Future developments in remote sensing systems should extend this capability to other molecular species with improved sensitivity and vertical resolution.

One of these programs, Measurement of Air Pollution from Satellites (MAPS), which uses a nondispersive gas-filter correlation instrument, is currently an approved payload for an early Space Shuttle flight. The objective of the experiment is to measure the interhemispheric mixing ratio of carbon monoxide in the global troposphere. The aircraft version of the MAPS instrument has been used in studies to measure the dispersion of urban plumes over Lake Michigan from the Chicago area, and recently was used in the Monsoon Experiment (MONEX) to measure the transport of carbon monoxide in the Indian Ocean region during the monsoon season.

Earth-observation satellite systems originally developed for Earth resource and meteorological investigations are currently being studied by NASA and the scientific community for detection and measurement of elevated pollution episodes and total aerosol loading in the troposphere. A measurement strategy is currently emerging in which a combination of satellite observations, airborne flights, and ground-based networks of in situ and remote sensors play complementary roles in providing measurements of gaseous and aerosol species with wide-area coverage, high sensitivity, and high vertical resolution from the ground to the troposphere. One example of a requirement that has emerged during the past several years involves effects of sulfur pollution on a regional or mesospheric scale.

Even though a network of ground-based and aircraft sensors can provide accurate local measurements of species concentrations, such measurements have limited utility for tracking and evaluating episodes of regional dimensions, especially in formative stages. Earth-observation satellites presently using visible and infrared imagery and ultimately using species-sensitive instruments complement these measurements by providing global- and regional-scale coverage, identifying regional pollution episodes in formative stages, and tracking the episodes as they migrate. The combination of satellite observations, aircraft flights, and ground-based sensors can provide valuable information for the design and implementation of environmental quality control strategies and for improved scientific understanding of tropospheric processes.

In this section, the current status of four remote sensing technologies within the NASA program are reviewed, including Earth-observation satellite systems, passive remote sensing systems, active remote sensing systems for application to tropospheric investigations, and remote sensing of aerosols. Comments on limitations of the current status of these systems are presented as well as the need to implement new technology to fully realize the potential of these systems for global monitoring.

3.6.1.1 Earth-observation satellite systems.- NASA has developed a number of Earth-observation satellite systems for various meteorological and resource applications. Table 6 is a summary of these systems which have been developed for specific applications. None of the satellite systems listed in table 6 were specifically designed to detect or measure aerosol loadings in the troposphere. In fact, a great deal of effort has been expended to minimize the effects of atmospheric haze, especially in the Landsat systems. An increasing number of investigators have noted that certain types of air pollution patterns can be detected in satellite imagery. The instruments in table 6 are generally classified as Visible/Infrared Spectroradiometers and operate in selected spectral bands ranging from the visible (0.45-0.70 μm) through the infrared (≥0.70 μm). Spatial resolutions of the instruments range from 0.03 km to 16 km. Table 6 contains, for each instrument, the spectral coverage, spatial resolution, satel-

TABLE 6.- EARTH OBSERVATIONS SATELLITE SYSTEMS

Instruments	Spectral coverage, µm	Spatial resolution, km	Satellite system	Orbit	Launch schedule	Applications/objective
VISSR	IR images (10.50 to 12.60) VIS images (0.55 to 0.75) VIS images (0.55 to 0.75) VIS images (0.55 to 0.75)	8 4 2 1 and 2	SMS-1, 2, 3 GOES-2, 3	Geosynchronous	SMS-1 5/74 SMS-2 2/75 SMS-3 10/75 GOES-2 6/77 GOES-3 6/78	Cloud images Sea surface temperature High-resolution images
VAS	Same as VISSR plus IR (3.73 to 8.00) IR (8.00 to 14.70)	16	GOES D/E/F (NOAA Reimbursable)	Geosynchronous	D 7/80 E 2/81 F 7/83	Atmospheric sounding Sea surface temperature Cloud top temperatures Meteorological high resolution Earth images
AVHRR	VIS images (0.55 to 0.70) Near-IR images (0.73 to 0.90) IR images (3.55 to 3.93) IR images (10.50 to 11.50)	1.1 1.1 1.1 1.1 1.1	TIROS N NOAA A Thru G	Sun synchronous	TIROS N 10/78 NOAA A 4/79 B* 79 C* 80 D* 81 E* 82 F* 83 G* 84	Cloud images Sea surface temperature High-resolution images
MSS	VIS (0.50 to 0.60) VIS (0.60 to 0.70) IR (0.70 to 0.80) IR (0.80 to 1.10)	0.08	Landsat 1 and 2	Sun synchronous 910 km	1 7/72 to 1/78 2 1/75	Land use Water resources Agricultural survey
RBV	Blue-green (0.48 to 0.58) Orange-red (0.58 to 0.68) Near IR (0.69 to 0.83)					
MSS	Same as Landsat 1 and 2 with additional MSS channel	0.080	Landsat 3	Sun synchronous 917 km	3/78	Land use Water resources Agricultural survey
RBV	IR (10.40 to 12.60)	.237				
Thematic mapper	VIS (0.45 to 0.52) VIS (0.52 to 0.60) VIS (0.63 to 0.69) IR (1.55 to 1.75) IR (1.55 to 1.75) IR (10.40 to 12.50)	0.03 .03 .03 .03 .03 .12	Landsat D	Sun synchronous	3rd quarter 1981	Land use Water resources Agricultural survey

*As needed.

lite system, orbit, launch schedule, and applications/objectives of each satellite system. Several systems, such as the Landsat type, represent a continuing series of launches. Further information for each satellite system can be found in references 5 to 7.

NASA is currently sponsoring research to further study the usefulness of satellite imagery in assessing regional-scale pollution episodes. The objective of one study is to provide the capability to quantitatively monitor tropospheric aerosols over land masses by evaluating the relationship between upwelling near-infrared radiance over inland bodies of water and the atmospheric-aerosol thickness. Raw data tapes from the Landsat 2 Multispectral Scanner (MSS) are being used. This study focuses on five inland sites for which ground-truth data were obtained in a previous Landsat study. The objective of a second study is to perform a comparative analysis of satellite imagery and ground-based visibility and to obtain aerosol measurements for selected periods encompassing significant sulfate-pollution episodes in the Northeastern United States. The Geostationary Operational Environmental Satellite (GOES) visible-band images (see table 6) were used to observe a high-sulfate episode which formed in the Ohio River Basin on July 21, 1978. Results of these studies are presented in reference 8. The current studies demonstrate high potential for qualitative identification of elevated pollution episodes over land for high-sulfate episodes and quantitative measurements of aerosol loadings using inland bodies of water. However, several problems still remain in discriminating aerosol loadings and elevated haze from clouds and in detecting low levels of haze, especially for widely varying ground albedos. Improvement of satellite observation systems for haze and aerosol measurements will require continued analysis of existing satellite imagery, simulations of upwelling radiance at various wavelengths and for various instrument bandpasses, and development of new satellite systems specifically designed to determine the concentrations of minor constituents of the troposphere.

3.6.1.2 Passive remote sensing technology.- The feasibility of utilizing passive remote sensors to measure tropospheric constituents from aircraft and space platforms was discussed in a study for NASA performed in 1969 (ref. 9). One of the major conclusions of the study was that the infrared region of the spectrum is very important for remote sensing of tropospheric species because it contains characteristic spectral features and because two measurement methods can be used - upwelling Earth-scattered sunlight can be detected in the 3- to 5-μm window and upwelling thermal radiation can be detected in the 8- to 14-μm window. In the first method, measurements are restricted to daylight portions of the globe; however, the dependence of the measurement on accurate knowledge of the atmospheric temperature profile is not as severe as it is at longer wavelengths. In the years following this study, various passive instruments and associated software systems have undergone laboratory testing and aircraft flight tests. As a result, a passive CO measurement instrument (MAPS) is approved to fly on the second NASA Shuttle flight.

A summary of the current passive remote sensors under development and in use for remote sensing within the NASA Air Quality Program is given in table 7. The instruments are categorized generically into four categories: Gas filter correlation (GFC), Interferometry, Infrared heterodyne radiometry, and Spectroradiometry. Instrument characteristics, including detectable species, spectral

TABLE 7.- PASSIVE REMOTE SENSORS

Category and instruments	Species	Spectral coverage, μm	Field of view	Vertical resolution, km	Viewing mode	Platform	Current status
Gas filter correlation (GFC):							
AC/MAPS	CO, CH_4 Extendable to other gases	4.52 to 4.80	7.5°	<5	Thermal IR	A/C	A/C operational
OFT MAPS (Shuttle)	CO Extendable to other gases	4.52 to 4.80	4.5°	<5	Thermal IR	Shuttle	CY 80 flight test
PMR	CH_4, CO, N_2O, NH_3 SO_2	4.52 to 4.80 8.00 to 11.00	4.5°	<5	Thermal IR	A/C	Proposed engineering model development
DCR	CH_4, NH_3, CO, N_2O, HCl, NO_2, SO_2, (NMHC)	4.00 to 9.00	2° to 7°	<5	Solar reflected	A/C	Proposed A/C development
Interferometry:							
COPE	CO, CH_4	2.35	7°	Total burden	Solar reflected	A/C	A/C operational
CIMATS	NH_3, H_2O, N_2O, CO, CH_4 CO, SO_2	2.00 to 2.40 4.00 to 9.00	2° to 7°	<5	Solar reflected Thermal IR	A/C	Engineering model developed
HSI	Spectrally scanning	1.00 to 6.00	2°	Total burden	Direct solar	Balloon/gnd-based	Balloon/gnd-based operational
Infrared heterodyne radiometry:							
IHR	O_3, NH_3	9.00 to 12.00 (Discrete steps with CO_2 laser)	0.25 mrad	<5	Direct solar	A/C	A/C gnd-based operational
					Thermal IR	A/C	Requires technology development in photomixer quantum efficiency
LHS	Spectral coverage (continuous)	7.50 to 13.00	0.25 mrad	<5	Direct solar	Gnd-based	Laboratory engineering model
Spectroradiometry:							
SBUV-TOMS	O_3, 12 selected channels	0.25 to 0.34	3°	Total burden	Scanner, solar reflected (UV)	Nimbus 3 Nimbus 4 Nimbus 7	Satellite operational
MOPS	SO_2, O_3, NO_2	0.30 to 0.60	Multispectral imaging	Total burden (1 ppm-m)	Direct solar nadir	A/C	A/C operational

coverage, field of view, and vertical resolution, are given. Three "viewing modes" are delineated, including the thermal IR (≧4.5 μm), solar reflected (2.0 to 4.5 μm), and direct solar (3.0 to 15.0 μm). Although the latter viewing mode is only applicable from a ground-based platform for the troposphere, it has been included because there are significant scientific investigations involving well-mixed gases in which selected geographical measurements would provide significant measurements for utilization by current photochemical models. An example of this type of investigation is the measurement of tropospheric ammonia to determine its seasonal and diurnal variations for selected land masses such as marshlands, agricultural terrain, and deserts. Another important application of this viewing mode for the troposphere is to utilize spectrally scanning instruments, such as the Michelson type, to obtain high-resolution spectra of tropospheric molecules at periodic intervals over extended periods of time to serve as sentinel measurements of new tropospheric species, and to obtain a long-term data base of well-known tropospheric species.

In general, the generic classes listed in table 7 represent the four major technologies for development of passive remote sensors for application from space and airborne platforms for tropospheric species. However, within each generic class, other remote sensing systems have been developed within NASA for applications to stratospheric monitoring, and by other organizations for long-path, integrated-burden measurements of tropospheric species. A comprehensive summary of these instruments is beyond the scope of this chapter; however, additional information is given in reference 10.

The remote sensing technology developed or proposed for measurement of stratospheric trace constituents can have important applications in tropospheric trace-gas measurements. For example, the high spectral resolution of stratospheric remote sensing instruments reduces spectral interferences from major tropospheric gases such as H_2O, CO_2, and O_3 when applied to the troposphere. Several technological developments expected to occur in future stratospheric and tropospheric remote sensors include the use of linear and two-dimensional arrays of infrared detectors, cryogenic cooling of optical receivers, charge-coupled detector technology for increased integration time from airborne and space platforms, high quantum efficiency and wideband photomixers for heterodyne detection, and microprocessor technology for higher efficiency data reduction and data analysis.

Technological improvements in the sensitivity of passive remote sensors should expand the number of instruments within each generic class listed in table 7 as potential payloads for airborne and space platforms. For GFC instruments, this could include dispersive correlation techniques, currently used for plume dispersion studies, and SO_2-NO_2 transboundary mass-flux measurements from mobile vans and stationary platforms. For interferometry instruments, this could include the development of Fourier transform spectrometers currently being used on mobile platforms in 1-km integrated-burden measurements of a variety of molecules in the 2.0- to 16.0-μm spectral region and other interferometric spectrally scanning techniques currently being applied from balloon platforms for monitoring the upper atmosphere (e.g., the High Speed Interferometer, HSI).

Despite the potential improvements in sensitivity of passive remote sensors through technological improvements in systems and detector technology, several fundamental limitations in passive sensors will limit the use of these instruments for some of the scientific requirements listed in earlier sections of this report. Passive sensors operating in the thermal IR have an inherent difficulty measuring molecules in the biosphere and are limited to measuring in broad vertical layers of the middle and upper troposphere. The somewhat long integration times required to measure low-concentration species will restrict the horizontal resolution of the measurement to broad geographic areas, and will probably require the use of geostationary satellite platforms to investigate regional areas such as the Northeastern corridor of the United States. Instruments using Earth-scattered sunlight are not sensitive to details of the lower tropospheric temperature profile and are thus capable of near-surface concentration measurements as well as vertical-profile and total-burden measurements. They are, of course, restricted to measurements over sunlit portions of the Earth. The technique is also restricted to detection of species with vibrational-rotational lines in the 3.0- to 5.0-μm region, where for some interesting tropospheric gases only overtone absorption lines are available, limiting the sensitivity of these instruments with respect to those based on thermal emission.

Despite these limitations, passive remote sensors do exhibit several attractive characteristics for a global-measurement strategy for the troposphere: The systems and technologies are the most advanced for satellite missions. The instruments are effective for measuring transport effects on a regional and global scale. Passive instruments using upwelling thermal radiance have the potential for measuring a large number of important tropospheric molecules simultaneously, in the middle and upper troposphere, and should be effective in studying the chemistry of selected chemical chains. Finally, passive instruments using Earth-scattered sunlight have the capability of measuring vertical profiles and total burdens of several major tropospheric gases. A satellite mission incorporating both types of instruments should be investigated in light of the scientific requirements for an early satellite payload dedicated to the lower atmosphere. The feasibility of using both types of remote sensors simultaneously could effectively be tested in an aircraft field-measurement study of the troposphere.

3.6.1.3 Active remote sensing technology.- Considerable effort has been expended by NASA and other organizations during the past decade to develop laser systems for active remote sensing of the atmosphere. The first systems used pulsed ruby lasers to measure aerosols by means of Mie backscattering in a technique known as lidar (light detection and ranging). In the early 1970's, Raman-scattering lidars were used to remotely measure species concentrations. By the mid-1970's, the advent of high-power tunable lasers spurred the development of differential absorption techniques for the measurement of gases, often replacing the less sensitive Raman-scattering technique. Such systems can be used to gather range-resolved information when the power is high enough to use atmospheric backscattered radiation and operate in the differential absorption lidar (DIAL) mode. Otherwise, a fixed target is used to provide column-content information unless some other variable, such as the spectral line-width dependence on atmospheric pressure, can provide altitude information.

Table 8 is a partial survey of the differential absorption laser systems that have been or could be used to measure atmospheric gases. The species listed are primarily those already detected in the atmosphere with laser sys-

TABLE 8.- DIFFERENTIAL ABSORPTION LASER SYSTEMS

Laser	Wavelength region, m	Tunability				Species (variables)	Viewing mode			Platform (a)		
		Discrete	Continuous	Pulsed	cw		Atmospheric backscatter	Topographic scatter	Cooperative reflector	Ground-based	Aircraft	Space Shuttle
Doubled dye, Nd:YAG Pumped	0.28 to 0.32		X	X		SO_2, O_3	X	X	X	A, B	B	C
Dye, Nd:YAG pumped	0.44 to 0.45		X	X		NO_2	X	X	X	A, B	C	D
Dye, ruby pumped	0.70 to 0.75		X	X		H_2O (p, T)	X	X	X	A (C)	C	D
Stimulated Raman scatter (Nd:YAG pumped)	1 to 3	X		X		H_2O, others	X	X	X	B	C	C
Optical parametric oscillator	1.4 to 3.7		X	X		CH_4, SO_2, CO H_2O, NH_3, H_2S, HC		X X	X X	A, B B	C C	D D
Dye, Nd:YAG mixed	1.4 to 4.4		X	X		Same as preceding		X	X	B	C	D
Color center	1 to 3.5		X		X	H_2O			X	C	D	D
Hydrogen fluoride (HF)	2.8 to 3.4	X		X		HF		X	X	A	C	D
Deuterium fluoride (DF)	2.8 to 3.4	X		X		H_2O, CH_4, HCl, HDO		X	X	A	C	D
Carbon monoxide (CO)	4.7 to 7.5	X		X	X	NO		X	X	A	C	D
Diode	1 to 16		X		X	CO			X	A, B	D	D
Carbon dioxide (CO_2)	8 to 12	X	X	X	X	O_3, NH_3, C_2H_4, H_2O, HC, SF_6, CO_2 (p, T)	X	X	X	A, B	A	C
CO_2 pumped crystals	4 to 6	X	X	X		CO_2	X	X	X	B	C	C
Spin flip Raman	2 to 3 5 to 6 9 to 14		X X X	X X X		NO			X X X	C A C	D C D	D D D

[a]A - Demonstrated B - Under development C - Untested, but considered feasible D - Untested, considered unfeasible

tems. Other species within the tuning ranges of the lasers can be measured as well if the concentrations are high enough, if spectral interference is not an overwhelming problem, and if the laser emits sufficient power at the appropriate wavelengths.

Although an eventual goal is to place lidar systems on Space Shuttle (both the continuous-wave (cw) CO_2 laser and the Nd:YAG laser are considered space-qualified), much of the work with active remote sensors for measurement of the troposphere in the near future will have to be from the ground or from aircraft. Several van-mounted dye-laser systems are being developed by NASA and other organizations for range-resolved measurements of NO_2, SO_2, O_3, and aerosols. Several IR DIAL systems and long-path systems are also being used or developed for field-measurement programs.

3.6.1.4 Remote sensing of aerosols.- The first lidar systems used pulsed ruby lasers for the measurement of aerosols by means of Mie backscattering. Ruby lidars are still used to map plumes and measure clouds and dust. Shorter wavelength lidars suffer from larger interference from Rayleigh scattering by molecules. Longer wavelength lidars avoid the Rayleigh-scattering problem but suffer from additional detector noise and weaker Mie scattering. It has recently been realized that wavelengths from 3.0 to 11.0 μm can be better used to measure mass concentrations of aerosols than can the shorter wavelengths, presumably because the wavelength is larger than the mean particle diameter so that the Mie-scattering cross section varies less rapidly with particle diameter. Work is also in progress to demonstrate the differential-scattering (DISC) technique to allow differentiation between different aerosol species (water droplets, ice crystals, sulfuric-acid droplets, etc.). Laser Doppler velocimeters are being developed to measure aerosol velocities. Table 9 summarizes the various lasers used to measure aerosols.

TABLE 9.- LASERS USED TO MEASURE AEROSOLS

Laser	Wavelength, μm	Property measured
Dye - second harmonic	0.28 to 0.32	Quasi-concentration
Ruby - second harmonic	.35	Quasi-concentration
Nd:YAG - second harmonic	.53	Visibility, quasi-concentration
Ruby	.69	Quasi-concentration
Nd:YAG	1.06	Quasi-concentration
HF or DF	2.8 to 3.4	Mass-concentration
CO_2	8 to 12	Mass-concentration, species (DISC), and aerosol velocity (Doppler)

A summary of the current active remote sensing systems in the NASA Air Quality Program is given in table 10. This summary classifies the instruments into fixed- and tunable-wavelength systems. The former are primarily important in measurements of tropospheric and stratospheric aerosols, aerosol extinction, and measurements of heights of inversion layers. For molecular species in which vibrational-rotational lines overlap wavelengths of the transmitting laser (e.g., O_3 and NH_3 for the CO_2 laser), the CO_2 Laser Absorption Spectrometer (LAS) has been developed for measuring total column concentrations from an airborne platform, and is readily extendable to Spacelab with existing technology. Tunable-wavelength lidar systems currently have the highest potential for measuring a variety of trace gases in the troposphere simultaneously, with vertical range extending to the ground and vertical resolution approaching 1 km. The lower limit on vertical resolution is generally governed by the power of the transmitting laser, the concentration and distribution of gas being measured, the size of the collecting telescope, and the intensity of the absorption line in a window of the atmosphere.

Table 10 summarizes, for each laser system, several instrument parameters including some of the species detectable with the instrument, spectral range, type of transmitting laser, receiver telescope diameter, viewing mode, and the current platform used or proposed for the sensor. The last two columns summarize the current status and the most probable field applications of the sensors. Other organizations are currently developing laser systems for applications to tropospheric monitoring. A recent survey of active ground-based and airborne remote sensors (including NASA sensors and sensors from other organizations) which potentially are available for studying elevated pollution haze was presented at the EPA Seminar/Workshop on Persistent Elevated Pollution Episodes (PEPE) held March 19 to 23, 1979, in Durham, N.C.

Within the NASA Air Quality Program, three active remote sensors have been used in a joint EPA/NASA regional field-test program from airborne platforms in the summer of 1980. These sensors are the Airborne Ultraviolet (UV) DIAL System, High Spectral Resolution Lidar (HSRL), and Laser Absorption Spectrometer (LAS). Additional joint studies are being considered for 1982.

The Airborne UV DIAL System has been designed to simultaneously measure aerosols and either O_3 or SO_2, with the potential of modifying the system to measure all three simultaneously. Other species detectable with the present system include NO_2 and H_2O. The HSRL system was developed to measure the vertical and horizontal distributions of atmospheric optical-extinction coefficients, the aerosol-to-molecular-scattering ratios, and aerosol-backscattering phase functions. The HSRL operates from an aircraft platform with the transmitting laser wavelength in a Fraunhofer line, permitting day/night operation. The LAS has undergone extensive aircraft flight testing, including flights on the NASA CV-990 and the JPL Beechcraft B80 Queen Air aircraft. The LAS has also been used in the Southeastern Virginia air quality study and successfully measured the transport of O_3 in parcels of air which originated in urban areas during morning hours and were subsequently transported by the prevailing winds.

The development of active remote sensors is not as advanced as the development of passive systems. Active remote sensors, however, have high potential

TABLE 10.- ACTIVE REMOTE SENSING SYSTEMS

Category and instrument	Species	Spectral range, μm	Transmitting laser	Receiver telescope diam, cm	Viewing mode	Platform	Current status	Field Applications
Fixed wavelength:								
Large telescope lidar system	Stratospheric aerosols	0.69	Ruby	122	Atmospheric backscatter	Mobile gnd	Operational	Gnd truth for satellites (SAM II, SAGE) Volcanic eruptions
A/C stratospheric aerosol lidar system	Stratospheric aerosols	.69	Ruby	36	Atmospheric backscatter	A/C	Operational	Gnd truth for satellites (SAM II, SAGE)
Gnd-based ruby lidar system	Tropospheric aerosols	.69	Ruby	31	Atmospheric backscatter	Mobile gnd	Operational	Power-plant plume studies
Laser Absorption Spectrometer (LAS)	O_3, NH_3	9.00 to 12.00 (discretely tunable)	CO_2 waveguide laser	15	Reflected gnd (molecular absorption)	A/C	Operational	Total burden
High Spectral Resolution Lidar (HSRL)	Aerosol extinction	0.40 to 0.45	N_2-pumped dye	36	Atmospheric backscatter	A/C	Under development	Regional aerosol extinction profiles
Tunable wavelength:								
UV DIAL	SO_2, O_3, NO_2, aerosols	0.28 to 0.31	Nd:YAG pumped dye	31	Differential absorption from atmospheric backscatter	Mobile gnd	Operational	Regional/urban plume studies
Near-IR DIAL	H_2O, pressure, temperature profiles	0.70 to 0.75	Ruby pumped dye	51	Differential absorption from atmospheric backscatter	Gnd/ vertical profiles	Operational	Tropospheric meteorological parameters
Mid-IR DIAL	CO, HCl, CH_4, CO_2,H_2O, N_2O, NH_3, H_2S, NMHC	1.40 to 3.70	Optical parametric oscillator	36	DIAL, gnd reflection	A/C	Under development	Regional (HC) and tropospheric species survey
A/C DIAL system	SO_2, O_3, NO_2, H_2O, aerosols temperature, pressure	0.28 to 0.90	Nd:YAG pumped dye	36	Differential absorption from atmospheric backscatter	A/C	Under development	Regional study of O_3, SO_2, aerosols, tropospheric H_2O profiles
Differential absorption pollution sensor	N_2O, CO, NH_3	0.45 to 0.60 7.50 to 13.00	Tunable diode lasers	6	Laser absorption in 20-m path	A/C	Operational	Regional study of tropospheric budgets and dynamics
Shuttle lidar	Multiple species, clouds, aerosols meteorological parameters	0.30 to 13.00	Evolutionary lidar system	125	Atmospheric backscatter flourescence DIAL	Spacelab	Phase-B study complete	Global troposphere stratosphere mesosphere thermosphere

for being designed to instrument specifications which meet some of the major scientific requirements for measurements in the troposphere from an airborne platform. These include vertical resolution of approximately 1 km for major species, vertical range extending to the ground, day/night operation, true column content measurements, and inherent high spectral resolution and tunability to measure tropospheric species simultaneously and uniquely in a background of interfering gases. However, for applications to space platforms, major technological breakthroughs must be made in the sources themselves, including higher power and efficiency, improved collimation and spectral purity, wider tunability, and higher frequency and amplitude stability. The NASA Shuttle Lidar Working Group has recognized the fact that at the present stage of laser technology, only two types of lasers are suitable for a Space Shuttle mission: The Nd:YAG laser and the cw CO_2 laser. No far-infrared lasers are currently suitable for spaceborne applications. In order to perform many of the scientific investigations of this plan, it will be necessary to further develop appropriate sources for active remote sensing systems.

Existing instruments must be tested under flight conditions not only to demonstrate their operational reliability and sensitivities, but also to provide data which can be interpreted and analyzed under conditions as close to an actual mission as possible. Such flights, either with aircraft or balloon platforms, must be performed for any instrument being proposed for spaceborne application. The Shuttle lidar experiments can serve as the technology demonstration flights and scientific investigations pointing to development of dedicated satellite laser instruments for studying the troposphere in long-duration satellite missions. The time scale for utilization of laser systems in research-satellite investigations is currently difficult to project due to the rapidly emerging technology of these systems. Therefore, in generating scientific requirements for satellite missions, the requirements must be tempered by the status of laser technology; in some cases, priorities for missions must be dictated by the availability of suitable laser technology.

3.6.2 In Situ Sensors

In situ sensors can be categorized in several different ways. One of the most general methods is that based on the time required to carry out a measurement. In this context, we can define two experimental approaches: Real-time and discontinuous sampling. In real-time field sampling, the time required to make a measurement (which can be either directly or indirectly related to a concentration value for a chemical species) is short compared with the natural time of variability of the species in the atmosphere or the time period of the field-sampling operation itself (typically 2 to 12 hr), whichever is shortest. In the discontinuous sampling, the time required for a measurement is defined to be longer than that specified for the natural time of variability of the species or the total time period for sampling, whichever is shortest. Each of these general sampling approaches, in turn, can be subdivided according to detection method. These include direct spectroscopic detection, indirect spectroscopic detection, gas chromatography, and wet-chemical analysis. Several specific instrument types which fall into these four categories are listed in the following:

A. Direct spectroscopic detection:

  (1) Long-path UV absorption
  (2) Long-path IR absorption
  (3) Single-photon laser-induced fluorescence
  (4) Multiphoton laser-induced fluorescence
  (5) Conventional fluorescence detection

B. Indirect spectroscopic detection:

  (1) Chemiluminescence
  (2) Neutron activation analysis - filter matte collection

C. Gas chromatography:

  (1) Electron capture detection
  (2) Flame ionization detection
  (3) Mass spectrometric detection
  (4) Flame photometric detection

D. Wet-chemical analysis:

  (1) Ion chromatography
  (2) UV-liquid chromatography

A more complete description of several of the more commonly used in situ sensors is given in table 11.

Based on the recommendation for a global aircraft field-sampling program, it follows that further development of in situ tropospheric sensors should also be given a high priority. Of particular concern should be the development of new real-time instrumentation capable of detecting tropospheric species at concentration levels given in table 12. Species for which instrumentation either does not exist or for which present instruments are inadequate are of the highest priority and include NO_x, C_2 to C_{10} hydrocarbons, peroxides (e.g., HO_2, H_2O_2, and CH_3O_2), hydrogenated sulfur compounds (e.g., H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3, and $CH_3\underset{O}{S}CH_3$), and NH_3.

Also, because of the importance of flux measurements in the overall assessment of local-regional sources and sinks for atmospheric trace gases, it is recommended that NASA give especially high priority to the funding of real-time instrumental techniques capable of generating data at repetition rates of at least 10 Hz. At the latter sampling rate, the newly developed meteorological correlation technique can be used to measure the net downward or upward flux of a trace gas directly from an aircraft platform.

TABLE 11.- SUMMARY OF IN SITU INSTRUMENTAL TECHNIQUES FOR MEASURING NATURAL BACKGROUND LEVELS OF GAS-PHASE TROPOSPHERIC SPECIES

(a) Real-time sampling

Detection method	Species detected	General status of technique (a)	Sensitivity limit (S/N = 2:1)	Time resolution for concentration twice sensitivity limit	Status of sampling platform (a)		
					A/C	Ship	Gnd base
Laser-induced flourescence	OH	A	3.5×10^5 OH/cm^3 ($p_t \leq 350$ torr) 1.0×10^6 OH/cm^3 ($p_t = 760$ torr - tropical marine boundary layer)	4 min	A	D	D
	NO	B	~0.5 ppt[b] ($p_t \leq 350$ torr) ~1.0 ppt[b] ($p_t = 760$ torr)	4 min	B	C	C
	SO_2	B	~3.0 ppt[b] ($p_t \leq 350$ torr) ~6.0 ppt[b] ($p_t = 760$ torr)	4 min	B	C	C
	CH_2O	B	50.0 ppt[b] ($p_t \leq 350$ torr) 100.0 ppt[b] ($p_t = 760$ torr)	4 min	B	C	C
Chemiluminescence	NO	[c]B,A	1.0 to 2.0 ppt	~1 min	B	A	A
	O_3	A	1.0 to 2.0 ppb	~1 min	A	A	A
	H_2O_2	B	0.1 ppb[b]	10 min	C	C	C
Chemiluminescence with chemical converter	NO_2	B	5.0 ppt	~1 min	B	B	B
Cryo-trapping GLC-FPD sulfur analyzer	SO_2	A	15.0 ppt	~4 min	A	C	A
	COS	A	2.0 ppt	~4 min	A	C	A
	H_2S	[c]A,B	~10.0 ppt	~4 min	B	C	A
	CH_3SCH_3	B	5.0 to 20.0 ppt[b]	—	B	C	B
	CS_2	B	5.0 to 20.0 ppt[b]	—	B	C	B
UV absorption	O_3	A	1.0 to 2.0 ppb	1 sec	A	A	A
UV photofragmentation UV fluorescence	H_2O	A	0.1 ppm ($p_t \leq 350$ torr)	1 min	A	D	D
	H_2O_2	B	1.0 ppb ± factor of 10[b]	—	B	C	B

[a] A = Tested, measurements reported in the literature; B = Under development; C = Untested, considered to be practical platform; D = Untested, considered to be impractical platform.

[b] Estimated sensitivity limit only.

[c] Technique has been successfully used in ground-base sampling and is under development for use on aircraft platforms.

TABLE 11.- Continued

(a) Concluded

Detection method	Species detected	General status of technique (a)	Sensitivity limit (S/N = 2:1)	Time resolution for concentration twice sensitivity limit	Status of sampling platform (a)		
					A/C	Ship	Gnd base
IR absorption diode laser	CO	B	5.0 to 10.0 ppb	0.5 to 2 min	A	C	B
	NH_3	B	50.0 ppt[b]	0.5 to 2 min	C	C	C
Mercury oxide	CO	A	2.0 to 5.0 ppb	Few seconds	A	A	A
	H_2	A	≈2.0 ppb	Few seconds	A	A	A
Gas chromatography flame ionization and electron capture detectors	CCl_4	A	3.0 ppt	8 min	A	A	A
	CF_2Cl_2	A	5.0 ppt	8 min	A	A	A
	$CFCl_3$	A	2.0 ppt	8 min	A	A	A
	CH_3Cl	[c]B, A	10.0 ppt[b]	8 min	B	A	A
	CH_3CCl_3	A	5.0 ppt	8 min	A	A	A
	C_2Cl_4	[c]B, A	20.0 ppt[b]	8 min	B	A	A
	C_2HCl_3	[c]B, A	20.0 ppt[b]	8 min	B	A	A
	CH_4	A	5.0 ppt	3 min	A	A	A
	C_2H_2	B	30.0 ppt[b]	5 min	B	A	A
	C_2H_4	B	30.0 ppt[b]	5 min	B	C	C
	C_2H_6	B	15.0 ppt[b]	5 min	B	C	C
	C_3H_8	B	30.0 to 60.0 ppt[b]	5 min	B	C	C
	C_3H_6	B	30.0 to 60.0 ppt[b]	5 min	B	C	C
	C_4H_{10}	B	30.0 to 60.0 ppt[b]	5 min	B	C	C
	CO	A	5.0 ppb	3 min	A	A	A
	N_2O	A	2.0 ppb	3 min	A	A	A
	CO_2	A	5.0 ppb	3 min	A	A	A
Frost-point hygrometer	H_2O	A	Dew pt., 243 to 233 K, or Dew pt. depression, 248 to 243 K	1 sec	A	A	A

[a] A = Tested, measurements reported in the literature; B = Under development; C = Untested, considered to be practical platform; D = Untested, considered to be impractical platform.

[b] Estimated sensitivity limit only.

[c] Technique has been sucessfully used in ground-base sampling and is under development for use on aircraft platforms.

TABLE 11.- Continued

(b) Discontinuous sampling

Detection method	Species detected	General status of technique (a)	Sensivity limit (S/N = 2:1)	Time resolution for concentration at sensitivity limit	Status of sampling platform (a)		
					Aircraft	Ship	Gnd base
High-volume collection with treated filter mattes - lab analysis	HNO_3	A	10.0 ppt	≈1 hr	A	A	A
	SO_2	B	20.0 ppt	≈1 hr	B	B	B
	HCl	B	50.0 ppt	≈1 hr	B	B	B
	HBr	B	100.0 ppt[b]		B	B	B
	NH_3	B	20.0 ppt[b]		B	B	B
	CH_3Br	A	10.0 ppt[b]		C	A	A
	CH_3I	A	1.0 ppt	≥1 hr	C	A	A
Cryo-trapping-Matrix Isolation - lab analysis	HO_2	B	$5.0 \times 10^7/cm^3$ [b]		D	C	B
C^{14}-CO Chamber Reactor - lab analysis	OH	B	$\approx 10^5$ OH/cm^3		D	C	B
Column adsorption - lab GC-mass spectrometric analysis	C_3 to C_{18}	B	20.0 to 50.0 ppt for each species[b]	≈1 hr	B	B	B
Grab sampling - Lab GLC or GLC-mass spectrometric analysis	CCl_4	A	2.0 ppt	Not meaningful quantity: time resolution in principle could be the rate at which can samples could be opened, filled, and then closed	A	A	A
	CF_2Cl_2	A	2.0 ppt		A	A	A
	$CFCl_3$	A	1.0 ppt		A	A	A
	CH_3Cl	A	4.0 ppt		A	A	A
	$CHFCl_2$	A	3.0 ppt		C	A	A
	$CHClF_2$	A	3.0 ppt		C	A	A
	CH_2ClF	A	3.0 ppt		C	A	A
	CH_3CCl_3	B	3.0 ppt		B	B	B
	C_2Cl_4	B	10.0 ppt		B	B	B
	C_2HCl_3	B	10.0 ppt		B	B	B
	CF_4	B	2.0 ppt		B	B	B
	CH_4	A	2.0 ppt		A	A	A
	C_2H_2	A	15.0 ppt		A	A	A
	C_2H_4	A	15.0 ppt		A	A	A
	C_2H_6	A	7.0 ppt		A	A	A
	C_3H_8	B	30.0 ppt		B	B	B
	C_3H_6	B	30.0 ppt		B	B	B
	C_4H_{10}	B	30.0 ppt[b]		B	B	B
	C_4-C_8	B	30.0 ppt[b]		B	B	B
	CO	B	2.0 ppt		B	B	B
	N_2O	A	1.0 ppt		A	A	A
	CO_2	A	2.0 ppt		A	A	A

[a] A = Tested, measurements reported in the literature; B = Under development, C = Untested, considered to be practical platform; D = Untested, considered to be impractical platform.

[b] Estimated sensitivity limit only.

TABLE 12.- INSTRUMENT SENSITIVITY REQUIRED FOR THE DETECTION OF SEVERAL CARBON, NITROGEN, OZONE, AND H_xO_y SPECIES UNDER DAYTIME CONDITIONS

Species measured	Estimated mean concentration level	Concentration range
OH	$1.5 \times 10^6/cm^3$	2×10^5 to $3 \times 10^7/cm^3$
HO_2	$3.0 \times 10^7/cm^3$	1×10^6 to $6 \times 10^8/cm^3$
H_2O_2	500 ppt	50 to 3000 ppt
H_2O	1.0 torr	0.02 to 20 torr
O_3	50 ppb	2 to 300 ppb
NO	5 ppt	1 to 200 ppt
NO_2	10 ppt	2 to 400 ppt
HNO_3	50 ppt	10 to 1000 ppt
HNO_2	$1 \times 10^6/cm^3$	1×10^5 to $1 \times 10^7/cm^3$
NO_3	$4 \times 10^6/cm^3$	4×10^5 to $2 \times 10^7/cm^3$
CO	90 ppb	40 to 300 ppb
CH_4	1.65 ppm	1.40 to 1.90 ppm
CH_2O	100 ppt	20 to 500 ppt
CH_3OOH	200 ppt	20 to 1000 ppt
CH_3OH	500 ppt	50 to 2000 ppt
CH_3O_2	$3 \times 10^7/cm^3$	1×10^6 to $6 \times 10^8/cm^3$

3.7 INTERAGENCY COORDINATION

The NASA research program in tropospheric environmental quality is continually coordinated with other agencies conducting related programs through mutual participation on interagency steering committees, through the exchange of and comment on programmatic documentation, through mutual participation in periodic progress reviews and planning workshops, and through discussion and critique at interagency committee meetings.

The overall coordination with related programs in the Environmental Protection Agency (EPA) is conducted by an interagency committee cochaired by the EPA Assistant Administrator for Research and Development and by the NASA Associate Administrator for Space and Terrestrial Applications. This committee administers an EPA/NASA interagency agreement focusing on cooperative programs in environmental quality. A current Memorandum of Understanding under this interagency agreement covers a cooperative project on regional-scale pollution episodes. As part of this project, NASA is conducting analytical and field studies in support of such EPA activities as the Sulfate Transport and Transformation Experiment (STATE), the Persistent Elevated Pollution Episodes (PEPE) activity, and other in-house research. NASA has been a participant in the EPA-coordinated Federal Interagency Energy/Environment Research and Development Program since 1975. Through these continuing programs and through frequent mutual participation in progress reviews and workshops, the NASA program is fully coordinated with EPA.

In addition to EPA, a number of other organizations are conducting programs related to the NASA Air Quality Program. The National Science Foundation (NSF) has sponsored Global Atmospheric Measurements Experiment on Tropospheric Aerosols and Gases (GAMETAG) and has established a new research program in atmospheric chemistry. NASA has reviewed the programmatic documentation on GAMETAG, and GAMETAG scientific investigators have kept NASA abreast of the results to date. NSF and NASA representatives have discussed potential collaboration on future aircraft measurements. NSF also managed the United States participation in the Monsoon Experiment (MONEX) in the spring of 1979, and several NASA investigators conducted environmental experiments as part of MONEX.

Other studies of interest to NASA are: (1) The Multistate Atmospheric Power Production Pollution Study (MAP3S) under the management of EPA through the Department of Energy to study the environmental impact of fossil-fuel burning, and (2) the now completed Sulfate Regional Experiment (SURE), which was conducted by the Electric Power Research Institute for validation of regional transport models. NASA has coordinated its program activities with MAP3S and SURE.

The NASA research program in air quality was further coordinated with a group of 16 Federal agencies conducting environmental programs through participation in the Interagency Task Force on Environmental Data and Monitoring. This Task Force was established in 1977 by the Council on Environmental Quality at the direction of the President to review present environmental data and monitoring programs and to recommend improvements that would make these programs more effective. In addition to pursuing its own objectives, the Task Force has provided an excellent mechanism for interagency coordination of federally sponsored environmental programs. The final report of the Task Force was issued in March 1980 (ref. 11).

The NASA research program in air quality is coordinated with related programs in other countries through NASA's International Affairs Division. Key NASA technical and management personnel participate in international technical meetings, serve as members of committees in support of the United Nations Environmental Progam (UNEP), and frequently visit other countries engaged in related programs to maintain an up-to-date knowledge of their progress and status. Additional coordination with foreign programs is achieved through active participation by scientists from other countries in NASA programs. Foreign scientists are principal investigators for experiments on NASA satellites, serve on NASA working groups, and participate in the NASA research programs through the Announcement of Opportunity (AO) and Applications Notice (AN) processes.

CHAPTER 4 - SUMMARY

This report has been devoted to the scientific rationale and recommended program elements for the NASA Tropospheric Research Program Plan. The overall goal of the research program is to increase our understanding of the chemical phenomena occurring in the troposphere with particular emphasis on those aspects that impact on environmental quality such as health, agriculture, climate, and weather. Thus, the tropospheric research plan focuses on those aspects of the general biogeochemical cycles of the Earth that concern the chemistry and dynamics of the troposphere.

The present research plan is centered around three general questions:

I. What are the principal processes governing the global carbon/nitrogen/ozone system?

II. What are the principal processes governing the global sulfur/ammonia/trace metal/carbon/aerosol system?

III. What are the relative roles of transport, transformation, and removal processes in governing the behavior of regional- and urban-scale polluted air masses? (This problem is of interest to NASA in responding to requests from EPA and other agencies for the development and application of space technology for monitoring tropospheric processes.)

Those research tasks that have been selected for implementation are divided into four basic categories:

1. Field measurements

2. Modeling

3. Laboratory measurements

4. Technology development

Each of the major scientific problems outlined in the tropospheric research plan has components that suggest theoretical and experimental research studies, and the experimental studies are divided according to those conducted in the field and in the laboratory. In view of the role of NASA as a developer of space-derived technology and as a catalyst for the adoption of this technology by other U.S. agencies and those of other countries, emphasis is also given to a number of technology-development tasks. This aspect is important because of the need for the continued development of advanced technology to achieve a global monitoring capability for the natural and the perturbed troposphere. Among the four basic categories mentioned, field-measurement programs and technology development are the areas of primary emphasis in the research plan in recognition of the unique role of NASA in orbital remote sensing and instrument development. The field-measurement programs proposed consist primarily of orbital remote sensing and airborne monitoring. Airborne measurements, and to some extent ground-based measurements, are proposed as high-priority programs early in the NASA tropospheric program because the in situ data to be obtained will be essential to improving our understanding of tropospheric processes.

NASA has played a central role in the development of mathematical models of the global troposphere, and continued refinement of such models is essential for the proper interpretation of tropospheric measurements. Because of the need to interface remote sensing data with the predictions of models both for the global troposphere and regional air pollution, the development of techniques for such integration is also viewed as an important task.

A variety of laboratory studies are needed to support the major components of field-measurement programs and technology development. The laboratory programs proposed are divided according to spectroscopy, calibration, and fundamental kinetic measurements. The fundamental kinetic studies proposed include the measurement of rate constants at tropospheric conditions and measurements aimed at explaining the processes of gas-to-particle conversion.

Technology development has been a cornerstone of NASA's mission. Several proposed programs are outlined for technology development in support of tropospheric research.

4.1 FIELD-MEASUREMENT MISSIONS

Two scientific goals in which the NASA program should attempt to make major gains during the coming two decades are establishment of global atmospheric distributions (i.e., budgets) of those elements believed to be of key importance in global biogeochemical cycles and determination of the cause-and-effect relationships between these observed distributions and the dominant controlling factors, such as atmospheric chemical transformations, biospheric and atmospheric source and sink strength, and atmospheric transport. Since an extraordinary amount of field sampling at a considerable cost will be required to satisfy these two goals, the decision on what type or types of sampling platforms to use in each case is obviously a critical one. Establishing the detailed relationships between concentration levels and source and sink strengths as well as chemical-transformation rates will require a combination of aircraft, ground-based, and ship sampling platforms coupled with limited satellite observations. The establishment of global distributions, on the other hand, conceptually could be most effectively carried out on satellite and/or Space Shuttle sampling platforms. The monitoring by means of satellite platforms of about 100 chemical species with high resolution in both the vertical and horizontal directions is highly unlikely. Two basic questions which then need to be answered in initiating a cost-effective satellite program are:

(1) Which of the approximately 100 chemical species are really the key ones?

(2) With what vertical and horizontal resolution must each of these key chemical species be measured?

Since the answer to the first question is strongly dependent on the cause-and-effect relationships as well as laboratory gas kinetic data, it is suggested that an extensive satellite monitoring effort be preceded by a well-conceived aircraft measurements program.

4.1.1 Tropospheric Aircraft Sampling Program

When considering tropospheric phenomena, it is convenient to divide the atmosphere spatially into global-scale, regional-scale, and mesoscale regimes. On a global scale, one is interested in those species that comprise the so-called natural troposphere. On the mesoscale, species usually considered as pollutants are of prime interest, whereas, both natural and anthropogenically derived (pollutant) species are important on the regional scale.

A key consideration in the design of the tropospheric aircraft sampling program is the spatial resolution required for measuring the particular chemical species. One of the factors that dictates the spatial resolution required for measuring a chemical species on a global scale is its atmospheric residence time. In general, the longer the residence time, the lower the spatial resolution required for the measurement. For species such as $CFCl_3$, CF_2Cl_2, and N_2O with very long residence times, two well-placed ground stations, one each in the Northern and Southern Hemispheres, would suffice for purposes of establishing the distributions of these species. For species with residence times on the order of a few days to a year, the existence of local regional sources and sinks in combination with the variable levels of free radicals dictates a fairly high level of spatial resolution for aircraft operations. For rapidly reacting species with residence times on the order of a few minutes to a day, local sources, sinks, and chemical-transformation rates are expected to strongly control the levels of these compounds. Higher spatial-resolution coverage than for longer residence-time species is necessary. Two possible aircraft sampling scenarios oriented toward studying the chemistry of the natural troposphere (as opposed to regional air pollution) are provided in this recommended plan. The first scenario restricts the aircraft sampling to 27 independent geographic regions and results in a sampling program of about 6.5 to 8 years duration. The second scenario expands the sampling to 43 regions and requires about 11.5 years to complete.

4.1.2 Lower Atmospheric Research Satellite (LARS)

The large spatial and temporal heterogeneities of tropospheric source and sink regions as well as the variability in meteorological variables make it imperative that a comprehensive global study of the carbon/nitrogen/ozone and sulfur/ammonia/carbon/trace metal/aerosol systems include the application of remote sensing technology on one or more orbital platforms. Although aircraft measurements can be quite important for characterizing various concentration domains, for many species for which abundance is affected by both transport and photochemistry, measurements from space are likely to be the best method to accurately map global distributions and to determine whether a concentration variation in a given location is due to Eulerian or Lagrangian effects.

Thus, a goal of the NASA Tropospheric Research Program Plan is the eventual implementation of a Lower Atmospheric Research Satellite (LARS). By chronologically following the tropospheric aircraft sampling program, it is envisioned that many of the mission and design specifications for atmospheric chemistry experiments on LARS can be formulated on the basis of the findings of the aircraft studies. The long-term global coverage that could be obtained by LARS will complement the data obtained by the aircraft program, which will be more detailed and precise but also more spatially and temporally limited than LARS. Appropriate atmospheric chemistry missions for LARS could include: (1) The detailed global mapping of species distributions and major source and sink regions, (2) a better understanding of the global importance of anthropogenic sources of key trace species, (3) the development and verification of detailed global and regional models of tropospheric trace-gas composition and air quality with capabilities to predict the impact of various anthropogenic emissions, and (4) a comprehensive record of the present global tropospheric trace composition which may ultimately be used in identifying long-term secular or cyclic variations in parameters relevant to regional and global air quality.

Because of the highly coupled nature of tropospheric photochemistry, simultaneous measurements from LARS of as many species as is realistically possible should be a major objective. Thus, implementation of this mission will depend on a vigorous program to develop a remote sensing technology as well as an intense field-measurements effort using ground-based instruments and aircraft measurements complemented by modeling calculations to determine which configuration of species measurements from a space platform would be most valuable. Thus, while the ultimate goal of the orbital program for the troposphere is the implementation of a comprehensive multiple-species measurement from space, smaller data-gathering missions using remote sensors either from space, ground-based stations, or from aircraft should be included in the tropospheric program.

4.2 MODELING

The objectives of global-scale modeling are to enhance our understanding of the chemical properties of the troposphere and to support the development of observing systems applicable to tropospheric pollution. The global-scale models being developed and applied in the current NASA Air Quality Program are primarily designed to explain the features of the various chemical budgets. Typically these models contain a detailed description of tropospheric photochemistry and adopt an eddy diffusion approach to transport. The output of such models is the spatial and temporal distributions of the concentrations of selected tropospheric species. Because of the large number of species involved in the chemical budgets, fully three-dimensional models are not yet computationally practical. In fact, it is unlikely that full operational utility of a global circulation model containing a detailed chemical component will be realized within the 5-year purview of this plan. Thus, heavy reliance is likely to continue to be placed on one- and two-dimensional models. It is anticipated that future development in the tropospheric modeling program will proceed along two lines. First, an increasing degree of sophistication will be incorporated in the treatment of physical and biological processes in current models. Second, current models will be extended to higher dimensionality, and the spatial and temporal variability of the troposphere will be investigated in increasing detail.

An example of the first type of development is the description of the sources of biologically produced gases as functions of the meteorological parameters (temperature, relative humidity, soil moisture, precipitation, etc.) on which they might depend. Coupling of aeronomic and meteorological processes within a single model would then permit a description of feedback loops within perturbation models. The second type of development involves the construction of time-dependent, two-dimensional models which may include at least part of the stratosphere. The principal advantage of such development will be the detailed description of stratospheric-tropospheric exchange and of species transport within the troposphere.

In addition, a key component for both the tropospheric aircraft sampling program and satellite missions should be the diagnostic and predictive modeling capability to analyze and simulate the data gathered. Because of the complexity of the photochemical system of the troposphere, a truly complete understanding of the data requires detailed numerical calculations.

A number of measurement programs, several based on remote sensing, have been proposed to further our understanding of the chemical and physical processes in regional air pollution. The measurements made in such programs must then be assimilated into and compared with model predictions to gain the desired understanding. The general problem of the assimilation of remotely sensed and in situ data into regional air pollution models has not received substantial attention. Therefore, development of theory applicable to the assimilation of data into regional-scale models should represent the principal NASA thrust in the area of regional air pollution modeling.

4.3 LABORATORY MEASUREMENTS

The measurement and evaluation of atmospheric properties and processes must be based upon relevant laboratory studies under controlled conditions.

4.3.1 Spectroscopy

Spectroscopy is the basis for essentially all of the remote sensing techniques for chemical species in the atmosphere. Consequently, it represents an important area for fundamental study prior to the deployment of a system for species detection. Since remote sensing instruments may operate in the microwave, far-infrared, mid-infrared, near-infrared, visible, or ultraviolet regions of the spectrum, spectroscopic investigations must be made in all of these regions. These studies must provide information on the following spectral properties for the molecular species of interest: Line positions, line strengths, line widths, and quenching cross sections.

4.3.2 Calibration Requirements

4.3.2.1 Remote sensors.- The measurement of tenuous atmospheric trace constituents imposes severe accuracy and precision constraints on experimental test and evaluation procedures for remote sensing instruments. Current techniques for calibrating remote sensors depend to a high degree on limited calibration information and extrapolation from laboratory measurements to expected atmospheric conditions of concentration, temperature, pressure, and radiometric input. Instrument performance and accuracy of the data-reduction process are severely limited by the assumptions and uncertainties in analytical procedures.

Measurements with in situ sensors or other remote sensing instruments are required for intercomparison of data. In order to improve the calibration of remote sensors, a dual calibration strategy should be developed, including improving the confidence of laboratory calibration data for remote sensors and improving both precision and accuracy of in situ instruments used in correlative data studies.

4.3.2.2 In situ sensors.- Although the calibration of in situ instrumentation should inherently be more direct and hence more reliable than for remote instrumental techniques, in situ devices are still subject to many types of errors. Within the last 3 to 4 years, for example, it has been convincingly demonstrated that even though multiple instruments may go through interlaboratory comparisons giving basically the same values, under field sampling conditions significantly different answers are generated. Variable temperatures, high humidities, aerosols, and unknown interfering chemical compounds, naturally in the atmosphere or produced by the sampling platform, frequently combine to produce systematic errors of unknown magnitude under field conditions. Thus, it is recommended that NASA give priority not only to standard calibration studies but also to strongly support field intercomparison investigations. In particular, it is recommended that any large field-sampling program have designed into it a well-conceived calibrations program.

4.3.3 Gas-Phase Chemical Kinetics

At the present time, one can identify at least two major tropospheric problem areas that are in need of further laboratory study. The first of these involves the complete explanation of the methane and higher molecular weight hydrocarbon degradation cycles; the second is concerned with the renewed effort to determine the absolute gas-kinetic rate constants for several key reactions under atmospheric conditions of pressure and composition.

4.3.4 Aerosol Physics and Chemistry

A problem of fundamental interest in virtually all aspects of atmospheric science is understanding the processes by which airborne particles form and evolve. Atmospheric particles, or aerosols, may be emitted into the atmosphere directly from sources (both natural and anthropogenic) or may be formed in situ by the nucleation of vapor molecules. From the point of view of assessing the climatic and human health effects of atmospheric aerosols, it is important to be able to measure and predict their size and chemical-composition distribution. Size and composition of atmospheric aerosols are strongly dependent on the mode of formation and growth of the aerosol. Unfortunately, many of the thermodynamic and kinetic parameters required for understanding formation and growth are not known for typical atmospheric aerosols. Laboratory programs are needed to obtain such parameters.

4.4 TECHNOLOGY DEVELOPMENT

4.4.1 Remote Sensors

In the current state of development of remote sensors, several active and passive systems have progressed to the stage where they are being used or proposed in field-measurement programs from airborne and ground-based platforms to measure gaseous species (e.g., CO, O_3, SO_2, H_2O, NH_3, and NO_2), tropospheric aerosols, mixing heights, and optical extinction coefficients. Future developments and remote sensing systems are aimed toward extending this capability to other molecular species with improved sensitivity and vertical resolution.

Passive remote sensors are categorized generically into four categories: (1) Gas filter correlation techniques, (2) interferometry, (3) infrared heterodyne radiometry, and (4) spectroradiometers. Technological improvements in the sensitivity of passive remote sensors should expand the number of instruments within each generic class as potential payloads for airborne and space platforms. Despite the potential improvements in the sensitivity of passive remote sensors through technological improvements in systems and detector technology, several fundamental limitations in passive sensors will restrict the use of these instruments for some of the scientific requirements listed in this document. Passive sensors in the thermal infrared have difficulty measuring molecules in the biosphere and are limited to measuring in broad vertical layers in the middle and upper troposphere. The relatively long integration times required to measure low-concentration species will restrict the horizontal resolution of the measurement to broad geographic areas and will probably require the use of geostationary satellite platforms to investigate regional areas, such as the U.S. Northeastern corridor. Instruments using Earth-scattered sunlight are capable of measuring total integrated burdens of molecular species but have inherently limited temporal and geographic coverage. Despite these limitations, passive remote sensors do exhibit several attractive characteristics for global measurements. Their systems and technology are the most advanced available for satellite missions. Passive instruments using upwelling thermoradiance have a potential for measuring a large number of interesting tropospheric molecules simultaneously and should be effective in studying the chemistry of selected chemical systems. Passive instruments using Earth-scattered sunlight have the capability of measuring the total burden of several major tropospheric gases. A satellite mission incorporating both types of instruments should be investigated in light of the scientific requirements for an early dedicated satellite for the lower atmosphere.

Considerable effort has been expended by NASA and other organizations during the past decade to develop active remote sensing techniques using lasers. The first systems used pulsed ruby lasers to measure aerosols via Mie backscattering in the technique known as lidar (light detection and ranging). In the early 1970's, Raman-scattering lidars were used to remotely measure species concentrations. By the mid-1970's, the advent of high-power tunable lasers spurred the development of differential adsorption techniques for the measurement of gases, often replacing the less sensitive Raman technique. The active remote-sensor systems in the NASA Air Quality Program can be classified into fixed- and tunable-wavelength systems. The former primarily are important in measurements of tropospheric and stratospheric aerosols, aerosol extinction, and measurements of inversion layer heights. Tunable-wavelength lidar systems currently have the highest potential for measuring a variety of trace gases in the troposphere simultaneously, with vertical range extending to the ground and with vertical resolution approaching 1 km. The development of active remote sensors is not as advanced as that of passive systems. Active remote sensors, however, have high potential for being designed to specifications that meet some of the major scientific requirements for measurements in the troposphere from an airborne platform, including vertical resolution of approximately 1 km for major species, vertical range extending to the ground, day/night operation, true column-content measurements, and inherent high spectral resolution and tunability to measure tropospheric species simultaneously and uniquely in a background of interfering gases. For applications to space platforms, however, major technological breakthroughs must be made in the sources themselves, including high power and efficiency, improved collimation and spectral purity, wider tunability, and higher frequency and amplitude stability. In order to perform many of the scientific investigations of the tropospheric research plan, it will be necessary to develop appropriate sources for active remote sensing systems. Further, existing instruments must be tested under flight conditions not only to demonstrate their operational reliability and sensitivities but also to provide data that can be interpreted and analyzed under conditions as close to an actual mission as possible. The time scale for utilization of laser systems and research satellite investigations is currently difficult to estimate due to the rapidly emerging technology of laser systems. Therefore, in generating scientific requirements for satellite missions, the science requirements must be tempered somewhat by the status of laser technology, and, in some cases, priorities for missions must be dictated by availability of laser technology.

4.4.2 In Situ Sensors

Based on the recommendation for a global aircraft field-sampling program, the further development of in situ tropospheric sensors should be given a high priority. Of particular concern should be the development of new real-time instrumentation capable of detecting tropospheric species at necessary concentration levels. Species of the highest priority (that is, those for which instrumentation either does not exist or for which present instruments are inadequate) are NO_x, C_2 to C_{10} hydrocarbons, peroxides (e.g., HO_2, H_2O_2, and CH_3O_2), hydrogenated sulfur compounds (e.g., H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3, $CH_3\underset{O}{S}CH_3$), and NH_3.

APPENDIX A

SCIENTIFIC RESEARCH OBJECTIVES IN TROPOSPHERIC POLLUTION

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APPENDIX A

CHAPTER 1 - OUTSTANDING SCIENTIFIC QUESTIONS AND RESEARCH TASKS

A. MEASUREMENTS OF THE GLOBAL DISTRIBUTIONS OF GASES AND AEROSOLS AND ELUCIDATION OF ATMOSPHERIC CYCLES

1. Tropospheric Ozone Budget

Although tropospheric ozone (O_3) is believed to play a key role in the free-radical photochemistry of the troposphere, the tropospheric budget of O_3 is not completely understood and is the subject of intense scientific investigation. Understanding the budget of tropospheric O_3 is essential for establishing a firm knowledge of tropospheric photochemistry and for establishing the potential impact of pollutants on the photochemical system. For instance, concern has been expressed that enhanced concentrations of carbon monoxide (CO), hydrocarbons (HC), and/or nitrogen oxides (NO_x) due to anthropogenic activities could lead to higher levels of tropospheric O_3.

Two theories have been advanced to explain the natural 30 to 40 parts per billion by volume (ppb) of O_3 commonly observed in the troposphere. The transport theory maintains that tropospheric O_3 is produced in the stratosphere where ultraviolet (UV) photons can dissociate oxygen and form ozone, is then mixed down into the troposphere by turbulent diffusion where it is chemically inert, and is eventually destroyed at the Earth's surface (Junge (ref. 12)). Supporting this theory is the immense amount of meteorological and radionuclide data that indicate a correlation between tropospheric ozone levels and stratospheric intrusions (Fabian and Pruchniewicz (ref. 13), Danielsen and Mohnen (ref. 14), and Falconer et al. (ref. 15)).

The photochemical theory of tropospheric ozone advanced by Frenkiel (ref. 16), and more recently by Crutzen (refs. 17 and 18) and Chameides and Walker (ref. 19), proposes that ozone is photochemically produced and destroyed in the troposphere through the interaction of natural hydrocarbons such as methane (CH_4), CO, and NO_x with sunlight. The photochemical production of tropospheric O_3 may occur from the generation of peroxyl radicals in the CH_4 oxidation chain and in the oxidation of CO. The peroxyl radicals (HO_2) may then react with NO

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$$

to form nitrogen dioxide (NO_2), which is photolyzed and leads to O_3 formation as follows:

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

The generation of HO_2 may also lead to the destruction of O_3 through the reaction

$HO_2 + O_3 \rightarrow OH + 2O_2$

Finally, ozone is destroyed in the generation of the hydroxyl radicals (OH):

$O_3 + h\nu \rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow 2OH$

The recent observations of tropospheric OH concentrations at the approximate levels predicted by photochemical models (Davis et al. (refs. 20 and 21) and Perner et al. (ref. 22)) at least confirm, by means of the previously given reactions, the existence of a chemical O_3 sink of about 7×10^{10} molecules/cm^2/s. This sink alone is comparable to estimates by Fabian and Pruchniewicz (ref. 13) of O_3 destruction at the Earth's surface. The presence of CO further implies the conversion of OH to HO_2 and thus implies more photochemical production and destruction of tropospheric ozone through the reactions involving HO_2.

Recent model calculations by several investigators, including Chameides (ref. 23), Nastrom (ref. 24), Danielsen and Mohnen (ref. 14), Fabian and Pruchniewicz (ref. 13), Chameides and Stedman (ref. 25), Stewart et al. (ref. 26), Fishman and Crutzen (ref. 27), Fishman et al. (ref. 28), Fishman and Crutzen (ref. 29), Galbally and Roy (ref. 30), Mahlman et al. (ref. 31), and Gidel and Shapiro (ref. 32), indicate that both photochemistry and transport probably play important roles in the tropospheric O_3 budget, with photochemistry acting as a net sink for O_3 in remote locations. (See table 13.) However, the intensity of the ozone photochemistry and whether the photochemistry supplies a net source or sink of O_3 are both uncertain and depend on a number of param-

TABLE 13.- ESTIMATES OF THE GLOBAL OZONE BUDGET

Ozone photochemistry and transport	Global ozone budget, 10^{11} molecules/cm^2/s, from -			
	Reference 23	Reference 24	Reference 14	Reference 13
Photochemical production	0.2 to 1.2			
Photochemical destruction	1.2 to 1.8			
Stratospheric-tropospheric flux	1.3 to 1.5	0.7	0.7	
Flux into Earth's surface	0.5 to 0.8			0.4 to 0.8

eters which include the concentration of nitrogen oxides, the concentration of CO, and the loss rate of free radicals due to heterogeneous processes and key rate coefficients which are still not accurately measured. The rate of transport of O_3 from the stratosphere to the troposphere is also uncertain; recent observations and model calculations imply that the O_3 exchange rate estimated from tropopause-folding processes is too small to account for estimated transport rates, and other processes may exist which transport O_3 across the tropopause. Observations with high vertical resolution are needed to address this question.

Scientific Questions:

A.1.1 What are the relative roles of stratospheric-tropospheric exchange, photochemistry, and surface sinks in the global tropospheric ozone budget?

A.1.2 Will variations in global CO and NO_x levels shift the ozone balance?

A.1.3 What is the detailed degradation chain for methane and what are its consequences on ozone and HO_x?

A.1.4 What is the role of nonmethane hydrocarbons in the ozone budget?

A.1.5 What are the detailed exchange mechanisms between the troposphere and stratosphere?

Research Tasks:

(1) Continue development of global tropospheric photochemical transport models.

(2) Measure the global distribution of ozone as a function of latitude, longitude, altitude, and time. Of special importance would be measurements of stratospheric ozone transport into the troposphere. These measurements could be carried out in two phases:

Phase I: Simultaneous measurement of ozone with NO_x, HO_x, CO, nonmethane hydrocarbons, and urban and stratospheric tracers. Resolution required: Vertical, 0.1 to 1 km; horizontal, 5 to 100 km; temporal, hourly.

Phase II: Long-term measurements of ozone after the initial program. Resolution required: Vertical, 2 km; horizontal, 100 km; temporal, daily to weekly.

In addition, supplemental local and regional measurements of ozone under conditions of enhanced tropospheric-stratospheric exchange would be desirable. Resolution required: Vertical, 0.25 km; horizontal, 1 to 10 km; temporal, continuous.

(3) Conduct flux measurements of ozone near the ground over various geographical locations.

(4) Develop remote capabilities for measuring tropospheric ozone.

2. Tropospheric Nitrogen Budget

Active nitrogen (NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, and HO_2NO_2).- Active nitrogen is of interest to atmospheric scientists because NO_x(NO + NO_2) acts to enhance tropospheric OH levels and, as in the urban environment, catalytically produces ozone in the presence of peroxyl radicals; that is,

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Furthermore, the conversion of NO_x to nitric acid (HNO_3) through the reaction

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

may contribute to acid rain. Unfortunately, the sources and sinks of atmospheric nitrogen oxides and their natural abundances are uncertain.

The sink for active nitrogen compounds is believed to involve heterogeneous removal by rainout and washout. The rate of this process is highly uncertain, but an estimate of about 60 to 90 million metric tons per year of nitrogen (60 to 90 Mt/yr of N) is usually made on the basis of existing data on the concentration of nitrate NO_3^- in precipitation. Inasmuch as photochemical models predict that HNO_3 is the most abundant form of active N in the unpolluted troposphere, it has been assumed that the removal process involves primarily HNO_3 removal.

The possible natural sources of active N include fixation of nitrogen by lightning, biospheric production from the soils (and ocean), and production from the oxidation of ammonia (NH_3) initiated by reaction with OH. The early estimates that lightning fixation was responsible for the production of 30 to 40 Mt/yr of N (Chameides et al. (ref. 33)) have recently been revised downward to about 3 Mt/yr of N (Dawson (ref. 34)). Because the NH_3 abundance is uncertain and the importance of heterogeneous removal is difficult to estimate, the production of NO_x from NH_3 is not accurately known. Similarly, the soil source rate is uncertain. Although laboratory studies have shown that NO is produced in acidic soils, other experiments indicate that the NO is absorbed and retained in the soil and eventually oxidized to NO_3 (Bartholomew and Clark (ref. 35)).

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Detailed measurements of NO_x fluxes from various soil types and terrains will be needed to understand the importance of biospheric production of atmospheric active N.

Inasmuch as estimates of anthropogenic NO_x emissions yield a global source rate for 1975 of about 20 to 25 Mt/yr of N, it would appear that man may have a significant impact upon the active nitrogen budget (Liu (ref. 36) and Chameides (ref. 37)). Calculations indicate that, if these anthropogenic emissions increase in the coming decades, they may lead to an increase in tropospheric O_3 and OH levels on a regional and, perhaps, global scale.

State-of-the-art measurements (Schiff et al. (ref. 38), and McFarland et al. (ref. 39)) indicate NO and NO_2 levels that are less than 0.04 ppb in remote marine and continental areas but are as high as 0.2 to 0.5 ppb in rural regions of the continental United States. It is not certain whether this enhancement is caused by anthropogenic influences. Tropospheric model simulations estimate an average NO_x level of about 0.05 ppb for the lower troposphere. (Even at these low concentrations, calculations indicate that NO_x still may play a significant role in generating OH and O_3.) Model calculations indicate that HNO_3 is the most abundant form of active N in the unpolluted troposphere, being about an order of magnitude more concentrated than NO_x. However, observations of HNO_3, which are unfortunately limited at this time, indicate that the ratio HNO_3/NO_x may be smaller than originally believed (Huebert and Lazrus (ref. 40)) and that it is possible that a key element in the active N system has not yet been identified. The importance of heterogeneous processes in controlling the abundance and distribution of HNO_3, which is highly soluble in water, is not well understood. If heterogeneous removal of HNO_3 is the major sink of atmospheric active nitrogen, it is important to understand the details of this mechanism. A concerted observational effort is needed to characterize the global distribution of NO, NO_2, and HNO_3 and to assess the impact of anthropogenic activities.

Scientific Questions:

A.2.1 What are the tropospheric concentrations of the active nitrogen compounds?

A.2.2 What are the natural sources of active nitrogen?

A.2.3 What are the major sinks of atmospheric NO_x and total active nitrogen?

A.2.4 Can increased levels of NO_x influence the tropospheric ozone balance?

Research Tasks:

(1) Measure the global concentration distributions of NO, NO_2, and HNO_3. These measurements could be carried out in two phases:

Phase I: Initial high resolution measurements in representative global regions with simultaneous observations of O_3, HO_x, and an urban tracer. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hourly. Concentration ranges expected: 0.002 to 1.00 ppb for NO and NO_2; 0.01 to 3 ppb for HNO_3.

Phase II: After the initial measurement program, long-term measurements of the most abundant active nitrogen compounds, for example, HNO_3, would be needed. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, daily to weekly. Concentration ranges expected: 0.002 to 1.00 ppb for NO and NO_2; 0.01 to 3 ppb for HNO_3.

(2) Carry out flux measurements of NO and NO_2 near the ground over various geographical locations.

(3) Measure the nitrate content in aerosols and rainfall on a global scale. Temporal resolution required: Monthly. Sensitivity desired: 10^{-6} moles/l.

(4) Develop remote and supportive in situ sensing methods to measure NO, NO_2, and HNO_3. Sensitivity desired for in situ instrument: 1 to 2 parts per trillion by volume (ppt) for NO and NO_2 and 10 ppt for HNO_3.

Ammonia (NH_3).- The role of NH_3 in atmospheric photochemistry cannot be assessed until accurate measurements characterize its global distribution and until the processes that produce and remove NH_3 are fully understood. Depending upon the NH_3 abundance, the oxidation of NH_3 by OH

$$NH_3 + OH \rightarrow NH_2 + H_2O$$

followed by further oxidation to NO may lead to significant production of NO_x. Ammonia may also affect the $SO_2 - SO_4$ system by forming ammonium sulfate $(NH_4)_2SO_4$.

Ammonia is believed to originate from the soil where, under the proper conditions, ammonium, which is produced in the decomposition of organic amino compounds, is volatized. It is estimated that about 140 Mt/yr of N in the form of NH_3 are produced by this process (Burns and Hardy (ref. 41)). There is some evidence to suggest that intense agricultural fertilization may lead to significant enhancements of NH_3 and NH_4^+ in precipitation on the regional scale. The known sinks for NH_3 include the reaction with OH and heterogeneous removal processes. Based upon lifetime arguments, it is likely that the heterogeneous process is dominant; Chameides et al. (ref. 33) estimate that less than 25 percent of atmospheric NH_3 reacts with OH and is eventually converted to NO. This estimate is uncertain, however, owing to our lack of knowledge of the heterogeneous processes and the exact abundance of OH.

Measurements of NH_3 indicate wide discrepancies, with concentrations varying from 10 ppb using analytic chemistry (Georgii and Mueller (ref. 42)) to less than 0.08 ppb using spectroscopy (Kaplan (ref. 43)). It is not known to what extent these differences reflect real variations in atmospheric NH_3 or merely systematic errors in one or both measurement techniques. Accurate techniques for measuring NH_3 need to be developed and applied to determine the global distribution of NH_3.

Scientific Questions:

A.2.5 What are the global concentrations, sources, and sinks of ammonia?

Research Tasks:

(1) Measure the global concentration distribution of ammonia. These measurements can be carried out in two phases:

Phase I: An initial measurement program in representative global regions with simultaneous measurements of ammonium in precipitation, OH, and NO_x. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, 0.3 to 1 day. Concentration range expected: 0.01 to 3.0 ppb.

Phase II: After the initial program, long-term measurements at lower spatial resolution of ammonia concentrations. Resolution required: Vertical, 2 km; horizontal, 100 km; temporal, weekly to monthly. Concentration range expected: 0.01 to 3.0 ppb.

(2) Carry out flux measurements of ammonia over various soils and terrain.

(3) Develop improved in situ and remote sensing methods to measure NH_3. Sensitivity desired for in situ measurements: 10 to 20 ppt.

Nitrous oxide (N_2O).- Nitrous oxide (N_2O), when transported to the stratosphere, may react with $O(^1D)$ to produce NO

$$N_2O + O(^1D) \rightarrow 2NO$$

and thus may have an impact upon stratospheric O_3. Radiative transfer calculations also indicate that N_2O, as an absorber of terrestrial radiation, contributes to the Earth's climate by means of the greenhouse effect (Yung et al. (ref. 44)).

Recent improvements in electron-capture gas chromatographic techniques for measuring ambient N_2O have established an abundance of about 330 ppb (Cicerone et al. (ref. 45)). The lack of variability in N_2O with season and location is characteristic of a long-lived gas and may indicate that the only significant sink for N_2O is photochemical destruction in the stratosphere at a rate of 9×10^8 molecules/cm^2/s. The sources of N_2O include denitrification in soils and possibly the oceans, as well as small production rates associated with anthropogenic activities. McElroy et al. (ref. 46) have argued that the oceans act as a sink for N_2O, but the data at present are conflicting and inconclusive. The possibility that atmospheric N_2O may increase due to increased industrial production of fertilizer has been addressed by several investigators; however, there is, at present, no consensus. A better knowledge of N_2O sources and sinks, as well as of the denitrification process, is needed before the impact of man's activities on N_2O in the atmosphere can be completely analyzed.

Scientific Question:

A.2.6 What are the natural sources and sinks of N_2O and what are the implications of increased use of nitrogenous fertilizers on the tropospheric N_2O budget?

Research Tasks:

(1) Conduct continuous monitoring of atmospheric N_2O concentrations. Resolution required: Vertical, 3 km; horizontal, 1000 km; temporal, monthly. Sensitivity desired: 6 ppb.

(2) Carry out N_2O flux measurements over soils and the ocean.

3. Tropospheric Carbon Budget

Carbon monoxide (CO).- Tropospheric CO is believed to be a key element in atmospheric photochemistry. The reaction

$$CO + OH \rightarrow CO_2 + H$$

is believed to be a major sink for OH and since H atoms are rapidly converted to HO_2 by

$$H + O_2 + M \rightarrow HO_2 + M$$

CO oxidation may lead to the photochemical production and/or destruction of O_3.

Before the early 1970's, the only known source of CO was anthropogenic, primarily from the internal combustion engine, and, in the absence of any known significant CO sinks, it was feared that CO levels might eventually rise to dangerously high levels. Weinstock (ref. 47), Levy (ref. 48), and McConnell et al. (ref. 49), however, alleviated these fears somewhat by pointing out that CO is produced in nature by the oxidation of CH_4 (by means of the methane oxidation chain) and that CO is photochemically removed from the atmosphere by reaction with OH. Preliminary model calculations indicated that the CO abundance was controlled by these natural photochemical processes and that anthropogenic sources of CO were probably relatively small. However, this view of atmospheric CO was hard to reconcile with observations that indicated significantly higher levels of CO in the Northern Hemisphere than in the Southern Hemisphere (Wilkniss et al. (ref. 50) and Seiler (ref. 1)). Since CH_4 has essentially the same abundance in the Northern and Southern Hemispheres, one would not expect to find a hemispheric asymmetry in CO if it was predominantly produced from CH_4 oxidation. Both Seiler (ref. 1) and Newell (ref. 51) argued that, in view of this latitudinal gradient in CO, the major source of CO must be anthropogenic emissions, which are most intense in the Northern Hemisphere.

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Although recent assessments of the CO budget indicate that 30 to 50 percent of the CO present in the atmosphere is from anthropogenic emissions that are produced at a rate of about 10^{11} molecules/cm^2/s (Seiler (ref. 1), Wofsy (ref. 52), Chameides (ref. 37), and Logan (ref. 53)), many uncertainties remain. The hemispheric asymmetry in CO is a possible measure of the importance of anthropogenic emissions of CO. Seiler (ref. 1) estimates that the average northern hemispheric and southern hemispheric CO abundances are 0.15 parts per million by volume (ppm) and 0.05 ppm, respectively. The natural sources and sinks of CO are also uncertain. The production of CO from CH_4 (on the order 10^{11} molecules/cm^2/s) is uncertain because of the lack of knowledge of the OH global distribution and the exact mode of the CH_4 decomposition; for example, if an intermediate of the CH_4 oxidation chain is removed by heterogeneous processes, the CO yield could be greatly reduced. The possible source of CO from nonmethane hydrocarbons (NMHC) is also not accurately known because of our lack of knowledge of NMHC abundances and the mode of decomposition for NMHC. The rate at which CO is attacked by OH (estimated to be as large as 3×10^{11} molecules/cm^2/s) is not accurately known because of uncertainties in both OH densities and the rate constant for the CO + OH reaction under tropospheric conditions.

The role of soils in the CO budget remains uncertain as observations indicate that, depending upon ambient CO levels and temperature, soils may act as a source or a sink for CO. Seiler (ref. 1) has suggested that the net effect is a large sink for atmospheric CO. This sink, however, is hard to reconcile with the known source strengths. Table 14 summarizes some estimates of the global budget of tropospheric CO.

TABLE 14.- GLOBAL BUDGET OF TROPOSPHERIC CO

Sources	Strength, Mt/yr
Oceans	60 to 300
Anthropogenic	500 to 700
CH_4 + OH	70 to 700
NMHC oxidation	20 to 500
Total	650 to 2200

Sinks	Strength, Mt/yr
Soils	300 to 500
CO + OH	1200 to 1900
Transport to stratosphere	10 to 60
Total	1510 to 2460

Wofsy (ref. 52) and Crutzen and Fishman (ref. 54) have found that the CO hemispheric asymmetry implies an asymmetry in OH, and Sze (ref. 55) and Chameides et al. (ref. 56) have calculated that, if CO emissions continue to increase, significant perturbations in the tropospheric photochemistry, and ultimately in the climate, may occur. The major effect thus far identified involves an increase in CO, which leads to a decrease in OH, and, consequently, to an increase in CH_4 and other gases scavenged by OH. Since CH_4 takes part in the atmospheric greenhouse effect, an increase in CH_4 will probably lead to an increase in surface temperature (Wang et al. (ref 57)). These calculations, however, remain uncertain because of uncertainties in the CO budget as well as the impact of simultaneous anthropogenic emissions of NO_x which tend to enhance OH (Liu (ref. 36) and Chameides (ref. 37)).

Photochemical model calculations, in agreement with observations of the variabilities of CO, indicate that tropospheric CO has a residence time of months. This residence time implies that both transport and photochemistry are important in controlling the CO abundance and distribution. Thus, in order to understand the detailed CO distribution, both the dynamics and photochemistry should be studied. In particular, interhemispheric exchange processes need to be investigated to understand the importance of anthropogenic processes in causing the CO hemispheric asymmetry.

Scientific Questions:

A.3.1 Are higher carbon monoxide levels in the Northern Hemisphere as compared with the Southern Hemisphere due to natural or anthropogenic processes and will continued CO emissions perturb atmospheric OH levels, especially the relative abundance in the two hemispheres?

A.3.2 Do soils always act as a sink of atmospheric carbon monoxide?

A.3.3 What is the role of nonmethane hydrocarbons in the CO budget?

A.3.4 What are the exchange mechanisms between the two hemispheres, and how important are they in controlling the CO abundance?

Research Tasks:

(1) Conduct long-term measurements of the global distribution of carbon monoxide. Simultaneously, study the global OH distribution. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hours to days. Concentration range of CO expected: 30 to 250 ppb.

(2) Measure the global distribution of nonmethane hydrocarbons. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hours to days. Concentration range expected: 0.01 to 2 ppb.

(3) Develop improved remote CO sensor.

Methane (CH_4).- Atmospheric CH_4 is produced primarily as a by-product of microbial fermentation in tropical rain forests, swamps, and rice-paddy fields, as well as a by-product of enteric fermentation in mammals. The total source strength is estimated to be about 10^{11} molecules/cm^2/s. The major sink of CH_4 is the reaction with OH

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

which leads to a long series of reactions known as the methane oxidation chain. The methane oxidation chain ultimately leads to the production of CO and H_2. The conversion of OH to HO_2 in the methane oxidation chain is also believed to affect the photochemistry of tropospheric O_3. (See section entitled "Tropospheric Ozone Budget.") It should be noted that the exact sequence of reactions in the methane oxidation chain is not well-known. Depending upon the branching ratio of several reactions, the oxidation chain could lead to either a source or a sink of HO_x free radicals. If any of the intermediate species of the methane oxidation chain are removed by heterogeneous processes, the yield of CO could be significantly less than unity.

The lifetime of CH_4 is estimated to be of the order of 10 yr and thus CH_4 exhibits very little short-term variability. The global abundance of CH_4 is believed to be about 1.6 to 1.7 ppm. Table 15 presents a summary of estimates for sources and sinks of the global budget of tropospheric CH_4.

TABLE 15.- GLOBAL BUDGET OF TROPOSPHERIC CH_4

Sources	Strength, Mt/yr
Oceans	4 to 20
Soils	500 to 800
Anthropogenic	10 to 50
Total	514 to 870

Sinks	Strength, Mt/yr
CH_4 + OH	200 to 400
Transport to stratosphere	10 to 70
Total	210 to 470

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A recent analysis of ten years of continuous data from three urban/suburban sites has led to the hypothesis of a secular trend of increasing ground level CH_4 concentrations (Graedel and McRae (ref. 58)). The possibility of a secular variation in CH_4 is of concern in view of its importance in the atmospheric photochemistry as well as its role in the atmospheric greenhouse effect as an absorber of terrestrial radiation in the 7.7-μm window region. Model calculations indicate that the CH_4 variation may be caused by a variety of processes including increases in CO, increases in NO_x, changes in stratospheric O_3, and changes in the atmospheric temperature, as well as changes in the flux of CH_4 from the surface. Many uncertainties remain. For instance, it is not clear if the CH_4 ground flux is presently increasing, decreasing, or remaining constant; increased cultivation of rice-paddy fields would increase the CH_4 flux, while deforestation of tropical rain forests and drainage of swamps would lower the CH_4 flux. A better understanding of the budgets of CO and NO_x is needed to more accurately assess the impact of future emissions of these species upon the CH_4 balance.

Research Tasks:

(1) Conduct long-term measurements of the global distribution of methane. Simultaneously, measure the OH distribution. Resolution needed: Vertical, 10 km; horizontal, 1000 km; temporal, seasonally.

(2) Conduct satellite monitoring of global land types and resources to infer the impact of man's activities upon areas of methane production.

(3) Carry out flux measurements of methane over various geographical areas.

(4) Develop remote CH_4 sensor.

Formaldehyde (H_2CO).- Atmospheric H_2CO is believed to be produced from the CH_4 oxidation chain. The oxidation of nonmethane hydrocarbons may also lead to significant H_2CO production. The chemical lifetime of H_2CO is about 1 day and is destroyed by photolysis

$$H_2CO + h\nu \rightarrow H_2 + CO$$

$$H_2CO + h\nu \rightarrow H + HCO$$

and reaction with OH

$$H_2CO + OH \rightarrow HCO + H_2O$$

Measurements of the H_2CO abundance under a variety of conditions may help to elucidate some of the steps in the methane oxidation chain as well as help to indicate the importance of nonmethane hydrocarbons relative to CH_4 in the H_2CO and CO budgets.

Research Tasks:

(1) Conduct measurements of the distribution of formaldehyde with simultaneous observations of CH_4, NMHC, OH, NO_x, and light intensity at selected global locations. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hourly. Concentration range expected: 0.02 to 1 ppb.

(2) Develop in situ and remote sensing methods to measure formaldehyde. Sensitivity desired for in situ measurements: 20 to 50 ppt.

Nonmethane hydrocarbons (NMHC).- The role of NMHC remains highly uncertain due to our lack of knowledge of the concentrations and sources of these species. Although highly reactive NMHC emitted in urban areas are believed to be responsible for photochemical smog, their short photochemical lifetimes probably preclude their having an impact in the background troposphere. However, longer lived NMHC may be important in the tropospheric photochemistry. For instance, Chameides and Cicerone (ref. 59) have found that 1 ppb of C_2H_6 and C_2H_2, with 0.1 ppb of C_3H_8, C_4H_{10}, and C_5H_{12}, can lead to a source of CO of as much as 3×10^{10} molecules/cm^2/s. Other investigators have attempted to estimate the source strength of terpenes from vegetation and have found that terpenes may lead to significant production of CO (Zimmerman et al. (ref. 60)). These NMHC may also have a significant effect upon tropospheric O_3, depending upon their degradation mode.

Research Tasks:

(1) Measure the global distribution of nonmethane hydrocarbons. These measurements can be carried out in three phases.

Phase I: High resolution spot measurements to determine which NMHC are most abundant. Concentration range expected: 0.01 to 2 ppb.

Phase II: Simultaneous NMHC measurements with CH_4, CO, OH, NO_x, O_3, and an urban tracer. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hourly. The sensitivity would be determined by the phase I studies.

Phase III: Long-term measurements of representative NMHC. Resolution required: Vertical, 1 km; horizontal, 100 km; temporal, weekly.

(2) Carry out flux measurements of nonmethane hydrocarbons over various geographical areas.

(3) Develop new in situ and remote sensing NMHC instruments for detection of C_2-C_{12} species. Sensitivity desired for in situ measurements: 0.01 ppb.

Carbon dioxide (CO_2).- The atmosphere presently contains about 330 ppm of CO_2, equivalent to 700×10^3 Mt of C. The atmospheric C content is ultimately determined by oceanic conditions (i.e., ocean temperature) since the large ocean reservoir of about 35 × 10^6 Mt of C, primarily in the form of HCO_3^-, drives the smaller atmospheric reservoir. However, because of the slow mixing time of water between the surface and deep ocean, it takes about 1000 yr for the ocean-atmosphere CO_2 system to reequilibrate after a perturbation. Thus, any process that leads to an imbalance between the rapid cycle of CO_2 production (respiration, decay, and combustion of organic material) and removal (photosynthesis) can cause a relatively long-term perturbation in the atmospheric CO_2 abundance. In view of the dominant role CO_2 plays in controlling the climate by means of the greenhouse effect, the observed increase in CO_2 of about 0.3 to 0.4 percent per year or about 2×10^3 to 3×10^3 Mt/yr of C is cause for concern - possibly the most significant environmental problem to be faced.

The increase in CO_2 has been primarily attributed to fossil-fuel burning which is growing at a rate of about 4 percent per year and currently adds about 5×10^3 Mt/yr of C to the atmosphere. The observed rate of increase of CO_2 has been explained by the fact that about 50 percent of the extra CO_2 is taken up by ocean surface layer. This view of the CO_2 buildup has been confused by the recent findings that deforestation and wood burning have been producing CO_2 at a rate approximately equivalent to the fossil-fuel burning source (Adams et al. (ref. 61)). To explain this situation, Wong (ref. 62) has proposed a more efficient oceanic pump of atmospheric CO_2 involving phytoplankton. Apparently, more research into the detailed global CO_2 cycle is needed before the relative importance of deforestation, wood burning, and fossil-fuel burning can be fully understood.

Scientific Questions:

A.3.5 Is the deforestation and wood-burning hypothesis plausible for the increase of CO_2 global concentration?

A.3.6 What are the climatic implications of changes in the atmospheric composition of trace gases such as CO_2, CH_4, N_2O, fluorocarbons, and aerosols?

Research Task:

Conduct satellite monitoring of land types, resources, and oceanic productivity to assess key parameters in the CO_2 cycle and their variation with time. Resolution required: Vertical, 3 to 5 km; horizontal, 200 km; temporal, seasonally.

4. Tropospheric Gaseous Sulfur Budget

Globally, natural emissions of hydrogen sulfide (H_2S) and/or dimethyl sulfide (CH_3SCH_3) are believed to be the single largest source of atmospheric sulfur. These emissions have been estimated to be in the range of 100 to 200 Mt/yr (Hitchcock (ref. 63) and Friend (ref. 64)). However, both the relative release rates of H_2S and CH_3SCH_3, as well as the absolute quantity of natural biospheric sulfur, are still considered to be poorly defined due to a lack of in situ concentration and flux data. The atmospheric fate of H_2S and CH_3SCH_3 has now been reasonably well established and is believed to consist of a multiple-step oxidation to SO_2, the initiation of which is reaction with OH (Cox and Sandalls (ref. 65)). In the case of H_2S, some contribution to oxidation is also thought to be made by heterogeneous O_3 reactions (Penkett (ref. 66)). The chemical conversion time for these oxidation processes can range from a few hours to a few days, depending on the steady-state concentration of the hydroxyl radical and/or ozone concentration.

Anthropogenic emissions of SO_2 are now estimated to be approximately 70 Mt/yr (Friend (ref. 64)). With the predicted increased usage of coal as an energy source, it is thus quite possible that anthropogenic sulfur emissions may soon equal those from natural biospheric sources. Recently reported global SO_2 data (Maroulis et al. (ref. 67)) suggest natural concentration levels for this species to be in the range of 207 to 37 ppt; however, at present, still too few data exist to ascertain what impact anthropogenic emissions might be having on natural SO_2 concentration levels, either on a regional or a global scale. Among the many possible concerns related to anthropogenic SO_2 emissions overtaking natural sulfur emissions is the possible effect that this acidic species (once converted to H_2SO_4) might have on global or regional levels of NH_3. An overtitration of atmospheric NH_3 could result in long-term changes in soil pH which, in turn, could have a major impact on plant-growth patterns.

The atmospheric fate of SO_2 in natural tropospheric air is chemical oxidation to H_2SO_4 and sulfates, which leads to the formation of sulfur aerosol species. Both homogeneous (predominantly reaction with OH) and heterogeneous reactions are now believed to be important in this conversion (Davis and Klauber (ref. 68), Davis et al. (ref. 21), Sander and Seinfeld (ref. 69), Calvert et al. (ref. 70), Junge and Ryan (ref. 71), and Penkett (ref. 66)). The relative importance of each mechanism, however, will obviously depend on a very large number of atmospheric variables. Under warm weather conditions where moderately high OH concentrations would exist, a chemical conversion time for SO_2 of a few days is expected.

Carbonyl sulfide, COS, has only recently been identified in the troposphere (Maroulis et al. (ref. 72)). Recent global measurements of this species (Torres et al. (ref. 73)) indicate that a near-uniform distribution exists throughout the lower atmosphere. The sources of this sulfur gas are presently poorly defined. Its chemical lifetime would appear to be several years; thus, it is quite possible that diffusion into the lower stratosphere, followed by photodissociation, is the most likely sink for COS. If the major source of COS is anthropogenic emissions (possibly CS_2), the resulting formation of H_2SO_4 aerosol in the lower stratosphere could have possible long-range consequences in terms of its effect on the atmospheric radiation balance (Crutzen (ref. 74).

Scientific Questions:

A.4.1 What is the yearly quantity of sulfur now being released from the natural biosphere, and what are the major chemical forms in which this sulfur is being released?

A.4.2 What is the global distribution of SO_2?

A.4.3 What are the short-term and long-term impacts of anthropogenic emissions of SO_2 on the tropospheric sulfur budget and on the budgets of other trace gases such as NH_3?

A.4.4 What is the relative importance of homogeneous versus heterogeneous processes in the SO_2 gas-to-particle conversion cycle?

A.4.5 What are the major sources of tropospheric COS? And, if man's activities are a major source, what might be the climatic implications of a COS buildup in the atmosphere?

Research Tasks:

(1) Carry out flux measurements of H_2S and CH_3SCH_3 over different geographical areas.

(2) Measure the global distribution of SO_2. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, daily to weekly. Concentration range expected: 0.01 to 1.0 ppb.

(3) Measure the global distribution of COS as well as the concentrations in the vicinity of volcanoes, power plants, and swamps. Resolution required: Vertical, 1 to 3 km; horizontal, 100 km; temporal, monthly.

(4) Measure the distribution of sulfates in aerosols and rainwater.

(5) Develop one new in situ and remote sensing method for measuring COS. Sensitivity desired for in situ measurements: 10 to 20 ppt.

(6) Develop one new in situ and remote sensing method for monitoring SO_2. Sensitivity desired for in situ measurements: 10 ppt.

(7) Develop one new in situ method to measure H_2S, CH_3SCH_3, and CS_2. Sensitivity desired for in situ measurements: 5 to 10 ppt.

5. Tropospheric H_xO_y (OH, H, HO_2, and H_2O_2)

On the basis of both kinetic data (ref. 75) and recent OH field measurements (refs. 20, 21, 76, 77, and 78), it has now been established that the OH radical plays a major role in the oxidation of several tropospheric trace gases, for example,

$$\text{(R31)}\quad SO_2 + OH \xrightarrow{M} HSO_3\cdot \xrightarrow[\text{steps}]{\text{Multiple}} H_2SO_4$$

(R32) $H_2S + OH \longrightarrow HS\cdot + H_2O \xrightarrow[\text{steps}]{\text{Multiple}} SO_2$

(R33) $CH_3SCH_3 + OH \longrightarrow CH_3SCH_2\cdot + H_2O \xrightarrow[\text{steps}]{\text{Multiple}} SO_2, CO$

(R34) $CH_4 + OH \longrightarrow CH_3\cdot + H_2O \xrightarrow[\text{steps}]{\text{Multiple}} CO$

(R35) (High MW hydrocarbons)$RH + OH \longrightarrow R\cdot + H_2O \xrightarrow[\text{steps}]{\text{Multiple}} CO$

(R36) $C_xH_uCl_vF_w + OH \longrightarrow C_xH_{u-1}Cl_vF_w\cdot + H_2O \xrightarrow[\text{steps}]{\text{Multiple}} CO, HF, HCl$

(R37) $CO + OH \longrightarrow CO_2 + H$

(R38) $NO_2 + OH \xrightarrow{N_2/O_2} HNO_3$

where MW is molecular weight.

The relative importance of the OH oxidation process as compared with other possible mechanisms is strongly dependent on a large number of atmospheric variables which collectively control the steady-state concentration of the OH radical. As a direct result of this, the tropospheric OH concentration is highly variable both spatially and temporally. Even in the Tropics, where average midday boundary-layer OH levels were found to be $8.5 \times 10^6/cm^3$, variations of a factor of five to six were observed in the midday OH concentration, due primarily to changes in the O_3 level at different times of the year. In the same geographical area, still larger variations in OH concentration were observed in the middle free-troposphere, reflecting major variations in H_2O and, to a lesser extent, O_3 levels. Variations in the NO concentration may also have been important; however, only upper limit measurements of the concentration of this species were possible at that time.

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The primary mechanism by which atmospheric OH radicals are generated is given by the reaction scheme

$$\text{(R39)}\quad O_3 + h\nu \xrightarrow{\lambda<3150\text{Å}} O(^1D) + O_2$$

$$\text{(R40)}\quad O(^1D) + N_2 \longrightarrow O(^3P) + N_2$$

$$\text{(R41)}\quad O(^1D) + H_2O \longrightarrow 2\ OH$$

Thus, the UV solar flux, ozone concentration, and the absolute water content of the atmosphere have a near-linear effect on the rate of production of OH. Possible loss processes for the OH radical are reactions (R34) and (R37). Taking the coupled set of reactions (R39), (R40), (R41), (R34), and (R37) as the major formation and loss processes that control the OH concentration, the OH concentration at photochemical equilibrium (PE) is given by

$$[OH]_{PE} = \frac{2k_{41}[H_2O]\dfrac{J_{39}[O_3]}{k_{40}[N_2] + k_{41}[H_2O]}}{k_{34}[CH_4] + k_{37}[CO]} \qquad (1)$$

Equation (1), however, is based on the assumption that all CH_3 radicals generated from reaction (R34) go on to react in such a way that no additional OH radicals are produced or destroyed. In fact, depending on the levels of other atmospheric trace gases (e.g., NO) and on the detailed degradation cycle chosen for the CH_3 radical, as many as three OH radicals could be generated from each CH_3 species. Thus, the possibility exists that reaction (R34) could lead to a net secondary source of OH radicals. This secondary OH source can be incorporated into equation (1) by modifying the term $k_{34}\ [CH_4]$ to read as shown in the following:

$$[OH]_{PE} = \frac{2k_{41}[H_2O]\dfrac{J_{39}[O_3]}{k_{40}[N_2] + k_{41}[H_2O]}}{k_{37}\ [CO] - k_{34}(x - 1)[CH_4]} \qquad (2)$$

where the values of x can be 0, 1, 2, etc., and correspond to

$CH_3 \rightarrow 0\ OH,\ x = 0$

$CH_3 \rightarrow 1\ OH,\ x = 1$

$CH_3 \rightarrow 2\ OH,\ x = 2$

A final complication not taken into consideration by the scheme of reactions (R39), (R40), (R41), (R34), and (R37) involves the assumption that all H atoms produced in reaction (R37) react with O_2 to produce HO_2 radicals which, in turn, are systematically converted into hydrogen peroxide (H_2O_2). It is further assumed that this H_2O_2 species is completely removed from the atmosphere via washout processes, that is,

(R42) $H + O_2 \xrightarrow{N_2/O_2} HO_2$

(R43) $HO_2 + HO_2 \longrightarrow \underset{\text{Washout and/or rainout}}{H_2O_2\downarrow} + O_2$

There are, however, at least two significant shortcomings with the preceding scheme. First, H_2O_2 may not be removed from the atmosphere by heterogeneous processes with 100-percent efficiency: H_2O_2 can undergo photolysis to produce two new OH radicals or it may react with OH to produce H_2O and an HO_2 radical. Second, the HO_2 species can react in at least two additional modes other than reaction (R43); that is,

(R44) $HO_2 + NO \longrightarrow OH + NO_2$

or

(R45) $HO_2 + OH \longrightarrow H_2O + O_2$

Reaction (R44) would, in effect, decrease the efficiency of reaction (R37) as a removal process for OH whereas reaction (R45) would tend to increase the apparent efficiency of reaction (R37). The net effect of these additional reactions on the photochemical stationary state concentration of OH cannot be specified in any simple expression. Detailed modeling calculations show that the impact of this additional chemistry is critically dependent on the absolute HO_x radical concentration, as well as on the NO level. Nitric oxide concentrations as low as 10 to 20 ppt now appear to have a significant impact on the calculated values of $[OH]_{PE}$.

Only within the last year has it even been possible to carry out a quantitative test of the validity of equation (2). The comparisons made between experimentally measured OH concentrations and calculated OH values, by using simultaneously collected data on CO, O_3, H_2O, CH_4, and the UV flux, have now shown reasonable agreement (to within a factor of 1.5) for clean tropospheric air (ref. 79). More extensive comparisons will require reliable data on NO, H_2O_2, CH_2O, and CH_3OOH plus more accurate values for several gas kinetic rate constants.

Scientific Questions:

A.5.1 What is the reliability of present photochemical theory in predicting H_xO_y distributions in both urban and remote atmospheric air parcels?

A.5.2 Can the asymmetry in global CO levels lead to asymmetry in global OH distributions?

A.5.3 What is the lifetime of H_2O_2 in the atmosphere, and what are major sinks for this compound?

Research Tasks:

(1) Measure the global concentration distributions of OH and HO_2. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hourly. Concentration range expected: 10^5 to 10^9 molecules/cm^3.

(2) Measure the global concentration distribution of H_2O_2. Resolution required: Vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, hours to days. Concentration range expected: 0.01 to 10 ppb.

(3) Develop new in situ methods to measure OH, HO_2, and H_2O_2. Sensitivity desired for in situ measurements: 10^6 molecules/cm^3 for OH, 1 ppt for HO_2, and 50 ppt for H_2O_2.

(4) Develop a remote sensing instrument for measuring H_2O.

6. Tropospheric Gaseous Halogens

At the present time, those halogenated species which have been detected in the troposphere are listed in table 16 (from refs. 79 and 80).

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TABLE 16.- ATMOSPHERIC HALOGEN SPECIES

Compound		Quality of data (a)	Mixing ratio, ppt
Natural	CH_3Cl (methyl chloride)	B	[b]~800; 630
	CH_3Br (methyl bromide)	C	<10
	CH_3I (methyl iodide)	C	~10
	HCl (hydrochloric acid)	C	100 to 1000 (200 typical)
?	CH_3CCl_3 (methyl chloroform)	B	~100
Anthropogenic	CCl_4 (tetrachloride)	B	~135
	CF_2Cl_2	B	200 to 230
	$CFCl_3$	B	100 to 140
	$CHCl_2F$	C	<10
	C_2Cl_3F	C	~20
	$CHCl_3$ (chloroform)	C	~20
	C_2Cl_4 (ethylene)	C	~30
	C_2HCl_3 (ethylene trichloride)	C	~20
	SF_6 (sulfur hexafluoride)	C	~0.2

[a] A - Excellent data base; uncertainty in global distribution no greater than 5 percent
B - Fair data base; uncertainties still equal to or exceeding 15 percent
C - Fragmentary information

[b] 800 ppt in tropical and subtropical boundary-layer air; 630 ppt in tropical and subtropical free tropospheric air.

As noted in table 16, of the 14 halogen species that have now been detected in the troposphere, only 4 can be clearly characterized as resulting from predominantly natural emissions. Good evidence now exists that indicates that all four of these species have an oceanic source. Recent data indicate that CH_3Cl, CH_3Br, and CH_3I are released directly into the atmosphere. On the other hand, HCl would appear to be the product of both gas-phase chemistry and heterogeneous chemistry. The gas-phase source involves the OH-initiated degradation of CH_3Cl (Davis et al. (ref. 21)); that is,

$$\text{(R46)}\quad CH_3Cl + OH \longrightarrow CH_2Cl + H_2O$$

$$\text{(R47)}\quad CH_2Cl \xrightarrow{\text{Multiple steps}} HCl,\ CO,\ H_2O$$

In this system, the rate determining step for the formation of HCl from CH_3Cl is reaction (R46). The second source of HCl is now believed to involve the reaction of HNO_3 with Cl^- in cloud droplets, the net reaction being

$$\text{(R48)}\quad HNO_{3(g)} + Cl^-_{(s)} \xrightarrow{H_2O} HCl_{(g)} + NO^-_{3(s)}$$

where subscripts (g) and (s) indicate gaseous and solid forms, respectively.

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More data are needed to determine the relative importance of reactions (R46) and (R48) in the production of HCl. The chemical lifetimes of both CH_3Cl and CH_3Br are dictated by their rates of reaction with atmospheric OH radicals; whereas for CH_3I, both photodegradation and reaction with OH would appear to be important. The atmospheric lifetime of HCl is undoubtedly controlled by washout and rainout; however, the efficiency of these processes is still poorly documented. Recent global tropospheric data would strongly suggest that the acidity of rainwater in remote areas of the world is primarily controlled by the presence of HCl and HNO_3.

The atmospheric origin of methyl chloroform has, up until recently, been considered anthropogenic in nature. Earlier measurements designed to determine the average interhemispheric gradients for this species resulted in reported values of approximately 1.5 (Singh (ref. 81)). However, recent field measurements have suggested an average interhemispheric gradient of 10 to 25 percent. Since the principal mode of degradation for this compound is reaction with OH, several investigators have used the interhemispheric concentration gradient to calculate an average global OH concentration (Singh (ref. 81) and Crutzen and Fishman (ref. 54)). If these recent data are correct, one would be forced to conclude that either the average global OH concentration is insignificantly small ($<1 \times 10^5$ molecules/cm^3) or there are natural global sources of CH_3CCl_3. The former conclusion would appear to be inconsistent with existing OH field data.

The last set of compounds listed in table 16 are all believed to have anthropogenic sources. The chemical lifetimes of these species vary enormously, depending on whether a given compound is liable to be attacked by OH radicals. Those compounds having either a double bond or a C-H bond fall into the latter category (i.e., $CHCl_2F$, C_2Cl_3F, $CHCl_3$, C_2Cl_4, and C_2HCl_3). On the other hand, CCl_4, CF_2Cl_2, and $CFCl_3$ are projected to have lifetimes in the range of 20 to 200 yr. For those molecules having lifetimes greater than about 10 yr, approximately 10 percent of the tropospheric burden would diffuse into the stratosphere and be photodecomposed. For a 20-yr lifetime, approximately 25 percent of the released halocarbon would end up being removed by means of diffusion into the stratosphere. In all cases, it is believed that released chlorine in the stratosphere would result in a systematic reduction in the stratospheric mixing ratio of ozone.

For comparison purposes, the lifetimes of several compounds listed in table 16 have been given in table 17. These lifetime calculations are based on rate constants k (ref. 75) for reaction with OH, taking 268 K as the average tropospheric temperature. The global average OH concentration $[OH]_{av}$ was taken to be either 9×10^5 or 3×10^5 molecules/cm^3.

TABLE 17.- CHEMICAL LIFETIMES

Compound	k at 268 K, cm^3/molecule/s	Lifetime, yr, for $[OH]_{av}$ of -	
		9×10^5 molecules/cm^3	3×10^5 molecules/cm^3
CH_3Cl	3.0×10^{-14}	1.2	3.6
CH_3Br	2.7×10^{-14}	1.3	3.9
$CHCl_2F$	1.7×10^{-14}	2.1	6.3
$CHCl_3$	6.4×10^{-14}	.6	1.8
CH_3CCl_3	8.0×10^{-15}	4.4	13.2
C_2Cl_4	1.0×10^{-14}	3.2	9.6

Scientific Questions:

A.6.1 What importance (in terms of a global average concentration value for OH) can be assigned to the interhemispheric gradient in methyl chloroform?

A.6.2 What are the major sources of atmospheric HCl and how important is this in determining rain acidity in both remote and urban areas?

A.6.3 What are the stratospheric implications of anthropogenic releases of halocarbons (such as CH_3CCl_3, $CHCl_2F$, and $CHClF_2$) in terms of their OH-controlled chemical lifetimes in the troposphere?

Research Tasks:

(1) Conduct global measurements of the distribution of halogen species (e.g., CH_3CCl_3, CH_3Cl, fluorocarbons, HCl, and Cl^-). Resolution required: For CH_3CCl_3 and fluorocarbons - vertical, 3 to 5 km; horizontal, 1000 km; temporal, seasonally; and for CH_3Cl and HCl - vertical, 0.2 to 1 km; horizontal, 5 to 100 km; temporal, daily to weekly. Concentration range expected: For CH_3Cl, 0.3 to 1.0 ppb; and for HCl, 0.01 to 3 ppb.

(2) Develop one new in situ and remote sensing method to measure HCl and CH_3Cl. Sensitivity desired for in situ measurements: 20 ppt.

7. Global Aerosol Budget

It is now well established that one of the major consequences of fossil-fuel combustion is the increased aerosol burden of the atmosphere. On a global basis, it is estimated that approximately 10 percent of the total particulate emission to the atmosphere results from anthropogenic activities, the remaining 90 percent being from such natural sources as ocean spray, wind blown dust, and volcanic eruption. However, all atmospheric particles are eventually returned to the ground through such processes as sedimentation, diffusion, rainout, and washout. The lifetime of atmospheric aerosols may range from a few days in the lower troposphere to several months in the stratosphere.

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Aside from their potential health effects in heavily polluted areas, atmospheric aerosols are of interest because of their effect on visibility, on rain pH, and on the radiation balance of the atmosphere. They are also known to affect the precipitation process and may have other inadvertent weather modification effects.

A major concern of increased fossil-fuel combustion, particularly the combustion of coal containing sulfur, is the increased emission of SO_2. In the atmosphere, SO_2 is photooxidized to form sulfuric acid and sulfates, both of which exist in particulate form. These particles containing sulfur can cause reduced visibility. They also lower the pH of rain and other forms of precipitation, with potentially disastrous effects on aquatic life in fresh water lakes and on agricultural production through modification of soil pH and chemistry.

Although many of the consequences of an increased atmospheric aerosol burden have been identified or postulated, the quantitative understanding of the processes involved remains at best incomplete. There is a need for a carefully planned program of scientific study in order to gain a better understanding of the processes involved in the generation, conversion, transformation, transport, and removal of atmospheric particulates. With improved understanding, the environmental consequence of increased atmospheric aerosol burden can then be more accurately assessed.

The behavior of the aerosol and the effects it produces are dependent upon the concentration, size distribution, and the chemical composition of the particles. The concentration of atmospheric aerosols may range from a few $\mu g/m^3$ at remote and background sites in the lower troposphere to several hundred $\mu g/m^3$ in heavily polluted areas. The size distribution of the aerosol is typically bimodal, with a fine-particle mode located at about 0.3 μm and a coarse-particle mode in the 5- to 50-μm range, depending on the specific location involved. Near combustion sources, a third mode in the 0.01- to 0.1-μm range sometimes also appears. The major constituents of atmospheric particles include sulfate, nitrate, organics, soot, and inorganic matter (including Na, Si, etc.). Most of the data on the concentration, size distribution, and chemical composition of atmospheric aerosols are for urban areas. There are comparatively fewer data for remote and background sites, and even more limited data on the vertical profile of atmospheric aerosols. One of the major needs is to obtain a more extensive data base on the spatial and temporal distributions of atmospheric aerosols, including the concentration and size distribution in the 0.002- to 10-μm-diameter range, and under special conditions in the 0.002- to 50-μm-diameter range. The chemical composition of the aerosol must also be determined for various classes of conditions.

One of the major questions regarding the climatic effects of increased atmospheric aerosol burden is the effect of the aerosol on the radiation balance of the atmosphere. In order to make an accurate assessment of the effect of aerosol on the radiative balance of the atmosphere, the optical properties of the particles must be known. This would require measuring the refractive index and absorption coefficient of the particles. Lack of data on the optical properties of atmospheric aerosols has made past predictions somewhat uncertain.

There is considerable controversy regarding the relative role of homogeneous and heterogeneous reactions in the conversion of gaseous pollutants, particularly SO_2, into particulate form. Experiments should be designed and conducted in order to assess the relative importance of the homogeneous and heterogeneous reaction mechanisms.

The recent observation of the extensive areas of haze covering thousands of square kilometers of areas in the United States through satellite photographs suggests that there is large-scale transport of pollutants across the continental United States. The origin and movement of such hazes should be more carefully studied and their implication in terms of ambient air quality standards assessed.

Scientific Questions:

A.7.1 What are the optical properties of tropospheric aerosols?

A.7.2 What are the physical and chemical properties of tropospheric aerosols?

A.7.3 How do aerosols influence the tropospheric radiation balance?

A.7.4 What is the origin and fate of large-scale tropospheric haze?

Research Task:

Measure globally the size distribution, refractive index, chemical composition, and vertical distribution of aerosols.

B. REGIONAL AIR POLLUTION AND LONG-RANGE TRANSPORT

1. Meteorological Aspects of Long-Range Pollutant Transport

Some of the meteorological processes that play a dominant role in the dispersion of pollutants on large temporal and spatial scales have a negligible effect at smaller scales, and vice versa. Among the processes that have a significant impact on dispersion over regions of 1000 km in size and over periods of several days but which are usually insignificant on smaller scales (and hence are neglected in most urban diffusion models) are the following:

(1) Vertical velocities induced by horizontal divergence in the synoptic scale flow, by Ekman pumping in the boundary layer, by convective clouds, and by other phenomena

(2) Wet and dry removal processes; that is, rainout, washout, and deposition

(3) Fluctuations in the horizontal flow where scales are larger than that of turbulence but smaller than that resolvable by the wind data network

(4) Wind shear

The effects of these processes and particularly their combined effects are presently the most poorly understood meteorological aspects of long-range pollutant transport, dispersion, and removal.

Vertical velocities.- Divergence in the synoptic and mesoscale horizontal wind regimes leads to vertical air motions. Also, vertical currents, which give rise to the phenomenon known as Ekman pumping, are generated by viscous forces in the boundary layer and can be particularly large in regions of complex terrain. Although the vertical velocities generated by these processes have a magnitude of only 1 to 10 cm/s, they can carry pollutants to the upper reaches of the troposphere in the time required to traverse a horizontal distance of 1000 km.

The effects of vertical velocities on material transport in diffusion models can be described, but it is not known whether the estimates of the magnitudes of these velocities that are inferred from available meteorological data are sufficiently accurate to provide an adequate description of the vertical transport of pollutants. To resolve this question, measurements are needed of the vertical profiles of inert pollutant species concentrations over a region of about 1000 km in size with a horizontal resolution of roughly 10 km and a vertical resolution of 1 km.

Convective clouds can produce vertical velocities 100 times larger than those produced by the two processes cited previously. Although individual clouds may be no larger than about 1 km in width, large populations of them act in concert to transport heat, momentum, moisture, and pollutants out of the mixed layer (or boundary layer) adjacent to the earth and into the so-called free atmosphere above (the layer above about 1 km). At the same time, these clouds force air from the free atmosphere down into the mixed layer. Clouds also provide a liquid water medium in which chemical reactions other than those observed in dry air can occur.

At present, there is no detailed information about the effects of clouds on pollutants; there are only unanswered questions. For example, is the net upward flux of pollutants in a large population of convective clouds (and the compensatory downward flux of material from the free atmosphere) uniquely related to some averaged, measurable properties of the atmosphere? Are pollutants that are transported upward in convective clouds deposited at some specific level such as cloud top height, or are they more uniformly distributed in the cloud layer? What chemical processes occur among pollutants in clouds and what products are ejected by clouds or left behind when clouds evaporate?

In order to answer these questions, detailed measurements of inert and reactive pollutant concentrations in and around large cumulus clouds are needed, particularly those deeper than about one-half the mixed-layer depth. To investigate the cloud flux questions, vertical concentration profile measurements of an inert pollutant are needed over a horizontal area several hundred kilometers in size and extending from the ground to an elevation of about 5 km. Vertically integrated concentrations would suffice, provided they are given for both the cloud layer (i.e., the region between cloud base and mean cloud top) and the subcloud layer. A horizontal resolution of at least 10 km is required.

APPENDIX A

Wet and dry removal processes.- Rainout, washout, and dry deposition are the only processes by which pollutants are eventually removed from the atmosphere. Since each of these phenomena tends to be correlated to some extent with horizontal flow direction, it is likely that the region over which pollutants from a given site are eventually removed displays distinct directional characteristics. For example, southwesterly flows on the east side of troughs are usually associated with ascending motion and hence clouds and precipitation. Conversely, northwesterly flows on the east side of ridges are generally associated with subsidence and hence clear skies and the trapping of pollutants below low-level inversions. The trapping effect would tend to elevate ground-level concentrations, and this, in turn, might enhance the rate of dry removal (although in the case of SO_2, the deposition process might be inhibited by the photooxidation of SO_2 to sulfate). On the basis of this simplified picture, one might expect that, averaged over a long period of time, a given pollutant source will have the greatest impact on ground-level concentrations to the southeast of the source and the greatest contaminating effect on precipitation (e.g., acid rain production) at sites to the northeast.

Knowing whether such patterns exist is of obvious importance to national land-use planning and emissions-control strategy studies. For these and other purposes, quantitative knowledge is required of the regions over which pollutants from a given source site are deposited, both by rainfall and surface uptake, and of the amounts deposited annually at all points within this region. One of the major issues that must be faced before removal patterns can be delineated by modeling studies is determining the amount of material removed as a function of rainfall rate, material concentration, and perhaps other parameters in both convective and frontal precipitation systems. Estimates of removal rates on convective precipitation can be obtained from vertically integrated pollutant concentrations made continually for about a 24-hr period over a region in which an isolated thunderstorm occurs. Integration through the depth of the troposphere and over the horizontal area covered by the storm during its lifetime (about 100 km) is required. Horizontal resolution is not essential. Estimates of pollutant removal rates in frontal precipitation systems (e.g., extratropical cyclones) require similar observations except, in this case, the horizontal area covered must be about 1000 km and horizontal and vertical resolutions of about 10 km and 500 m, respectively, are desirable. Vertically integrated concentrations combined with surface measurements might suffice.

Horizontal wind fluctuation effects.- The wind data required in models of long-range pollutant transport are obtained either from historical wind measurements or from a simulation of the wind fields. Measured data are available from a network of stations spaced roughly 100 km apart; simulated wind data can be obtained on horizontal grids as small as about 10 km. Regardless of the wind data source, the effects on pollutant transport of wind fluctuations or eddies that are larger than the spatial resolution of the data are treated explicitly in the diffusion model. Eddies smaller than about 1 km are categorized as turbulence and their combined effects are parameterized in dispersion models by a diffusivity term. An important question at present is whether the diffusivity approximations used to represent turbulence effects can be "scaled up" to describe the impact on pollutant dispersion of eddies larger than the turbulence scale but smaller than the spatial resolution of the wind data. To answer this question, point-source plume observations are needed over distances up to 1000 km from the source. Vertically integrated concentrations of an inert pollutant with a horizontal resolution of about 1 km would suffice for this purpose.

Wind shear effects.- During daylight hours when the mixed layer is unstably stratified and confined below an inversion layer, wind shear in the mixed layer is confined to a very shallow layer next to the ground. Under these conditions, the flow has approximately the same speed and direction at all levels in the mixed layer and pollutant transport is rather easily described. At night, conditions are much more complicated. Contaminants that are in the lower portion of the mixed layer at sundown may become stalled in the calms that accompany ground-based radiation inversions, or the direction of motion of these contaminants may be altered by the shallow drainage winds that are common in regions of complex terrain. At the same time, contaminants that were in the upper portion of the mixed layer at sunset may continue on their way through the night unimpeded or they may be accelerated by the low-level nocturnal jet. As a result, by morning, contaminants that were part of the same vertical column the previous afternoon may be scattered over horizontal distances of tens or even hundreds of kilometers. The same type of distortion process is active during all hours when the boundary layer is neutrally stratified.

To investigate wind-shear effects and to develop ways of treating them in long-range transport models, elevated point-source plume observations are needed, especially at night. Vertical profiles of inert species concentrations are required over distances up to several hundred kilometers from the source and extending from the ground to an elevation of about 1 km. A horizontal resolution of about 100 m and a vertical resolution of about 50 m are required in the concentration measurements. To facilitate both the interpretation of these data and their ultimate use in long-range transport model development, wind measurements should be made concurrently with the concentrations. It is also important that the plume and wind observation be made over both smooth and complex terrain.

Relationship of measurements and model predictions.- The disparity between the spatial and temporal scales of measurements and model predictions often leads to difficulty in assessing model performance. Measurements may be made in any of the following four combinations:

		Spatial scale	
		Point	Spatial average
Temporal scale	Instantaneous measurement		
	Time-average measurement		

Model predictions are usually based on solutions of equations that involve both spatial and temporal averaging. An important need in model development and evaluation is reconciliation of the scales of measurements and predictions.

Scientific Questions:

B.1.1 What are the meteorological processes governing the long-range transport of pollutants?

B.1.2 What is the relative importance of the various removal processes on the long-range transport of pollutants?

Research Tasks:

(1) Develop mesoscale models of atmospheric transport, transformation, and removal of pollutants.

(2) Measure pollutant removal during precipitation processes.

(3) Measure the long-range characteristics of pollutant plumes, especially during nighttime conditions.

(4) Conduct detailed measurements of the flow fields in complex terrain.

(5) Measure transport rates between the mixed layer and the free troposphere.

(6) Continuously measure vertical temperature profiles, mixing depth, and surface heat flux to support model development and validation.

(7) Develop techniques to relate measurements (both in situ and remote) to model predictions.

2. Chemical Processes During Pollutant Transport

The object of the study of transport and removal processes of pollutant species is development of the capability to predict their atmospheric residence time as they are transported downwind from a source-rich area. Several recent investigations have been made in which measurements (usually airborne) have been conducted downwind of large urban complexes to obtain material balances on gaseous and particulate pollutants. A goal of these studies is to determine the relative roles of transport, conversion of gaseous to particulate pollutants, and removal.

The general behavior of pollutants in the urban plume can be described as follows. Primary gaseous emissions are converted partly to secondary gaseous species within the urban atmosphere as a result of gas-phase reactions. Simultaneously, the secondary species are converted to the particulate phase by further chemical reaction or by absorption into existing particles. The mixture of gases and particles is transported downwind of the urban region, accompanied by continuous conversion of more of the primary gases to particulate material. Occurring simultaneously is surface absorption of primary gases as well as particles containing secondary species. Eventually, rainout and washout will serve to remove the remaining gases and existing particles.

Transformation of SO_2 to sulfate.- Sulfur dioxide undergoes chemical reactions in the atmosphere which leads to a change in oxidation state, principally to $SO_4^=$ in the particulate form. The questions of main concern relative to the conversion of SO_2 to sulfate pertain to (1) the mechanism and rate of conversion and (2) the chemical and physical properties of the particulate sulfur.

From the point of view of understanding sulfate levels, the most important questions are:

(1) Are the oxidizing agents of SO_2 man-made and can they be controlled? If SO_2 oxidation is promoted by man-made oxidizing agents (as it is now suspected), then the specific role of those substances (e.g., the hydroxyl radical) should be established and the means of their control should be explored.

(2) Do natural (e.g., meteorological) parameters influence SO_2 conversion? Temperature, humidity, solar radiation, or any other natural parameter may influence the conversion rate.

(3) What is the chemical composition of the particulate sulfur? Acidic aerosol is believed to be environmentally more harmful than neutral aerosol. The conditions that favor acid aerosol formation should be established.

In order to answer these questions, an understanding of the SO_2 conversion mechanisms is necessary. There are four mechanisms that are believed to be of significance for atmospheric SO_2 conversion:

(1) Indirect photooxidation

(2) Catalytic SO_2 oxidation

(3) Oxidation in the liquid phase by strong oxidants

(4) Surface catalyzed oxidation of SO_2

(1) Indirect photooxidation occurs following gas-phase reaction of SO_2 with strong oxidizing radicals such as OH, HO_2, and CH_3O_2. The sources of these radicals in the polluted troposphere are hydrocarbon and NO_x emissions which, in the process of daytime photooxidation, produce oxidizing radicals as intermediate products. The SO_2 oxidation step is therefore indirectly linked to smog photochemistry. The chemical kinetics of this mechanism have been formulated in models using measured rate constants (Sander and Seinfeld (ref. 69), Calvert et al. (ref. 70), and Davis et al. (ref. 21)). An unambiguous confirmation of the importance of the homogeneous conversion mechanism would require the direct observation of the participating free radicals (e.g., OH, HO_2, and CH_3O_2) simultaneously with SO_2 and $SO_4^=$ under a variety of atmospheric conditions. Currently, such data are not available. Simulations of chemical kinetics for typical urban mixtures indicate conversion rates of 2 to 4 percent per hour for sunny days (refs. 21 and 70). Eggleton and Cox (ref. 82), in a summary of European results, conclude that in the western European summer, SO_2 oxidation

rates due to gas-phase, radical reactions in sunlight are expected to be between 0.5 and 5 percent per hour, depending on the degree of pollution of the atmosphere. In the winter, because of the reduced sunlight intensity and duration, the conversion rates are expected to be slower by at least a factor of 2 to 5. The specific roles of temperature, dew point, solar radiation intensity, and so forth on the indirect photooxidation require systematic future studies.

(2) Catalytic SO_2 oxidation in droplets has been studied extensively but the results regarding its role in the atmosphere are uncertain. The concensus at the International Symposium on Sulfur in the Atmosphere is as follows (ref. 83):

> "The catalyzed oxidation of SO_2 in solution by transition metals (e.g., Fe, Mn) is believed to be important in situations in which relatively high ($>10^{-5}$ M[molar]) concentrations of catalyst are present in the droplet and in which the total atmospheric concentrations of the catalytic elements are also high. Such conditions can exist in urban and stack plumes and perhaps in urban fogs. In cleaner rural air this reaction would occur only in clouds. However, unless the pH and metal concentrations in cloud water are substantially different from those in rain water, this process is unlikely to be of significance. Both laboratory and field studies of such reactions are necessary."

(3) Oxidation in the liquid phase by strong oxidants, such as ozone and H_2O_2, can be comparable with or exceed the indirect photooxidation rate (Eggleton and Cox (ref. 82) and Beilke and Gravenhorst (ref. 84)). However, current oxidation-rate data vary too widely to permit quantitative assessment of their atmospheric importance. The ozone and H_2O_2 in urban atmospheres arise in photochemical smog. Within clouds or fogs, such gases are rapidly absorbed into water droplets. Measurements of H_2O_2 in polluted and clean atmospheres are necessary to assess the importance of this mechanism of SO_2 oxidation.

(4) Surface catalyzed oxidation of SO_2 upon collision with solid particles, particularly elemental carbon (soot), has been demonstrated (Novakov et al. ref. 85)). Measurements of aerosol soot levels in plumes are needed to assess the applicability of laboratory studies to the atmosphere. Common features of the SO_2 conversion mechanisms are that the rate-controlling species can be identified and may, in principle, be controlled independently from SO_2.

The residence time and transport distance of sulfur are determined by the overall removal rate of sulfur compounds from the atmosphere. The overall removal has four major components: (1) Dry removal of SO_2, (2) wet removal of SO_2, (3) dry removal of $SO_4^=$, and (4) wet removal of $SO_4^=$. Dry removal of SO_2 and wet removal of $SO_4^=$ appear to be the two major components and are described as follows:

> Dry removal is a mass transfer process whereby SO_2 is first transported to surfaces by turbulent and molecular diffusion and then removed by adsorption or absorption at the surface. The overall mass

transfer rate can be characterized by a mass transfer coefficient, called a deposition velocity, and the difference between the bulk and surface concentrations.

Wet removal of sulfur compounds involves collection of material into cloud droplets with the subsequent deposition in rain. The wet removal rate, therefore, can be estimated from the sulfur content and the rate of rainfall.

Wet and dry removal rates are evidently of comparable magnitude; dry deposition dominates the SO_2 removal (about 60 percent of the total) and wet deposition dominates the $SO_4^=$ removal (40 percent). Both removal processes limit the lifetime of sulfur compounds to 2 to 3 days. The residence time of SO_2 is determined by the competing rates of transformation to sulfate and removal of SO_2 and $SO_4^=$. For a conversion rate of 1 to 2 percent per hour and an overall removal rate of 2 to 5 percent per hour, a characteristic residence time of 14 to 33 hr is obtained for SO_2. The residence time of sulfate is the sum of the formation and removal times. According to current estimates, the sulfate residence time is between 3 and 5 days. A typical transport speed in the planetary boundary layer is about 500 km/day; hence, transport distances are on the order of 500 km for SO_2 and 3000 km for sulfate. The meteorological framework in which sulfur transport needs to be considered is therefore the synoptic scale.

Transformation of NO_x to nitrate.- Figure A1 depicts the potential paths by which particulate nitrate species may be formed from NO and NO_2. Path 1

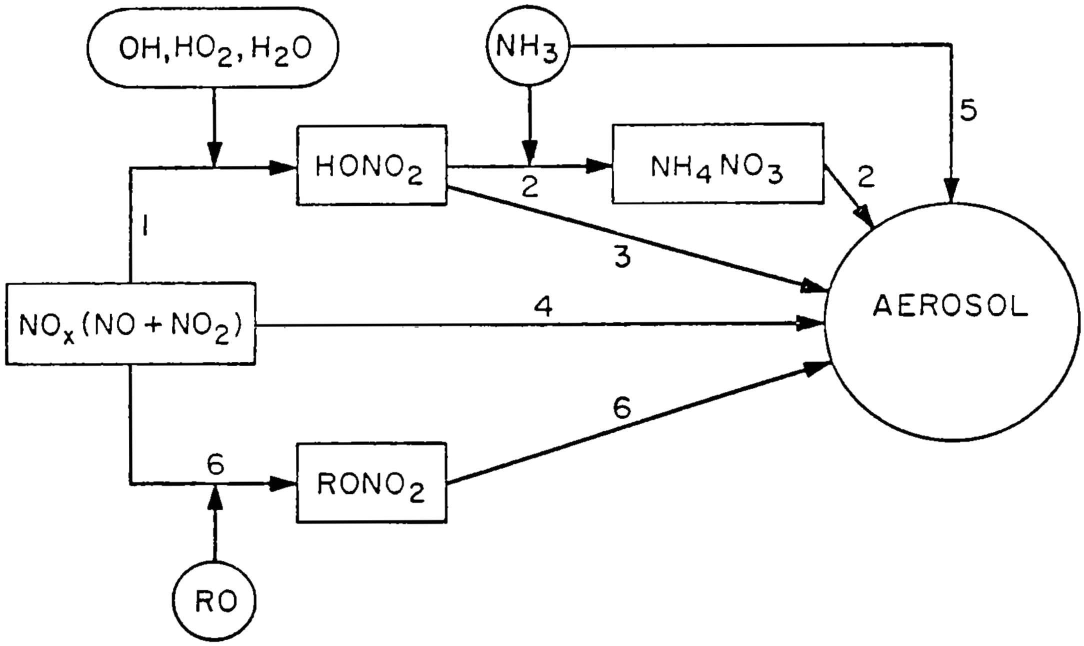

Figure A1.- Paths of nitrate formation in the atmosphere.

involves the formation of gaseous nitric acid. Nitric acid vapor, once formed, may then react with NH_3, a ubiquitous atmospheric constituent with both natural and anthropogenic sources, to produce ammonium nitrate, NH_4NO_3 (path 2), which at standard temperature and pressure exists as a solid. Alternatively, the nitric acid vapor may be absorbed directly into a particle (path 3) although thermodynamic and kinetic considerations favor reaction with NH_3 to form NH_4NO_3 to convert gaseous nitric acid to nitrate in particulate form (Morris and Niki (ref. 86) and Stelson et al. (ref. 87)). Path 4 involves the direct absorption of NO and NO_2 into an atmospheric particle, a route that is likely for certain aqueous particles, particularly when accompanied by the absorption of ammonia (path 5) (Orel and Seinfeld (ref. 88)). Path 6 depicts the formation of organic nitrates followed by absorption of these nitrates into particles. At present, little is known about the importance of paths, such as path 6.

There have been a number of measurements of nitric acid and particulate nitrate concentrations in ambient air (Huebert and Lazrus (ref. 40)). Many of the measurements have identified the particulate nitrate as NH_4NO_3, suggesting that the aerosol may consist of solid NH_4NO_3 or NH_4^+ and NO_3^- in solution in approximate stoichiometric balance. It is difficult to estimate the relative importance of the paths in figure A1 for several reasons. First, the rate of reaction of nitric acid and ammonia is not well-known although the forward reaction is probably rapid and, in fact, can be presumed to be in equilibrium with the dissociation of solid ammonium nitrate

$$NH_{3(g)} + HONO_{2(g)} \rightleftarrows NH_4NO_{3(s)}$$

Second, the rate of absorption of NO and NO_2 into existing particles depends on the composition and size of each particle and cannot generally be predicted a priori. In either case, it is apparent that the presence of NH_3 is required, either to form NH_4NO_3 or to neutralize the acidity of a liquid droplet in which NO and NO_2 dissolve.

The current state of understanding of atmospheric nitrate formation can be summarized as follows. The principal gas-phase nitrate-forming reaction is the reaction of NO_2 and OH. The nitric acid vapor formed in this way probably reacts rapidly with ammonia to form small particles of solid ammonium nitrate; thus, the equilibrium of the previously given reaction is established. In competition with the nitric acid/ammonium nitrate path is the path consisting of direct absorption of NO and NO_2 into aqueous droplets. The relative rates of these two paths cannot be determined in general. In either case, however, the presence of ammonia appears to be required.

Ozone/oxidant formation.- Ambient concentrations of photochemical oxidants in urban atmospheres are well documented. Although certain details of the chemical processes that are responsible for formation of oxidants in urban atmospheres are still unresolved, the basic qualitative aspects of the process are understood. Recently, the existence of oxidant/ozone concentrations in nonurban atmospheres that exceed what has been thought to be natural background levels has been of intense interest. In principle, there are three routes by which oxidant may be produced in rural[3] areas at levels exceeding the natural background level of ozone: (1) Transport of precursor hydrocarbons and oxides of nitrogen from urban source areas, coupled with chemical reactions in the air mass to produce ozone at downwind nonurban sites; (2) long-range transport of ozone formed in the urban atmosphere to the nonurban site; and (3) interaction between natural hydrocarbon emissions and man-made emissions of oxides of nitrogen.

Measurements in the last 5 to 6 yr have showed oxidant/ozone concentrations in many rural areas to exceed 0.08 ppm, with a frequency comparable to or even exceeding that observed in many urban areas. Such elevated oxidant/ozone levels in rural areas are almost certainly caused by anthropogenic oxidant/ozone and/or precursors generated locally or transported into such areas from urban centers. Evidence attesting to the anthropogenic nature of rural oxidant, in part or in whole, is the elevated concentrations of chlorofluoromethanes or acetylene, as well as the fact that wind back-trajectory analysis indicates passage of the rural air over urban sources. Downward intrusion from layers aloft of transported anthropogenic oxidant/ozone concentrations can explain the occurrence of elevated oxidant/ozone concentrations in rural areas and during the night in the summer and fall months.

The occurrences of oxidant/ozone concentrations in remote areas and during the winter months constitute strong evidence that natural sources must exist and thus provide an atmospheric background upon which the anthropogenically generated oxidant/ozone concentrations are superimposed. The question of the strengths of natural sources needs to be answered for the purpose of more accurately estimating the benefits to be derived from anthropogenic emission reduction. Evidence derived from analysis of data on ozone concentrations in remote areas suggests stratospheric intrusions that may reach ground level.

An air interchange between stratosphere and troposphere is known to occur by means of four mechanisms: (1) Mean meridional circulation, (2) large-scale eddy transport, (3) seasonal adjustment of tropopause level, and (4) mesoscale and small-scale eddy transport. Each of these mechanisms is characterized by short-term seasonal and long-term fluctuations. Their impact in terms of surface concentration of stratospheric ozone varies with latitude. Specific research needs include: (1) More definitive information on the frequency of occurrence and intensity of cyclonic events resulting in stratospheric ozone intrusion, (2) more definitive information on the ozone decay attending the subsidence of stratospheric ozone within the lower tropospheres, especially within the planetary boundary layer, (3) development of techniques for forecasting stratospheric ozone intrusions, and (4) further analysis of tropospheric ozone measurements to delineate the stratospheric and anthropogenic contributions to such ozone.

The role and importance of naturally emitted organics in the oxidant/ozone problem is a question of current interest. It is well established that vegeta-

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[3] The term "rural" is used to signify areas or atmospheres that are nonurban but are occasionally susceptible to anthropogenic pollutants, and the term "remote" is used to signify areas so far removed from anthropogenic pollutant sources that contamination by such pollutants is highly unlikely.

tion emits organic vapors and that certain of these vapors (terpenes) play the dual role of oxidant/ozone precursors and destructive agents. Relevant questions are:

(1) What is the net effect upon oxidant/ozone precursors of the atmospheric reactions of terpenes and other natural organics?

(2) What reactive organics other than terpenes are emitted by natural sources and at what rates?

It is critical that convincing measurements be provided on the chemical identity, ambient concentrations, and emissions of natural organics. There is sufficient evidence to show that monoterpenes do occur in the ambient air but only within forested areas. In such areas, total terpene concentrations averaged 10 to 50 ppb of carbon. The evidence further shows that terpenes have extremely short lifetimes; therefore, with the exception of isoprene, they are not transported downwind from the sources in appreciable quantities. Within urban areas, terpenes have not been found to occur in measurable concentrations. Thus, the evidence does not support an important direct role of terpenes in the urban oxidant/ozone problem. It is conceivable, of course, that terpenes may contribute to the rural oxidant problem and, therefore, indirectly, to the urban problem by way of oxidant transport to urban areas.

The fact that ozone is relatively insoluble in water - despite evidence that the oceans remove some ozone - suggests that rainout and washout cannot be important sink processes for ozone. The reaction of ozone with NO and with hydrocarbons is an important sink process which accounts for the complete removal of ozone from the surface air layers in urban areas at night. Surface adsorption and some destruction from locally emitted NO and hydrocarbons account for the nighttime absence of ozone from the rural atmospheres at ground level. In air layers aloft that are relatively free of fresh precursor and surface influences, ozone has been observed to remain extremely stable over time periods on the order of hours to days. Thus, the chemical sink processes for ozone are qualitatively well established; quantitatively, the dry deposition sink processes for ozone are not well defined. Adsorption and/or destruction of ozone on ground surfaces (soil, vegetation, water, etc.) constitute a major sink for this gas on a global basis. Measurements of uptake rates of different pollutants by certain forms of vegetation show the ozone rate to be comparable to that for NO_2 and somewhat lower than that for SO_2. Thus, the evidence presently available indicates that, of the various possible sink processes for ozone, chemical reaction and surface destruction are the most important.

Scientific Questions:

B.2.1 What chemical processes influence O_3 formation in point-source and urban plumes?

B.2.2 What chemical processes govern the conversion of SO_2 to sulfates in point-source and urban plumes?

B.2.3 What chemical processes govern the conversion of NO_x to nitrates in point-source and urban plumes?

B.2.4 What are the contributions of photochemistry involving man-made and natural hydrocarbons, long-range transport of O_3 and precursors, and stratospheric intrusions in producing elevated O_3 concentrations in rural areas?

B.2.5 What is the source and composition of acid rain?

Research Tasks:

(1) Conduct detailed measurements in and near point-source (e.g., power plant) plumes of SO_2, NH_3, $SO_4^=$, OH, HO_2, H_2O, H_2O_2, aerosols (size distribution), trace metals, wind fields, and temperature.

(2) Conduct detailed measurements in urban and point-source plumes and in rural areas of hydrocarbons, NO_x, O_3, CO, H_2O, OH, HO_2, HNO_3, and tracer molecules such as C_2H_2 or fluorocarbons.

(3) Measure the pH and composition of rainwater.

(4) Simultaneously measure visibility, aerosol properties, and tracer molecules in rural and remote areas.

APPENDIX A

CHAPTER 2 - SUMMARY OF SCIENTIFIC QUESTIONS AND RESEARCH TASKS - THEIR CORRESPONDENCE AND PRIORITIES

The scientific questions posed in chapter 1 are summarized in table 18. In tables 19 and 20 the research tasks outlined in chapter 1 are presented. In these two tables, the research tasks have been divided according to operational needs (table 19) and instrument development needs (table 20).

For virtually all trace gases in the troposphere, remote measurements (especially by means of satellite) would be desirable. Establishing the operating parameters for instruments of this class, however, is very difficult at this time since information is just now being obtained on the variability of trace gases on vertical and horizontal scales. Thus, more extensive in situ sampling should take place before large-scale investments are made in remote sensing instrumentation. At this time, the general guidelines for resolution that are suggested for remote instruments are: Vertical, 1 km; horizontal, 100 km. (For the long-lived species N_2O, CO_2, $CFCl_3$, and CF_2Cl_2, the needed resolutions would be more like 3 to 5 km (vertical) and 1000 km (horizontal).)

The characteristics required in new in situ instrumentation depend greatly on the nature of the sampling platform. For static platforms, integration times (time resolution) as long as 1 hr would be acceptable to achieve signal-to-noise ratios of 2. On the other hand, for aircraft sampling platforms, a time resolution no greater than 5 to 10 min would be desired if acceptable vertical and horizontal spatial resolutions are to be achieved.

Corresponding to each research task in tables 19 and 20 are the questions relevant to that task. The Working Group recognized that the research tasks listed in these tables are not all of equal priority with respect to increasing our understanding of tropospheric pollution. Consequently, it was decided that a two-level ranking system would be appropriate to indicate those research tasks that the Working Group viewed as high priority and somewhat lower priority. Thus, in the "Priority" column in tables 19 and 20, a research task is given a "1" or "2" ranking, depending on whether it is recommended as a high or low priority task. One object of the Working Group was to suggest research tasks that, in the opinion of the Group, would be of potential interest to EPA for a joint NASA-EPA research effort. Tasks that fall in this category are delineated with an asterisk.

Recently, several atmospheric species previously undetected have been discovered, which leads to suspicions as to what additional undetected compounds may be present. The Working Group wishes to propose that long-term monitoring of infrared spectra of the troposphere be initiated not only to measure changes in the concentrations of species already identified but also to detect the appearance of new species. This recommended research task appears as entry 38 in table 19.

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TABLE 18.- SUMMARY OF SCIENTIFIC QUESTIONS RELATED TO TROPOSPHERIC POLLUTION

Number	Question
A.1.1	What are the relative roles of stratospheric-tropospheric exchange, photochemistry, and surface sinks in the global tropospheric ozone budget?
A.1.2	Will variations in global CO and NO_x levels shift the ozone balance?
A.1.3	What is the detailed degradation chain for methane and what are its consequences on ozone and HO_x?
A.1.4	What is the role of nonmethane hydrocarbons in the ozone budget?
A.1.5	What are the detailed exchange mechanisms between the troposphere and stratosphere?
A.2.1	What are the tropospheric concentrations of the active nitrogen compounds?
A.2.2	What are the natural sources of active nitrogen?
A.2.3	What are the major sinks of atmospheric NO_x and total active nitrogen?
A.2.4	Can increased levels of NO_x influence the tropospheric ozone balance?
A.2.5	What are the global concentrations, sources, and sinks of ammonia?
A.2.6	What are the natural sources and sinks of N_2O and what are the implications of increased use of nitrogenous fertilizers on the tropospheric N_2O budget?
A.3.1	Are higher carbon monoxide levels in the Northern Hemisphere as compared with the Southern Hemisphere due to natural or anthropogenic processes and will continued CO emissions perturb atmospheric OH levels, especially the relative abundance in the two hemispheres?
A.3.2	Do soils always act as a sink of atmospheric carbon monoxide?
A.3.3	What is the role of nonmethane hydrocarbons in the CO budget?
A.3.4	What are the exchange mechanisms between the two hemispheres, and how important are they in controlling the CO abundance?
A.3.5	Is the deforestation and wood-burning hypothesis plausible for the increase of CO_2 global concentration?
A.3.6	What are the climatic implications of changes in the atmospheric composition of trace gases such as CO_2, CH_4, N_2O, fluorocarbons, and aerosols?

TABLE 18.- Continued

Number	Question
A.4.1	What is the yearly quantity of sulfur now being released from the natural biosphere, and what are the major chemical forms in which this sulfur is being released?
A.4.2	What is the global distribution of SO_2?
A.4.3	What are the short-term and long-term impacts of anthropogenic emissions of SO_2 on the tropospheric sulfur budget and on the budgets of other trace gases such as NH_3?
A.4.4	What is the relative importance of homogeneous versus heterogeneous processes in the SO_2 gas-to-particle conversion cycle?
A.4.5	What are the major sources of tropospheric COS? And, if man's activities are a major source, what might be the climatic implications of a COS buildup in the atmosphere?
A.5.1	What is the reliability of present photochemical theory in predicting H_xO_y distributions in both urban and remote atmospheric air parcels?
A.5.2	Can the asymmetry in global CO levels lead to asymmetry in global OH distributions?
A.5.3	What is the lifetime of H_2O_2 in the atmosphere, and what are the major sinks for this compound?
A.6.1	What importance (in terms of a global average concentration value for OH) can be assigned to the interhemispheric gradient in methyl chloroform?
A.6.2	What are the major sources of atmospheric HCl and how important is this in determining rain acidity in both remote and urban areas?
A.6.3	What are the stratospheric implications of anthropogenic releases of halocarbons (such as CH_3CCl_3, $CHCl_2F$, and $CHClF_2$) in terms of their OH-controlled chemical lifetimes in the troposphere?
A.7.1	What are the optical properties of tropospheric aerosols?
A.7.2	What are the physical and chemical properties of tropospheric aerosols?
A.7.3	How do aerosols influence the tropospheric radiation balance?

TABLE 18.- Concluded

Number	Question
A.7.4	What is the origin and fate of large-scale tropospheric haze?
B.1.1	What are the meteorological processes governing the long-range transport of pollutants?
B.1.2	What is the relative importance of the various removal processes on the long-range transport of pollutants?
B.2.1	What chemical processes influence O_3 formation in point-source and urban plumes?
B.2.2	What chemical processes govern the conversion of SO_2 to sulfates in point-source and urban plumes?
B.2.3	What chemical processes govern the conversion of NO_x to nitrates in point-source and urban plumes?
B.2.4	What are the contributions of photochemistry involving man-made and natural hydrocarbons, long-range transport of O_3 and precursors, and stratospheric intrusions in producing elevated O_3 concentrations in rural areas?
B.2.5	What is the source and composition of acid rain?

APPENDIX A

TABLE 19.- OPERATIONAL RESEARCH TASKS

Number	Research task	Relevant questions	Priority
1.	Continue development of global tropospheric photochemical transport models.	A.1.1, A.1.2, A.1.3, A.1.4	1
*2.	Measure the global distribution of ozone as a function of latitude, longitude, altitude, and time. Of special importance would be the measurements of stratospheric ozone transport into the troposphere.	A.1.1, A.1.5	1
*3.	Conduct flux measurements of ozone near the ground over various geographical locations.	A.1.1	2
4.	Measure the global concentration distributions of NO, NO_2, and HNO_3.	A.2.1, A.1.2, A.2.3, A.2.2	1
*5.	Carry out flux measurements of NO and NO_2 near the ground over various geographical locations.	A.2.2, A.2.3	1
*6.	Measure the nitrate content in aerosols and rainfall on a global scale.	A.2.3	2
7.	Measure the global concentration distribution of ammonia.	A.2.5, A.4.3	1
*8.	Carry out flux measurements of ammonia over various soils and terrain.	A.2.5	1
9.	Conduct continuous monitoring of the atmospheric N_2O concentration.	A.2.6	2
10.	Carry out N_2O flux measurements over soils and the ocean.	A.2.6	2
11.	Conduct long-term measurements of the global distribution of carbon monoxide.	A.3.1, A.3.2, A.3.3, A.3.4	1
12.	Conduct long-term measurements of the global distribution of methane. Simultaneously, measure the OH distribution.	A.1.1, A.1.3	1

*Candidate for NASA-EPA program.

TABLE 19.- Continued

Number	Research task	Relevant questions	Priority
13.	Conduct satellite monitoring of global land types and resources to infer the impact of man's activities upon areas of methane production.	A.1.3, A.3.6	2
14.	Carry out flux measurements of methane over various geographical areas.	A.1.3	2
15.	Conduct measurements of the distribution of formaldehyde, with simultaneous observations of CH_4, NMHC, OH, NO_x, and light intensity at selected global locations.	A.1.1, A.1.3, A.3.1	1
*16.	Measure the global distribution of nonmethane hydrocarbons. These measurements can be carried out in three phases.	A.1.1, A.1.4, A.3.3	1
*17.	Carry out flux measurements of nonmethane hydrocarbons over various geographical areas.	A.1.1, A.1.4, A.3.3	1
18.	Conduct satellite monitoring of land types, resources, and oceanic productivity to assess key parameters in the CO_2 cycle and their variation with time.	A.3.5, A.3.6	2
*19.	Carry out flux measurements of H_2S and CH_3SCH_3 over different geographical areas.	A.4.1	1
*20.	Measure the global distribution of SO_2.	A.4.2, A.4.3, A.4.4	1
21.	Measure the global distribution of COS as well as the concentrations in the vicinity of volcanoes, power plants, and swamps.	A.4.5	1
*22.	Measure the distribution of sulfates in aerosols and rainwater.	A.4.3, A.4.4	2

*Candidate for NASA-EPA program.

TABLE 19.- Continued

Number	Research task	Relevant questions	Priority
*23.	Measure the global concentration distributions of OH and HO_2.	A.1.1, A.1.3, A.1.4, A.3.3, A.4.4, A.5.1, A.5.2, A.6.1, A.6.2, A.6.3	1
24.	Measure the global concentration distribution of H_2O_2.	A.5.1, A.5.3	1
25.	Conduct global measurements of the distribution of halogen species (e.g., CH_3CCl_3, CH_3Cl, fluorocarbons, HCl and Cl^-).	A.6.1, A.6.2, A.6.3	1
*26.	Measure globally the size distribution, refractive index, chemical composition, and vertical distribution of aerosols.	A.7.1, A.7.2, A.7.3, A.7.4	1
*27.	Develop mesoscale models of atmospheric transport, transformation, and removal of pollutants.	B.1.1	1
*28.	Measure pollutant removal during precipitation processes.	B.1.2	1
*29.	Measure the long-range characteristics of pollutant plumes, especially during nighttime conditions.	B.1.1	1
*30.	Conduct detailed measurements of the flow fields in complex terrain.	B.1.1	2
*31.	Measure transport rates between the mixed layer and the free troposphere.	B.1.1	1
*32.	Continuously measure vertical temperature profiles, mixing depth, and surface heat flux to support model development and validation.	B.1.1	2
*33.	Develop techniques to relate measurements (both in situ and remote) to model predictions.	B.1.1	1

*Candidate for NASA-EPA program.

TABLE 19.- Concluded

Number	Research task	Relevant questions	Priority
*34.	Conduct detailed measurements in and near point-source (e.g., power plant) plumes of SO_2, NH_3, $SO_4^=$, OH, HO_2, H_2O, H_2O_2, aerosols (size distribution), trace metals, wind fields, and temperature.	B.2.2, B.2.3, A.4.4	1
*35.	Conduct detailed measurements in urban and point-source plumes and in rural areas of hydrocarbons, NO_x, O_3, CO, H_2O, OH, HO_2, HNO_3, and tracer molecules such as C_2H_2 or fluorocarbons.	B.2.3, B.2.4	1
*36.	Measure the pH and composition of rainwater.	B.2.5	1
*37.	Simultaneously measure visibility, aerosol properties, and tracer molecules in rural and remote areas.	B.1.2, B.2.1, B.2.2, B.2.3, B.2.4	1
38.	Long-term monitoring of infrared spectra of the troposphere.		1

*Candidate for NASA-EPA program.

APPENDIX A

TABLE 20.- INSTRUMENTAL DEVELOPMENT TASKS

Number	Research task	Relevant questions	Priority
*1.	Develop remote capabilities for measuring tropospheric ozone.	A.1.1	1
2.	Develop remote and supportive in situ sensing methods to measure NO, NO_2, and HNO_3.	A.2.1	1
3.	Develop improved in situ and remote sensing methods to measure NH_3.	A.2.5	1
4.	Develop new in situ and remote sensing methods to measure formaldehyde.		1
5.	Develop one new in situ and remote sensing method for measuring COS.	A.4.5	2
6.	Develop one new in situ and remote sensing method for monitoring SO_2.	A.4.2	1
7.	Develop one new in situ method to measure H_2S, CH_3SCH_3, and CS_2.	A.4.1	2
*8.	Develop new in situ methods to measure OH, HO_2, and H_2O_2. Study the feasibility of developing remote sensing methods for these species.	A.5.1, A.5.3	1
9.	Develop a remote sensing instrument for measuring H_2O.		2
10.	Develop a remote sensing capability for sulfate, nitrate, trace metals, and carbon in aerosols.	A.7.2	1
11.	Continue development of methods for measuring the optical properties of aerosols.	A.7.1	1
12.	Continue development of methods for measuring atmospheric state variables.	B.1.1	1

*Candidate for NASA-EPA program.

APPENDIX B

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ACRONYMS AND ABBREVIATIONS

A/C	Aircraft
ACE	Aerosol Climate Effects
AIDS	Aircraft Integrated Data System
alt	Altitude
AN	Applications Notice
Anthro.	Anthropogenic
AO	Announcement of Opportunity
ASDAR	Aircraft to Satellite Data Relay
AVHRR	Advanced Very High Resolution Radiometer
CIMATS	Correlation Interferometer for Measuring Atmospheric Trace Species
COPE	Carbon Monoxide Pollution Experiment
cw	Continuous wave
DCR	Differential Correlation Radiometer
DCS	Data Collection System
DIAL	Differential Absorption Lidar
DISC	Differential scattering
DMSP	Defense Meteorological Satellite Program
EDS	Environmental Data Service
EPA	U.S. Environmental Protection Agency
EQ.	Equator
ESA	European Space Agency
FGGE	First GARP Global Experiment

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FPD	Flame Photometric Detector
GAMETAG	Global Atmospheric Measurements Experiment on Tropospheric Aerosols and Gases
GARP	Global Atmospheric Research Program
GC	Gas chromatograph
GCM	General circulation model
GFC	Gas filter correlation
GLC	Gas-phase liquid chromatography
GMT	Greenwich Mean Time
gnd	Ground
GOES	Geostationary Operational Environmental Satellite
GOS	Global Observing System
HIRS	High Resolution Infrared Sounder
HSI	High Speed Interferometer
HSRL	High Spectral Resolution Lidar
IHR	Infrared Heterodyne Radiometer
IR	Infrared
JPL	Jet Propulsion Laboratory
LARS	Lower Atmospheric Research Satellite
LAS	Laser Absorption Spectrometer
LHR	Laser Heterodyne Radiometer
LHS	Laser Heterodyne Spectrometer
lidar	Light detection and ranging
MAPS	Measurement of Air Pollution from Satellites
MAP3S	Multistate Atmospheric Power Production Pollution Study
MASIR	Microwave Atmospheric Sounding and Imaging Radiometer
mb	millibar (1 mb = 100 Pa)

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MONEX	Monsoon Experiment
MOPS	Multispectral Observations of Pollutants
MSS	Multispectral Scanner
MSU	Microwave Sounding Unit
N	North
NASA	National Aeronautics and Space Administration
NCAR	National Center for Atmospheric Research
NESS	National Earth Satellite Service
N.H.	Northern Hemisphere
NMHC	Nonmethane hydrocarbons
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
OFT MAPS	Orbital Flight Test MAPS
PEPE	Persistent Elevated Pollution Episodes
PMR	Pressure Modulated Radiometer
ppb	Parts per billion by volume
ppm	Parts per million by volume
ppm-m	Parts per million-meter
ppt	Parts per trillion by volume
RBV	Return-Beam Vidicon Camera
R.H.	Relative humidity
rms	Root mean square
S	South
SAGE	Stratospheric Aerosol and Gas Experiment
SAM II	Stratospheric Aerosol Measurement II
SBUV	Solar Backscattered Ultraviolet

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SDM	Statistical dynamical model
SEM	Space Environment Monitor
SMS	Synchronous Meteorological Satellite
SOP	Standard operating procedures
SSEC	Space Science and Engineering Center
SST	Sea surface temperature
SSU	Stratospheric Sounding Unit
STATE	Sulfate Transport and Transformation Experiment
SURE	Sulfate Regional Experiment
Subtrop.	Subtropical
TIROS	Television and Infrared Observation Satellite
TOMS	Total Ozone Measurement System
TOVS	TIROS Operational Vertical Sounder
TWOS	Tropical Wind Observing Ships
UNEP	United Nations Environmental Program
UV	Ultraviolet
VAS	VISSR Atmospheric Sounder
VIS	Visible
VISSR	Visible and Infrared Spin Scan Radiometer
WEFAX	Weather Facsimile
WWW	World Weather Watch

SYMBOLS

A	constant
c_i	concentration of species i
c_n	average number density of clusters
ΔG_n	free energy

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h	Planck's constant
J	photochemical rate constant
k	Boltzmann's constant
n	number of particles
p	pressure
p_s	surface pressure
p_t	total pressure
r	droplet radius
S/N	signal-noise ratio
T	absolute temperature
T_c	cloud-top temperature
T_s	surface temperature
t	time
Δt	change in time
V	wind vector
x, y, z	location of point or region
$\Delta x, \Delta y, \Delta z$	specified dimensions or size
x_c, y_c, z_c	location of centroid
x_d, y_d, z_d	location of center of grid cell
z	geometric height
γ	surface tension
ε	error
λ	wavelength
ν	frequency of electromagnetic radiation
ρ_w	density of water vapor
Ω	region

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Subscripts:

(g)	gas
i	species i
m	model
r	remote
s	stationary (in situ)
(s)	solid or particle

APPENDIX C

MEASUREMENT OF ATMOSPHERIC STATE VARIABLES

Nearly all of the research objectives in tropospheric pollution require a knowledge of weather variables (e.g., the classical state variables of pressure, temperature, and density, plus such other parameters as water vapor, wind, sea-surface temperature, precipitation, cloud cover, and visibility). The weather-observing system in the United States is composed of four fundamental weather-observing programs - surface, upper air, radar, and meteorological satellites. Our national programs are complemented by observation programs of other countries. Taken together they constitute the Global Observing System (GOS), a part of the World Weather Watch (WWW), which, in turn is an element of the World Weather Program. (See refs. 89 to 92.)

U.S. WEATHER OBSERVING PROGRAMS

Surface observations are taken by the Departments of Commerce, Defense, Transportation, and Energy, and the National Aeronautics and Space Administration. Automatic stations and automated buoys are becoming increasingly popular in providing such observations as wind, temperature, dew point, pressure, precipitation, and even cloud and visibility information.

Data from the upper-air observing network provide the basic input to numerical analysis and forecasting. The Department of Commerce operates land facilities in the United States to make upper-air (balloon) observations. The Department of Defense participates both at U.S. and overseas areas through operations of its land and ship facilities. Supplemental upper-air data are provided by Department of Defense weather reconnaissance flights and by in-flight reports from commercial, general, and military aviation. Also, NASA and the Department of Defense use rocketsondes to obtain temperature and wind measurements at altitudes above balloon levels at selected sites.

A fundamental state-variable observation program consists of polar-orbiting and geostationary satellites. Operational systems include those of the Departments of Commerce and Defense. The Department of Commerce, through the NOAA National Earth Satellite Service (NESS), is the agency responsible for a national operational environmental satellite system.

The current polar-orbiting satellites in this system are in the TIROS-N/NOAA series. The TIROS-N payload consists of four instruments:

(1) Advanced Very High Resolution Radiometer (AVHRR): A four-channel (0.5 to 0.9, 0.7 to 1.1, 3.6 to 3.9, and 10.5 to 11.5 μm) scanning radiometer providing image and radiometric data in the visible, near-infrared, and far-infrared portions of the spectrum with a resolution of approximately 1 km (at the satellite subpoint).

(2) TIROS Operational Vertical Sounder (TOVS), consisting of the following:

(a) The High Resolution Infrared Sounder (HIRS/2), a 20-spectral-channel infrared radiometer used to infer tropospheric temperature and moisture profiles

(b) The Stratospheric Sounding Unit (SSU), a three-channel pulse-modulated, step-scanned, far-infrared spectrometer used to produce temperature profiles of the stratosphere

(c) The Microwave Sounding Unit (MSU), a four-spectral-channel radiometer with response in the 50- to 57-GHz O_2 band capable of sounding atmospheric temperatures even in the presence of clouds

(3) Data Collection and Platform Location System: A random-access system for platform location and the collection of meteorological data from both fixed and moving platforms, such as buoys and constant-density balloons.

(4) Space Environment Monitor (SEM): A multidetector unit used to monitor solar particulate energies in the vicinity of the satellite.

The geostationary satellites in the operational system are in the SMS/GOES (Synchronous Meteorological Satellite/Geostationary Operational Environmental Satellite) series. The SMS/GOES payload consists of the following:

(1) Visible and Infrared Spin Scan Radiometer (VISSR): This is basically a telescope with a precision latitude stepping mechanism. The radiometer scans within two broad bands (visible, 0.55 to 0.75 μm, and infrared, 10.5 to 12.6 μm) in the west/east direction as the spacecraft spins about its axis. There are eight identical visible channels and two redundant infrared channels. The eight visible channels are aligned in a linear array providing approximately 1-km image resolution at the satellite subpoint. The two infrared channels provide approximately 8-km resolution at the subpoint. At 100 rpm, the full disk image requires 18.2 min. Full Earth disk pictures are available at 30-min intervals throughout the day and night; partial disk pictures can be obtained at more frequent intervals to meet special requirements such as viewing the development and movement of severe storms. Approximately 1600 wind observations from two or three levels can be deduced daily from sequential satellite cloud images within 50° of the subpoint.

(2) Data Collection System (DCS): A system used to collect and relay environmental data observed by remotely located sensing platforms such as automatic weather stations, buoys, and river and tide gages.

(3) Weather Facsimile (WEFAX) System: A system used to broadcast environmental data to remote stations.

(4) Space Environment Monitor (SEM): A system to collect data for warnings of solar activity.

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The Defense Meteorological Satellite Program (DMSP) is an operational meteorological satellite system managed by the U.S. Air Force. DMSP data are similar to the data from NOAA satellites. NOAA receives the DMSP data for operational use and dissemination to other government agencies.

THE GLOBAL OBSERVING SYSTEM

The components of the Global Observing System (GOS) are depicted in figure C1. Radar systems are not shown in figure C1 because they primarily detect short-term mesoscale phenomena and, hence, are usually not considered to be "global" in nature. Also, rocketsondes are not shown in figure C1 because their observations are not sufficiently numerous or widely enough distributed to be considered as part of the routine observing system.

Important characteristics of the First GARP Global Experiment (FGGE) level II-B surface-based data and satellite data are shown in tables 21 and 22, respectively. Level II-B data refer to meteorological parameters resulting from a special delayed (up to 6 months) data collection and processing effort in order to assemble the most complete set of observations that is practical to obtain for subsequent FGGE research. (In the context of this report, it is hoped that the FGGE level II-B data represent the type of data that will become routinely available during the 1980's.)

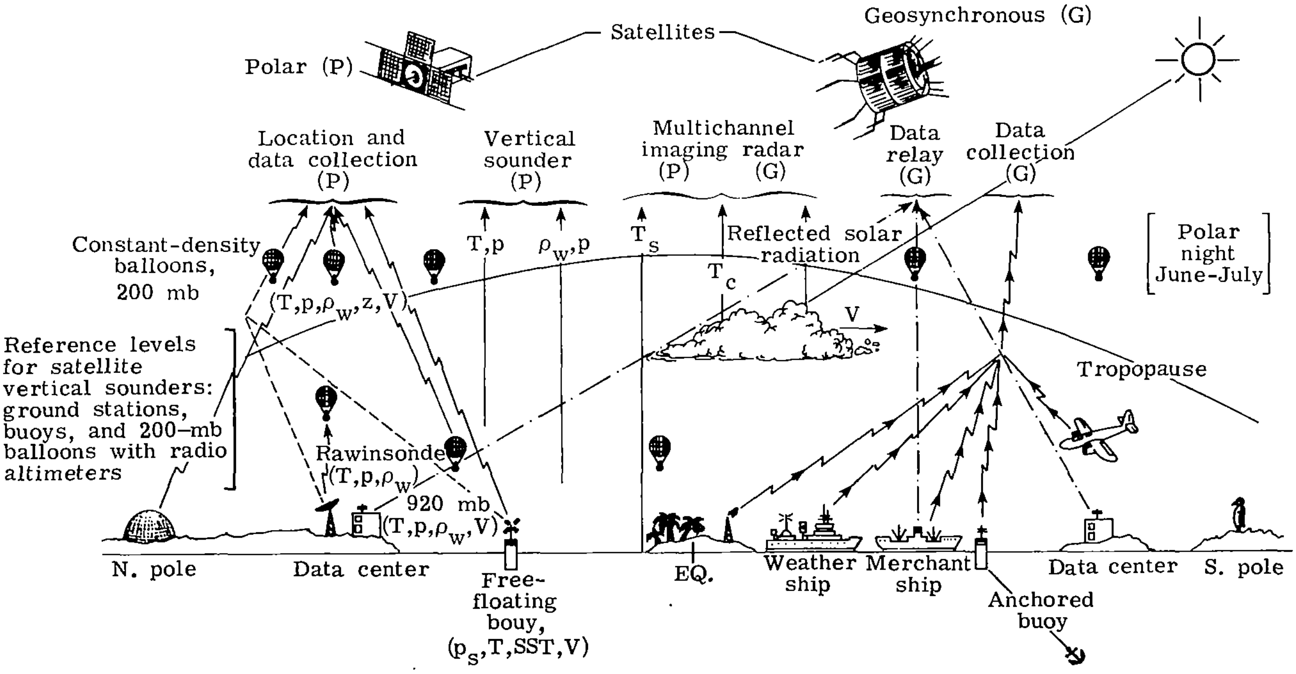

Figure C1.- Schematic of the Global Observing System. (Constant-density balloons are used only for special observations.)

TABLE 21.- FGGE LEVEL II-B SURFACE-BASED DATA

Observing system	Data types	Areal coverage	Observational period	Frequency observations	Geophysical parameters
Mobile ships	Surface marine reports	Global oceans	1 Jan 78 to 30 Nov 79	3 hourly (as available)	Conventional surface meteorological parameters Sea surface temperature (SST), wind wave, and swell data
Commercial aircraft	Aircraft flight-level reports	Global (along flight routes)	1 Jan 78 to 30 Nov 79	Asynoptic	Flight level wind, temperature, pressure/height
Oceanographic	Bathythermal observations Temperature, salinity, and current reports	Global oceans	1 Jan 78 to 30 Nov 79	Asynoptic	Temperature - depth profiles Temperature/salinity/current - depth profiles
Dropwindsonde aircraft	Upper-air reports	Equatorial (10°N to 10°S)	15 Jan 79 to 13 Feb 79; 10 May 79 to 8 June 79	Asynoptic	Wind, temperature, humidity, pressure/height
Constant-level balloons	Upper-air flight-level reports	Approximately 20°N to 40°S	5 Jan 79 to 5 Mar 79; 1 May 79 to 30 June 79	Asynoptic	Flight level, wind, temperature, pressure/height
Drifting buoys	Ocean surface reports	Southern Hemisphere (20°S to 65°S)	5 Jan 79 to 5 Mar 79; 1 May 79 to 30 June 79	Asynoptic	Sea level pressure, SST
Land and ocean stations (includes ocean weather stations and Tropical Wind Observing Ships (TWOS)).	Surface reports Upper-air reports	Global	1 Jan 78 to 30 Nov 79	Surface: 6 hourly Upper air: 12 hourly (some 6 hourly)	Surface: conventional meteorological parameters Upper-air: wind, temperature, humidity, pressure/height

TABLE 21.- Concluded

Observing system	Number of expected daily observations (approx.)	Expected accuracy of geophysical parameters	Availability of data (a)	Comments
Mobile ships	9000	SST - ±1.5 K Winds - accuracy of Beaufort scale or better	6 months to 1 yr	SST: 90% of all observations are from N.H.
Commercial aircraft	10 000 to 12 000	Winds - 1.5 m/sec rms T = ±1.5 K Alt = ±20 m	6 months	Approx. 100 observations/day from each of 80 AIDS and 17 ASDAR equipped aircraft
Oceanographic	150	T = ±0.2 K Salinity = ±1 part per thousand	6 months	
Dropwindsonde aircraft	100	Winds - 1.5 m/sec T = ±0.5 K (variable) p = ±2 mb	6 months	Coverage: Atlantic, Indian, and mid- and eastern-Pacific Oceans
Constant-level balloons	400	Winds - 1.5 m/sec T = ±0.7 K p = ±3 mb	6 months	Flight altitude: 140 mb
Drifting buoys	300 to 700	T = ±0.2 K p = ±1 mb	6 months	
Land and ocean stations (includes ocean weather stations and Tropical Wind Observing Ships (TWOS)).	10 000 (Synoptic surface reports) 1500 (Upper-air reports)	[b]Upper-air winds - ±1.0 m/sec below 10.0 m/sec T = ±1.0 K R.H. = ±5% p = ±1 mb	6 months	Max. 80 observations per day from TWOS from 10°N to 10°S for SOP's (5 Jan - 5 Mar, 1 May - 30 June 79)

[a] Available from World Data Center in Washington, D.C., after the time of observation.

[b] Accuracy ±10% above 10 m/sec. For TWOS, wind accuracy will depend on geographical area, time of day, availability of Omega stations, solar conditions, etc. Average expected accuracy, 2 m/sec; relative humidity accuracy above 300 mb (or tropopause), ±10%; atmospheric pressure accuracy near surface, ±0.5 mb.

TABLE 22.- FGGE LEVEL II-B SATELLITE DATA

Observing system	Geophysical parameters	Areal coverage	Observational period	Frequency of derived data	Resolution of derived data
Geostationary satellites (3 USA, 1 ESA, 1 Japan)	[a]Cloud vectors	[b]50°N to 50°S	[c]1 Jan 78 to 30 Nov 79	[d]12 hourly	[e]250 km
	SST (ESA, Japan)	50°N to 50°S	Uncertain	Uncertain	Uncertain
Operational polar-orbiting satellites (2 USA, 2 USSR)	SST	Global oceans	1 Jan 78 to 30 Nov 79	Daily	50 km
	Upper-air soundings and radiances	Global	1 Jan 78 to 30 Nov 79	12 to 24 hourly	250 to 500 km
Experimental polar-orbiting satellites (2 USA - Nimbus 7 and Seasat A)	SST, ocean-surface wind speeds, and atmospheric water vapor (Nimbus)	Global oceans (every 6 days from 64°N to 64°S	1 Dec 78 to 30 Nov 79	Duty cycle: 1 day on, 1 day off; Approx. 75% global coverage per day	150 km (SST) 100 km (wind speeds) 60 km (water vapor)
	Ocean-surface wind velocities (Seasat)	Global oceans (every 3 days)	5 Jan 79 to 5 Mar 79 1 May 79 to 30 June 79	As available	50 km
	Stratospheric temperature/height profiles (Nimbus)	At 320-km intervals along satellite track (outside 84°N and 64°S - no data)	1 Dec 78 to 30 Nov 79	As available; Duty cycle: 5 days on, 1 off	150 km, sounding resolution 320 km, sounding interval

[a] University of Wisconsin will provide daily, near-local noon mesoscale cloud motion vectors (100- to 200-km resolution) from 15°N to 15°S latitude for the mid- and eastern-Pacific and Atlantic Oceans (170°E to 20°W) for the period 1 Dec 78 to 30 Nov 79, as well as a high-density Indian Ocean wind set (resolution 200 to 300 km) from latitude 35°N to 20°S and longitude 30°E to 110°E at 0830 and 2045 GMT for the period 1 May 79 to 8 Aug 79 (100 days).

[b] University of Wisconsin will produce Indian Ocean wind set with latitude limits expected to be 55°N to 55°S and GOES Atlantic and Pacific limits of 45°N to 45°S.

[c] Indian Ocean set observational period 1 Dec 78 to 30 Nov 79 in contrast to 1 Jan 78 to 30 Nov 79 period for Atlantic and Pacific GOES.

[d] Indian Ocean derived wind times, 1000 and 2200 GMT. U.S. observations at 00, 1200, and 1800 GMT.

[e] Indian Ocean resolution, 250 to 500 km.

TABLE 22.- Concluded

Observing system	Geophysical parameters	Number of expected daily observations (approx.)	Expected accuracy of geophysical parameters	Availability of data (f)	Comments
Geostationary satellites (3 USA, 1 ESA, 1 Japan)	[a]Cloud vectors	[g]7500	Winds - ±3 to 6 m/sec	[h]6 months	
	SST (ESA, Japan)	Uncertain	T = ±2.0 K or better	6 months	
Operational polar-orbiting satellites (2 USA, 2 USSR)	SST	40 000	T = ±1.5 K	6 months	Limited by clouds; analysis resolution 100 and 500 km
	Upper-air soundings and radiances	6 000	T = approx. ±2.0 K	6 months	Based on 500-km resolution
Experimental polar-orbiting satellites (2 USA - Nimbus 7 and Seasat A)	SST, ocean-surface wind speeds, and atmospheric water vapor (Nimbus)	10 000 (SST) 20 000 (wind) 60 000 (vapor)	SST - ±1.5 to 2 K Winds - ±2 m/sec from 0 to 50 m/sec Water vapor - ±0.15 g/m^3	6 months	All weather, but will not provide a complete global coverage every day
	Ocean-surface wind velocities (Seasat)	20 000	Winds - ±10% from 4 to 26 m/sec	6 months	
	Stratospheric temperature/height profiles (Nimbus)	1 800	T = ±1.5 K	6 months	

[f] See footnote (a) on page 146.

[g] Winds are derived in areas with suitable cloud tracers. Vertical resolution is 2 to 3 levels.

[h] Raw VISSR image data from Pacific and Atlantic archived at NOAA/EDS. The Space Science and Engineering Center (SSEC) of the University of Wisconsin will record at full resolution the full digital output for the three active SMS/GOES satellites for the entire operational FGGE year. In addition, arrangements are being pursued by SSEC to obtain geostationary satellite images from ESA and Japan.

APPENDIX C

EXPERIMENTAL SATELLITES

In addition to the operational satellite systems previously described, NASA carries out an experimental satellite program to develop new or advanced sensors for the purpose of increasing our knowledge of environmental processes and/or providing improved data leading to improved forecasts. Two such satellites launched in 1978 were Seasat A and Nimbus 7. Unfortunately Seasat A, an oceanographic satellite launched on June 26, 1978, became inoperative on October 10, 1978. Nimbus 7, launched on October 24, 1978, carried eight sensors intended to measure upper atmosphere temperatures, trace gases/aerosols (pollutants), and oceanographic and meteorological parameters.

SOME FUTURE SYSTEMS

A geostationary sounding capability has been incorporated into the GOES-D and will be incorporated into subsequent spacecraft. The GOES-D spacecraft was launched in September 1980 and carried the VISSR Atmospheric Sounder (VAS) as its primary instrument. VAS retains the same imaging capability as before, but an infrared sounding capability has been added.

New sensors employing active remote sensing technology are under study for future satellite missions. Among these are the following:

(1) Lidar Temperature and Moisture Sounder

(2) Lidar Pressure Sounder

(3) Lidar Wind Sensor (Clear Skies)

(4) Lidar Aerosol Sensor (Troposphere)

(5) Precipitation Radar

(6) Active/Passive Multichannel Microwave Imager

New passive sensors are also under study. Among these are the following:

(1) Sensors for remotely sensing tropospheric pollutants: The Mapping of Atmospheric Pollution Sensor (senses emitted infrared radiation) and the Differential Correlation Radiometer (DCR, senses backscattered solar radiation) are examples.

(2) Microwave Atmospheric Sounding and Imaging Radiometer (MASIR): A microwave sounder/imager for sensing tropical cyclones and severe local storms from a geostationary platform; 100- to 200-GHz spectral region, $\Delta t < 1$ hr.

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15. Supplementary Notes
Appendix A by: John H. Seinfeld, William L. Chameides, Douglas D. Davis, Robert G. Lamb, and Benjamin Y. H. Liu

16. Abstract

The NASA Office of Space and Terrestrial Applications, seeking to strengthen the scientific foundation for its long-range tropospheric research program, formed a Working Group on Tropospheric Program Planning in 1978. The first task of the Working Group was to identify the major scientific questions in tropospheric pollution, to point out high priority scientific questions for current emphasis, and to recommend research tasks which could be achieved in a joint NASA/EPA program. That task was accomplished in 1978. The second task of the Working Group was to develop the scientific rationale and recommend research activities to be conduted by NASA, the execution of which would increase our understanding of the troposphere. This task is now complete.

The results from the Working Group are presented herein. The body of this report presents the scientific rationale and research activities recommended for NASA. Appendix A identifies the major scientific questions in tropospheric pollution, points out high priority areas for current emphasis, and recommends research tasks which could be achieved in a joint NASA/EPA program.

The following Working Group members contributed to this report: John H. Seinfeld, California Institute of Technology, Chairman; Frank Allario, Langley Research Center; William R. Bandeen, Goddard Space Flight Center; William L. Chameides, University of Florida (now at Georgia Institute of Technology); Douglas D. Davis, Georgia Institute of Technology; E. David Hinkley, Jet Propulsion Laboratory; Robert G. Lamb, U.S. Environmental Protection Agency; Benjamin Y. H. Liu, University of Minnesota; and Richard W. Stewart, Goddard Space Flight Center.

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