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ATMOSPHERIC CHEMISTRY

Problems and Scope

A Report of the
Panel on Atmospheric Chemistry
to the
·Committee on Atmospheric Sciences
National Research Council
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NATIONAL ACADEMY of SCIENCES
Washington, D.C.   *1975*

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The members of the panel selected to undertake this project and prepare this report were chosen for recognized scholarly competence and with due consideration for the balance of disciplines appropriate to the project. Responsibility for the detailed aspects of this report rests with that panel.

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Committee on Atmospheric Sciences

Panel on Atmospheric Chemistry

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Foreword

Atmospheric chemistry, the area of study dealing with the effects of chemical and meteorological processes on the gaseous and particulate composition of the atmosphere, has been getting a great deal of attention over the last decade. Scientists, government officials, and the public have become concerned about air pollution and the effects of the pollutants on weather and climate.

Federal and state governments have adopted legislation aimed at improving, or at least maintaining, the quality of the air. Environmental considerations have contributed to governmental decisions having major social impacts. For example, the development of a supersonic transport airplane in the United States was discontinued partly because of fear that engine emissions would adversely affect the composition of the upper atmosphere. Decisions on automobile emission control, having enormous economic consequences, have been made, in part, on the basis of information compiled by atmospheric chemists. It now appears that perhaps the decision to use catalytic converters was premature and based on inadequate information.

The most recent crisis in atmospheric chemistry is reflected in the recognition that a continuation of the widespread release of chlorofluoromethane (e.g., Freon) from *pressurized* spray cans and from refrigeration systems may lead to substantial reductions in the quantity of ozone in the atmosphere and a consequent increase in skin cancer and possibly other significant biological or atmospheric effects.

Over the last few years, atmospheric scientists and many others have begun to ask whether anthropogenic alterations of atmospheric composition are having significant effects on weather and climate. The evidence shows that since the mid-1940's the average temperature of the lower atmosphere has cooled by about half a degree Celsius, a small but significant amount. Have emissions into the atmosphere been contributors to this change? We still do not know, but it is crucial that we find out.

This report reviews a wide range of problems being addressed by atmospheric chemists. It assesses present activities, identifies problem areas, and makes recommendations for a national program that will assure an effective means of identifying potential problems before they become critical. It is effectively argued that a steady research effort over a continuing period would be more efficient than one involving responses to series of crises.

As the nation seeks alternative and less costly fuels, surveillance of atmospheric quality and increasing knowledge of atmospheric chemistry become even more important than they have been in the past. As world populations grow and as needs for greater supplies of food and water accelerate, it becomes essential that we learn how the earth's climate may be changed by emissions into the atmosphere.

This is the time for a greater investment of intellectual capital in the training of competent atmospheric chemists and in a national research program commensurate with the social costs and benefits involved.

Louis J. Battan, *Chairman*
Committee on Atmospheric Sciences

Preface

In 1971, the Committee on Atmospheric Sciences of the National Research Council published a report titled *The Atmospheric Sciences and Man's Needs: Priorities for the Future*. This report urged that the nation should establish the following objectives in atmospheric science, ranked according to priority:

OBJECTIVE I   *To extend the capability for useful prediction of the weather and atmospheric processes.*

OBJECTIVE II   *To contribute to the development of the capability to manage and control the concentrations of air pollutants.*

OBJECTIVE III   *To establish mechanisms for the rational examination of deliberate and inadvertent means for modifying weather and climate.*

OBJECTIVE IV   *To reduce substantially human casualties, economic losses, and social dislocations caused by weather.*

Objectives II and III both require substantial contributions from atmospheric chemistry, which is a relatively new, interdisciplinary branch of science dealing with the combined consequences of meteorological and chemical processes on atmospheric composition.

The Committee on Atmospheric Sciences subsequently established the Panel on Atmospheric Chemistry "charged with responsibility for recommending to CAS programs and policies needed to extend understanding of atmospheric chemical and photochemical processes and the interaction of chemical and dynamical processes occurring in the atmosphere." The Panel was asked to limit its considerations to that part of the atmosphere below about 80 km, since increasing ionization and grossly changing composition change the character of the problem at higher altitudes.

The Panel held several meetings and engaged in extensive discussions about the scientific problems of atmospheric chemistry and current efforts to solve them. The early discussions of the Panel resulted in a series of "resource papers," which are essentially documented reviews of a variety of problems in atmospheric chemistry, prepared in most cases by Panel members. These are included as Appendixes to this report. From these reviews, and from discussions and consultations with representatives of various interested governmental agencies, came the statements and recommendations that form the main portions of the report.

In this report, the Panel reviews the major problems of atmospheric chemistry. Based on this review, the Panel offers recommendations to strengthen the field and to ensure progress toward solutions of the problems at present—solutions that are essential for the development of constructive and effective environmental policies.

We have tried to organize this report in such a way that it will be useful to an audience with diverse backgrounds. In the Summary and Recommendations, our general findings are presented without substantial justification or detail. The substantive discussions of the scientific problems and issues constitute Part I of the report. The Appendixes, given in Part II, are intended for both scientists and others who desire additional detail, justification, and documentation of the points made in the main body of the report.

About two years have passed since the Panel last met in face-to-face discussion and prepared this report. Since then, there have been some important developments that merit comment but that do not change our main conclusions. We have entered these in an Epilogue, which can be most usefully considered by the reader after he has read the report itself.

The Panel wishes to acknowledge the assistance received from persons outside the Panel during the course of its studies. Particularly, the contributions of Halstead Harrison, of the Department of Atmospheric Sciences, University of Washington, leading to Appendix E of this report, are greatly appreciated. Although he was unable to participate as fully as originally hoped, the Panel is nonetheless grateful to Peter K. Mueller, Department of Public Health, State of California.

Richard A. Craig, *Chairman*
Panel on Atmospheric Chemistry

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Report of the Panel

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Summary and General Recommendations

Atmospheric chemistry, which combines certain aspects of meteorology and chemistry, is a relatively new branch of science, having achieved recognition as a separate subject only in the past decade. It deals with the effects of chemical and meteorological processes on the composition of the atmosphere, including both gaseous and particulate components and both naturally occurring substances and those resulting from human technological activities.

About 99.97 percent of the atmosphere below 80 km is composed of the gases oxygen, nitrogen, argon, and water vapor. Most of the remainder is carbon dioxide. However, there are also exceedingly small concentrations of a large number of other gases and particles. The temporal and spatial distributions and concentrations of these minor or "trace" constituents vary. Though occurring in small amounts, they may have important effects, for they can influence the precipitation process, the nature and amount of incoming solar radiation, and visibility and air quality in urban areas, and some interact with animal and plant life.

A trace constituent enters the atmosphere at one or more sources, is transported by atmospheric motions, reacts with other constituents, and finally is removed from the atmosphere at one or more sinks. At the earth's surface, natural processes and human activities serve as both sources and sinks; in the atmosphere, chemical reactions provide sources and sinks. The concentration of a trace constituent depends on the effectiveness of sources and sinks and on transport processes. Its lifetime determines how far it is transported in the atmosphere. To understand the trace constituent cycles and how human activities affect them is the central problem of atmospheric chemistry.

Much effort in atmospheric chemistry has been devoted to research on some critical atmospheric problem such as assessment of the effect of the supersonic transport (SST) on the stratosphere or

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the control of urban air quality. Such problems demand prompt attention and merit the manpower and funds allocated to them. But new and different problems will develop in the next 5 to 20 years and must be addressed and anticipated as far in advance as possible. The United States can no longer afford to drift from crisis to crisis, assuming that the atmosphere is an unlimited and unalterable resource. Not only is this policy economically costly and inefficient, but it is dangerous also, for some unanticipated effects could be irreversible by the time they are recognized and efforts to control or ameliorate them are mounted. The Panel's survey of the status of atmospheric chemistry in the United States suggests that far too little attention is being devoted to the identification of potential problems.

Such problems are apt to arise in connection with four general subject areas: urban air quality, stratospheric composition, migration and fate of atmospheric trace substance, and chemical aspects of climate change.

The problem of urban air quality, which has been of widespread concern for the longest period of time, results from a concentration of waste emissions in a limited area. The role of atmospheric chemistry is to understand the subsequent atmospheric transport and chemical transformation of the substance emitted. This knowledge is necessary to construct optimum control strategies that will protect health and comfort with the least possible economic dislocation.

The stratospheric problem has been highlighted in recent years by the question of the effect of emission from supersonic aircraft flying at high altitudes. The role of atmospheric chemistry is to understand the possible effect of human activities in ozone and on stratospheric particles, considering both atmospheric transport and chemical transformation.

Substances placed in the atmosphere by natural or anthropogenic processes may be transported long distances from this source and may be transformed chemically. These processes give rise to a problem of regional or even global air quality, since many of the substances have marked effects either in the atmosphere or at the removal site. The role of atmospheric chemistry in this problem is to understand the natural cycle and how it might be affected by human activities. Examples of concern are sulfur dioxide and carbon dioxide from fossil fuels and polychlorinated biphenyls and pesticides.

The problem of climatic change draws on atmospheric chemistry for detailed knowledge of the optical properties of trace particles and

gases, natural or man-made, that might affect the radiation balance. In addition, the nucleation properties of particles as they might affect the properties of clouds are of critical concern.

More detailed discussions of these questions are contained in the main body of the report (Part I) and in the Appendixes (Part II).

Atmospheric chemists are presently few in number, although the need for them is increasing rapidly as a result of a growing awareness of the impact of human activities on the environment. Not only is our scientific manpower for future efforts in atmospheric chemistry limited but so are the existing educational programs in atmospheric chemistry. In the field of education, the Panel is primarily concerned with doctoral programs, involving appropriate aspects of both chemistry and meteorology. As in any new interdisciplinary field, there are questions about the responsible department, the curriculum, and the appropriate degree for an atmospheric chemist. Answers will vary among institutions. Successful PhD programs will develop in institutions where there are atmospheric chemists who have the interest and initiative to mount research programs and lead students into the field. Once developed, the programs will maintain themselves at levels consistent with public support and student interest. However, currently, there are not enough such key people in universities to start this process.

To develop and sustain the continuing national effort that the Panel believes is necessary will require an increased level of national planning. While continuing vigorous attacks on the short-term problems that face the nation, and maintaining an adequate basic research program, the federal government should begin immediately to plan, fund, and carry out those programs that are foreseen as necessary for a balanced national effort.

Therefore, the Panel offers one central, general recommendation and several supporting and specific recommendations directed toward implementation of its various provisions. Following the supporting recommendations, we note parenthetically the Section of Part I in which the particular topic is discussed. It is assumed that the reader will peruse the brief Overview section that follows this Summary in order to become familiar with the field of atmospheric chemistry, the setting in which the conclusions and recommendations are made. Sections are similarly noted on which the four priority research areas identified in the first implementing recommendations are discussed. The remaining five implementing recommendations are discussed in Chapter 3, Sections III and IV. Addi-

tionally, footnotes in Chapter 3 direct the readers' attention to related and more technical and detailed discussions to be found in the Appendixes on the key problem areas identified in the report.

THE PANEL RECOMMENDS THAT THE FEDERAL GOVERNMENT ORGANIZE A NATIONAL PROGRAM IN ATMOSPHERIC CHEMISTRY THAT WILL ASSURE AN EFFECTIVE MEANS OF IDENTIFYING POTENTIAL PROBLEMS BEFORE THEY BECOME CRITICAL. THIS PROGRAM SHOULD PROVIDE FOR

(1) THE IDENTIFICATION OF POTENTIAL PROBLEMS AND STIMULATION AND COORDINATION OF RESEARCH DIRECTED TO THEM (Chapter 3, Sections I, II, and V);

(2) THE PERIODIC REVIEW OF RESEARCH IN ATMOSPHERIC CHEMISTRY FOR THE PURPOSE OF REASSESSMENT OF RESEARCH PRIORITIES (Chapter 3, Section III);

(3) THE STRENGTHENING OF COORDINATED BASIC RESEARCH IN ATMOSPHERIC CHEMISTRY IN BOTH SHORT-RANGE AND LONG-RANGE PROBLEMS (Chapter 3, Sections II.A–II.D);

(4) THE DEVELOPMENT OF EFFECTIVE EDUCATIONAL PROGRAMS TO PRODUCE THE INTERDISCIPLINARY SCIENTISTS NEEDED IN SHORT- AND LONG-RANGE ATMOSPHERIC CHEMISTRY RESEARCH PROGRAMS (Chapter 3, Section IV).

The following six recommendations relate to implementation of the proposed national program in atmospheric chemistry.

THE PANEL FURTHER RECOMMENDS THAT A CONTINUING, COORDINATED RESEARCH EFFORT BE UNDERTAKEN, IN ORDER OF PRIORITY (Chapter 3, Section II), IN (a) URBAN AIR QUALITY (Chapter 3, Section II.A), (b) STRATOSPHERIC COMPOSITION (Chapter 3, Section II.B), (c) MIGRATION AND FATE OF ATMOSPHERIC TRACE SUBSTANCES (Chapter 3, Section II.C), AND (d) CHEMICAL ASPECTS OF CLIMATE CHANGE (Chapter 3, Section II.D);

THOSE FEDERAL AGENCIES CHARGED WITH SPECIFIC AIR-RESOURCE MANAGEMENT RESPONSIBILITIES STRENGTHEN THEIR LIAISON WITH UNIVERSITY-BASED ATMOSPHERIC CHEMISTS AND ENCOURAGE RESEARCH EFFORTS DIRECTED TOWARD UNDERSTANDING AND SOLVING LONG-RANGE ENVIRONMENTAL PROBLEMS;

ATMOSPHERIC CHEMISTS OUTSIDE GOVERNMENT ACQUAINT THEMSELVES MORE FULLY WITH NATIONAL NEEDS AND GOALS TO WHICH ATMOSPHERIC CHEMISTRY CAN CONTRIBUTE IN ORDER TO RENDER MORE EFFECTIVE ASSISTANCE IN NATIONAL PROGRAMS;

BETWEEN 1977 AND 1979, THE NATIONAL SCIENCE FOUNDATION PRO-
VIDE FOR A REVIEW OF PROBLEMS AND PRIORITIES IN ATMOSPHERIC
CHEMISTRY RELATED TO ENVIRONMENTAL PROBLEMS;

DEPARTMENTS OF ATMOSPHERIC SCIENCE, CHEMISTRY, AND OTHER
RELATED DISCIPLINES, INDIVIDUALLY OR JOINTLY, EXAMINE
PROMPTLY THE PROBLEM OF ADEQUATE, WELL-BALANCED TRAINING
IN ATMOSPHERIC CHEMISTRY, PARTICULARLY IN PhD PROGRAMS;

LIMITED-TERM POSTDOCTORAL PROGRAMS BE ESTABLISHED TO
ENABLE PhD'S IN CHEMISTRY TO STUDY IN METEOROLOGY DEPART-
MENTS AND PhD'S IN METEOROLOGY TO STUDY IN CHEMISTRY
DEPARTMENTS FOR 1 TO 2 YEARS EACH.

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Atmospheric Chemistry – An Overview

I. THE NATURE OF THE FIELD

In Europe in the mid-1950's, atmospheric chemistry was first identified as a separate subdiscipline embracing chemistry and meteorology. Junge defined the field in 1963 as "the branch of atmospheric science concerned with the constituents and chemical processes of the atmosphere below . . . about 50 km." Recognition of the field came later in the United States. Even now few U.S. atmospheric science or chemistry departments offer courses in atmospheric chemistry, and its scope remains loosely defined.

The Panel's charge limited the scope of this report to the atmosphere below 80 km. In this region, it is concerned with all un-ionized constituents—whether gaseous or particulate; radioactive; natural or resulting from human activities—however small and variable their concentrations. Those constituents presenting scientific and practical problems receive special attention. Most such problems arise in relation to trace constituents, which occur in exceedingly small concentrations.

The major constituents of the atmosphere, oxygen (O_2), nitrogen (N_2), and argon (A), present no serious problems except on a geological time scale or when they interact with trace constituents. Carbon dioxide (CO_2) accounts for only about 0.03 percent of the atmosphere, and many other true constituents occur in much smaller concentrations. Many of these trace constituents have effects out of proportion to their abundance. For example, ozone because of its intense absorption of solar ultraviolet radiation, affects the temperature of the stratosphere and shields the biosphere from dangerous radiation. Aerosols, because they serve as condensation and freezing nuclei, influence the precipitation process and the chemical composition of rain. Carbon dioxide, because it absorbs radiation from the earth's surface, helps to regulate the temperature at the surface.

Human activities can affect the concentration, distribution, and character of trace constituents, and such changes can, in turn, affect the environment. Therefore, the challenge to atmospheric chemistry is to understand the occurrence and behavior of all trace constituents as a basis for assessing possible changes and the nature of the effects of such changes.

The behavior of a trace constituent depends in part on its source. Sources vary widely among constituents. For example, the principal source of ozone is the stratosphere and that of methane, the earth. Behavior depends also on residence time, the time between production and removal. The removal process, or sink, could be a terminating chemical process in the atmosphere, deposition at the earth's surface by various means, or escape from the top of the atmosphere.

The abundance of a trace constituent depends on the relative strengths of sources and sinks. For substances with long residence times, atmospheric transport is a critical determinant of geographic and vertical distribution. Consequently, problems of atmospheric chemistry often require an understanding of both meteorological and chemical processes. Therefore, atmospheric chemistry is an interdisciplinary subject requiring the complementary efforts of meteorologists and chemists in both research and education.

Urban air pollution by industrial and vehicular sources is a problem in atmospheric chemistry that has been recognized for many years and that clearly warrants special attention. In recent years, other important problems, such as the long-range transport of pollutants and contamination of the stratosphere, also have been recognized. A different problem is the effect of pollutants on weather and climate through interference with the normal energy balance of the atmosphere. The Panel has examined all of these critical problem areas.

As a complex, interdisciplinary subject dealing with vital questions about the natural environment, atmospheric chemistry has obvious scientific importance and challenge. The problems summarized in subsequent pages of this report, and discussed in more detail in the Appendixes, are those regarded by the Panel as most important at the present time. They clearly deserve recognition and attention in the general context of science's effort to understand natural processes. However, if this were the only rationale for the development of atmospheric chemistry, compelling as it may be, the Panel would not feel the same sense of urgency.

Atmospheric chemistry should provide the scientific knowledge needed to understand the impact of human activities on the atmospheric environment. The need already is great and is increasing rapidly. For example, the growing demand for energy in the face of declining supplies of conventional fuels has led to difficult problems of protecting the environment while ensuring the least possible economic dislocation. Unfortunately, there is insufficient information about the chemistry of the atmosphere—its composition, its chemical reactions, the sources and sinks of its constituents—to evaluate apparent changes in atmospheric composition and their effects. And there is a shortage, too, of scientists, with knowledge of both atmospheric transport processes and atmospheric chemistry, to collect, analyze, and interpret the data needed to address these and other critical problems and to anticipate and prepare for future ones.

A vigorous and well-coordinated research effort in atmospheric chemistry is essential. The erroneous conclusions, overreaction, uncertainty, and inefficient approach to policy development that have characterized recent years as a result of insufficient knowledge in this field provide ample support for this statement. For example, recent findings suggest that on a global basis polychlorinated biphenyls, rather than pesticides, could be the major form of chlorinated hydrocarbon contamination of ocean fish and that the principal means of transport to the ocean is the atmosphere. Current evidence also indicates that mercury in ocean fish may not be a contaminant and may not be strongly concentrated in food chains; yet only recently it was believed that air and water pollution sources of this element had seriously contaminated the living resources of the oceans. Prior to 1970, few people had even been aware that large-scale mercury pollution was possible.

As another example, circumstantial evidence in cities of a connection between carbon monoxide and human health brought about implementation of a policy to reduce carbon monoxide emissions in automobiles. Nitrogen oxide emissions also affect air quality, and provision for their control is equally important. Although lead can be removed from gasoline, aromatic or other substitutes could result in other, equally difficult problems. Knowledge of the occurrence and sources of other possibly more undesirable trace metals in urban atmospheres still is inadequate. Consequently, the development of sound and effective policies for the control of pollution of urban atmosphere is hampered.

The impact on global climate of particle input to the atmosphere as a result of human technological activities could be greater than that of carbon dioxide. However, only recently was such an effect considered, and, even now, whether the effect of particle concentrations in the atmosphere is to heat or to cool the earth is not clear. It was not until 1971 that nitrogen oxide contamination of the stratosphere from jet fuel combustion was considered as a factor in altering ozone concentration in the atmosphere.

The picture that emerges is that of a new field, developing unevenly, somewhat haphazardly, in response to crises and social pressures. What is needed is a coherent, well-coordinated program to acquire the necessary fundamental knowledge, respond constructively to current problems, and identify and, it is hoped, avert future ones.

II. CHALLENGING QUESTIONS

Atmospheric chemistry offers a number of scientifically challenging problems that also have broad and immediate applications to environmental management and control. This section summarizes briefly some of the key questions in these and other areas of atmospheric chemistry and their implications. The reviews that comprise the Appendixes present additional detailed information.

Activities that introduce a given primary constituent into the urban atmosphere are easily identified. These sources vary spatially and temporally, but the compilation of source inventories is a comparatively straightforward problem, requiring only adequate manpower and instrumentation. The crucial scientific question is what happens after the introduction of the material into the atmosphere. Few of the chemical reactions that take place in photochemical smog are known, nor have their rate coefficients been determined. These reactions take place in a complicated motion field that produces a variation in concentration over a wide range of space and time rather than in still air in a laboratory container. To understand them will require long-range monitoring of many chemical species and of the urban atmospheric motion field, as well as the development of realistic numerical models. This research would form the basis for the identification of the buildup, decay, and effects of a specific substance in the atmosphere with a specific source strength. Such information is necessary for effective control of urban air quality.

The mixtures known as smog and photochemical smog contain both gaseous and particulate components. In addition to their effect on air quality and visibility, such mixtures absorb and emit radiation and interact with water vapor; therefore, in principle, they can affect local weather. Two questions then are: Given a specified mixture blanketing a particular area, what is the effect of the resulting differential heating or cooling on local atmospheric circulation, and what is the effect of the aerosol load on cloudiness and the quantity and composition of rain in the area? There is evidence that such effects are signficant in the environment of large cities.

On a global scale, cities or large urban complexes can be regarded as individual sources of trace gases and particles. How much of what is produced at each source actually gets into the global atmosphere, and how much is destroyed in the immediate area of the source? A program of regional monitoring of constituents and the atmosphere around major urban sources is necessary to answer these questions.

Except for the regular increase of carbon dioxide in the atmosphere, the effects of human activities appear to be small perturbations on the natural cycles of production, transport, and removal of atmospheric constituents. For example, data are as yet insufficient to show whether human activities have increased the particle content of the global atmosphere. To establish baseline concentrations and detect trends, global monitoring of particles and many trace gases is necessary. Such a global monitoring program would serve also as the starting point for a systematic study of the natural cycles of gases and particles. These cycles must be understood as a basis for an assessment of the future impact of human activities on atmospheric composition. Monitoring of concentrations alone is insufficient to determine natural cycles; much additional scientific study and observation are required to understand exchange within the biosphere and across the air–sea interface. Complex reaction chains, which constitute a special problem in the urban atmosphere, occur also in the global atmosphere and should be studied there.

The principal sink for particles is precipitation. Much effort in precipitation chemistry and global precipitation sampling will be necessary to answer such questions as: To what extent would the atmosphere cleanse itself, if, for example, the particle load were doubled?

Atmospheric particles can affect weather and climate in at least two ways. They absorb and scatter radiation and therefore influence the global radiation balance. In addition, they act as condensation or ice nuclei, thereby influencing precipitation and possibly affecting

also the radiation balance by altering the type and amount of cloudiness that is responsible for the earth's high natural albedo. Calculating these effects is among the most challenging problems in meteorology. Global numerical models of the general circulation of the atmosphere, currently being developed, are the necessary tools for this calculation. The need for answers to the questions posed by the atmospheric aerosol now ranks with the need for improved weather forecasting as justification for the development of general circulation models. Recognition of this broader need is recent and attests to growing awareness among meteorologists of the chemical aspect of the atmosphere.

The understanding of atmospheric motion on all scales that is necessary to produce a general circulation model adequate for studying climatic effects has not yet been achieved. But even with such knowledge the question of the effects of aerosol on the atmosphere could not be answered, because the optical properties of the particles are not known. Models of the atmosphere less complex than current general circulation models have been advanced to give approximate answers, but because of lack of knowledge of fundamental properties of the particles there is not even agreement on whether the net effect of an increase would be to heat or to cool the atmosphere. Similarly, little progress can be made toward a calculation of the effects of an increase in aerosol load on cloud amounts and distribution until the nucleation properties of the aerosol, including those aerosols that are already present naturally, have been discovered. It appears that the most immediate problems begging for solutions regarding man's potential influence on climate are those in which the atmospheric chemist must have a central role.

Trace gases, too, have significant effects. Because of its influence on the general circulation of the atmosphere, water vapor is the most important of these gases. It has been monitored extensively throughout the world, and its cycle is now well known. Carbon dioxide affects the radiation balance and is known to be increasing on a global scale, but no definitive statement of the effect of this increase on climate is yet possible. Because the radiative properties are well known, the question here is meteorological and must be studied with models of the general circulation. Many other trace gases could affect climate because of numerous possible gas-to-particle conversions in the atmosphere, few of which have been identified.

Many chemically active trace gases from both natural and man-made sources are transported into the stratosphere or introduced

there by aircraft and rockets or nuclear explosions. The mass of the stratosphere is only 10 percent of that of the troposphere, the rate of exchange with the troposphere is slow, and there is no washout by precipitation. For these reasons the natural background chemistry of the stratosphere is easily altered on a global scale by the introduction of trace constituents resulting from human activities.

The most important trace constituent in the stratosphere is ozone, which shields the earth from a region of the ultraviolet spectrum that is potentially dangerous to life. Any possibility of decreasing the ozone content of the stratosphere by upsetting the natural chemical balance must be viewed with apprehension.

The outstanding applied problem in the study of the stratosphere is to assess the change in ozone content that could result from an operational fleet of commercial supersonic transports. Clearly, such an assessment will require an understanding of the natural chemistry and atmospheric dynamics that maintain the background ozone in the stratosphere. This is the basic problem. The chemistry was once thought to be relatively simple, but scientists now believe that numerous trace gases are involved. Few observations of the background concentrations of many constituents of potential importance to the ozone chemistry of the stratosphere have been made, and many key rate coefficients are not yet known. The level of expense, effort, and time required for laboratory determination of rate coefficients seems small compared with that which will be needed to effect the observational description required to understand the chemistry of the stratosphere.

The atmospheric motions that transport trace gases in the stratosphere must also be described by observations. More specifically, if a general circulation model is to be extended into the stratosphere to predict chemical distributions, then there must be a description of the actual motion fields against which to check the results of the model. In general, the higher one goes into the stratosphere, and above, the more closely the atmospheric motion system is coupled to the chemistry of the atmosphere. Consequently, in the high atmosphere there are numerous fundamental problems in atmospheric dynamics, and, in the region extending from the upper stratosphere to 100 km, the photochemistry is even more complex than in the lower stratosphere. These higher altitudes may be the region of future transportation systems or of pollution episodes brought about by the vertical traverse of rockets. Continued efforts to understand the photochemistry of the atmosphere and fundamental research in

atmospheric dynamics are essential to the solution of such problems.

A part of the quest for scientific understanding is the effort to discover the origin of the basic state. Therefore, the study of the origin and evolution of the earth's atmosphere and that of other planets is an important part of atmospheric chemistry. Research on the atmosphere of other planets helps to increase understanding of the base state of the earth's atmosphere.

III. FUNDING AND MANPOWER

One measure of the national effort in atmospheric chemistry is the amount of federal support provided for research in this field. To identify expenditures for it in federal agency budgets is often difficult, for atmospheric chemistry as we have defined it is not generally regarded as a separate field of endeavor in the United States. For example, in the annual reports of the Interdepartmental Committee on Atmospheric Sciences (ICAS), atmospheric chemistry is a subcategory under aeronomy but not under meteorology. For the purposes of this report we refer to atmospheric chemistry as it broadly concerns composition of the atmosphere below 80 km, that is, below that part of the terrestrial atmosphere of greatest interest to aeronomists.

Seven federal agencies provide significant support for atmospheric chemistry research: the Department of Defense (DOD), the National Aeronautics and Space Administration (NASA), the Energy Research and Development Administration (ERDA),* the National Science Foundation (NSF), the Environmental Protection Agency (EPA), the Department of Transportation (DOT), and the Department of Commerce (DOC). Budgetary information on their activities during fiscal year 1973 included in many cases expenditures for high-altitude chemistry research. For the purposes of this report, we have tried to distinguish between these and the expenditures for research in the central atmosphere. Care was taken to obtain as complete data as possible, but the current ambiguities of the field do not permit a perfect picture. However, we believe that the data summarized here are the best available at this time.

The total federal expenditure for atmospheric chemistry activities during fiscal year 1973 was approximately $34.5 million. Of this amount, about $7.7 million was for studies in the ionized portion of

*Formerly the Atomic Energy Commission (AEC).

TABLE 1 Support of Atmospheric Chemistry Research in the Neutral Atmosphere in Fiscal Year 1973

Category	Amount of Support ($ Millions)	Principal Agencies Providing Support
Atmospheric transport	6.9	AEC, DOT, NSF, EPA
Observation, measurements, and analysis	10.4	NASA, AEC, DOD, EPA
Chemical reactions	4.3	EPA, NSF
Instrumentation	5.2	EPA, NASA, DOT

the atmosphere, generally above 50 km. The largest federal expenditures in the high atmosphere were those of DOD, about $2.5 million, and NASA, about $3.5 million. The AEC and NSF also provided significant support for research in the high atmosphere.

Federal funds for atmospheric chemistry in the neutral atmosphere amounted to $26.8 million in fiscal year 1973. The principal agencies were NASA, $6.3 million; EPA, $5.4 million; DOT, $4.3 million [as part of the Climatic Impact Assessment Program (CIAP)]; NSF, $3.7 million; and AEC, $3.6 million. Other agencies supporting studies in this field are DOD and DOC.

A breakdown of activities in the field was attempted, with program activities assigned to four categories: atmospheric transport; observation, measurements, and analysis; chemical reactions; and instrumentation. Table 1 presents the findings.

The figures for support of these activities in the ionized high atmosphere are atmospheric transport, $0.3 million; observation, measurements, and analysis, $2.5 million; chemical reactions, $4.4 million; and instrumentation, $0.4 million.

Table 2 shows the differences in the percentages of the total budgets invested in these four categories.

Information obtained from federal agencies included in most cases the organization conducting a project, study, or activity contributing to a major program. Because this information was not available for all programs, some subjective determinations were necessary and were based on such criteria as who had been involved in the activity during the previous year or who the agency had employed for given types of requirements. The breakdown of information on where work was conducted—federal agencies and their laboratories, industrial or private organizations, and universities and associated

TABLE 2 Comparison of Percentages of Total Budgets for Research in the Neutral and Ionized Atmosphere Allocated to Four Activities

Category	Neutral Atmosphere (%)	Ionized Atmosphere (%)
Atmospheric transport	26	4
Observation, measurements, and analysis	39	33
Chemical reactions	16	57
Instrumentation	19	6

research laboratories—showed a wide variation among these three categories for different agencies.

Nearly 100 percent of the NSF budget in this field supported work conducted in universities. In sharp contrast, nearly 100 percent of the work supported by the DOC was conducted in its own laboratories. Fifty-two percent of the atmospheric-chemistry activities supported by DOT were carried out by industrial or private organizations, 23 percent by universities, and 25 percent by government laboratories, generally in agencies other than DOT. Other federal agencies allocated 20 to 25 percent of the amounts budgeted for this field to work performed by industry. The distribution of the total amount allocated to the support of atmospheric chemistry (including both neutral and ionized atmosphere) by seven federal agencies was government laboratories, 42 percent ($14.6 million); universities, 40 percent ($13.8 million); and industry, 18 percent ($6.1 million).

The Panel considered, but decided against attempting, a breakdown between applied and basic research. Definitions vary widely among agencies, research laboratories, and scientists themselves. Further, the state of knowledge about many problems in or closely related to the four cateogries of activities in this field results in a high degree of overlap between basic and applied research. The Panel believed that to attempt to distinguish between them probably would be more misleading than informative and such judgments too highly subjective to be useful.

It should perhaps be noted that widespread social concern about the deleterious effects of human activities on the environment has intensified during the past five years or so. Without such social pressure, the activities in atmospheric chemistry supported by the EPA, DOT, and NSF's Division of Environmental Systems and Resources

might not have been undertaken. The budgets of these three agencies for research in the neutral atmosphere were $5.4 million, $4.3 million, and $1.5 million, respectively, or approximately 42 percent of the total federal expenditures in this area, which could be interpreted as reflecting social concern, compared with the 58 percent of the expenditures by the other federal agencies on continuing mission requirements. The AEC has had a continuing program in this field since it was established. The programs of DOD and NASA reflect a positive but relatively smaller response to environmental impact.

Any attempt to analyze education and manpower data in atmospheric chemistry encounters the same problems of definition, interpretation, and categorization that characterize funding data. Neither atmospheric-science nor chemistry departments have taken the initiative in developing educational programs in atmospheric chemistry. Some scientists active in this field and holding doctorates have been trained in departments of geology, oceanography, civil engineering, or public health. Some currently working on PhD dissertations relevant to atmospheric chemistry come from atmospheric-science departments but have little formal training in chemistry; others come from chemistry departments but have little formal training in atmospheric sciences.

The University Corporation for Atmospheric Research publishes annually a *Report of Members* that lists the titles of all PhD dissertations judged by members as relevant to the atmospheric sciences. In three annual reports covering the period 1969–1972, some 460 such titles were listed. About 35 (7.6 percent) of these appear to be related to some aspect of atmospheric chemistry as broadly defined by the Panel. Topics ranged from observations of trace constituents, which do not imply any particular knowledge of chemistry, to laboratory determination of atmosphere-relevant rate coefficients, which does not require any particular knowledge of meteorology. Few of these dissertations, perhaps five to ten, depending on interpretation, clearly imply training in both fields.

3
Recommendations

I. LONG-RANGE PLANNING

The Panel noted that in a remarkably short time atmospheric chemistry has achieved a key position in the management and protection of air resources. Many potentially critical problems in air-quality control were not foreseen by specialists in meteorology or in chemistry and developed to crisis proportions. Consequently, many of the small number of atmospheric chemists in both government and private organizations are now devoted to solving these immediate problems.

The importance of these immediate problems cannot be denied. The Panel stresses that the problems of concern in some 5 to 20 years probably will be different, and an effort to anticipate them is needed, as events of the past few years show. For example:

1. Scientists engaged in long-range research recently recognized that previously unsuspected "new" substances—trace elements and organic compounds—are important atmospheric contaminants.

2. Urban air-pollution control standards and strategies are now continuously reviewed and revised in accordance with new research results. Advances in technology have already affected priorities.

3. Advances in related fields such as oceanography and soil microbiology have improved the understanding of long-range transport of certain atmospheric contaminants. Continuing close interaction among a wide range of scientific disciplines should facilitate the recognition of future problems.

4. Some of the most urgent problems have arisen because the environmental impact of widely applied technological developments, such as the increased use of automobiles and the development of high-flying aircraft, was not sufficiently understood. New technological developments will continue to bring new problems.

To ensure that potential problems are identified and the data needed to define, avert, or solve them are acquired,

19

THE PANEL RECOMMENDS THAT THE FEDERAL GOVERNMENT ORGA-
NIZE A NATIONAL PROGRAM IN ATMOSPHERIC CHEMISTRY THAT
WILL ASSURE AN EFFECTIVE MEANS OF IDENTIFYING POTENTIAL
PROBLEMS BEFORE THEY BECOME CRITICAL. THIS PROGRAM
SHOULD PROVIDE FOR
    1. THE IDENTIFICATION OF POTENTIAL PROBLEMS AND STIMU-
LATION AND COORDINATION OF RESEARCH DIRECTED TO THEM;
    2. THE PERIODIC REVIEW OF RESEARCH IN ATMOSPHERIC CHEM-
ISTRY FOR THE PURPOSE OF REASSESSMENT OF RESEARCH
PRIORITIES;
    3. THE STRENGTHENING OF COORDINATED BASIC RESEARCH IN
ATMOSPHERIC CHEMISTRY IN BOTH SHORT-RANGE AND LONG-RANGE
PROBLEMS;
    4. THE DEVELOPMENT OF EFFECTIVE EDUCATIONAL PROGRAMS
TO PRODUCE THE INTERDISCIPLINARY SCIENTISTS WHO WILL BE
NEEDED IN SHORT- AND LONG-RANGE ATMOSPHERIC CHEMISTRY
RESEARCH PROGRAMS.

II. PRIORITY PROBLEM AREAS

To implement a national program of coordinated research in atmo-
spheric chemistry requires, first, that considerable effort be devoted
to early identification and definition of key problems. Obviously, it
will never be possible to predict in complete detail the critical prob-
lems of the atmospheric environment some 5 to 20 years in advance,
for they will depend on various scientific, technological, economic,
and social developments that are equally difficult to foresee. How-
ever, intelligent estimates of probable developments, reviewed and
revised periodically, are preferable to drifting from crisis to crisis.

The Panel has identified four general subject areas that require a
continuing, coordinated research effort, not only to solve current
problems but to identify and to anticipate future ones. These are, in
order of the Panel's assessment of priorities:

    1. Urban air quality,
    2. Stratospheric composition,
    3. Migration and fate of atmospheric trace substances, and
    4. Chemical aspects of climate change.

Therefore,

THE PANEL RECOMMENDS THAT THE APPROPRIATE GOVERNMENT
AGENCIES DEVELOP PLANS FOR CONTINUING COORDINATED RE-
SEARCH EFFORTS IN URBAN AIR QUALITY, STRATOSPHERIC COMPO-

SITION, MIGRATION AND FATE OF ATMOSPHERIC TRACE SUB-
STANCES, AND CHEMICAL ASPECTS OF CLIMATE CHANGE, TAKING
INTO ACCOUNT THE GUIDELINES AND RECOMMENDATIONS PRE-
SENTED IN THE DISCUSSION THAT FOLLOWS.

We emphasize once again that priorities should be periodically
reviewed. For example, continuing research or new technological and
social developments may suggest a higher priority for studies of
acidified rain or of the effect of man's activities on the climate.

A.   Urban Air Quality *

Human activities adversely affect the composition of the air and alter
the climate of most cities. The location of many cities in regions
subject to frequent atmospheric inversions, as well as the construc-
tion of barriers to natural ventilation, enhance the impact of waste
emissions on air quality. Through processes not yet clearly under-
stood, these wastes condense and coagulate into aerosols that affect
visibility, the number density and size of water droplets in the atmo-
sphere, the transparency of the atmosphere for sunlight, and, pos-
sibly, dynamics and temperature structure of the atmosphere.

The resulting degradation of urban air quality is not only un-
pleasant but may be injurious to health. Scientists cannot accurately
specify either the meteorological processes or the chemical reactions
that significantly affect urban air quality. Consequently, they cannot
construct optimum models to assist in the evaluation of alternative
control strategies. Because of the current lack of knowledge, there
frequently is no way to detect errors in the control program, errors
that could lead to costly overcontrol or dangerous undercontrol. As
conventional energy sources decline, the need to avoid both over-
control and undercontrol will increase.

The Panel concluded that monitoring and control activities must
be supported by a strong continuing research program to ensure
protection of public health and comfort with the least possible eco-
nomic dislocation. A basic requirement for such a research program
is to obtain better measurements of meteorological and chemical
factors in the urban environment. Therefore,

THE PANEL RECOMMENDS DEVELOPMENT OF GREATLY IMPROVED
INSTRUMENTATION FOR URBAN AIR-QUALITY MEASUREMENTS AND

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*Additional information on this subject appears in Appendixes C, D, and E.

OPTIMUM DEPLOYMENT OF THE BEST AVAILABLE INSTRUMENTA-
TION IN GATHERING ATMOSPHERIC DATA AND DEVELOPING
ADEQUATE AIR-POLLUTION MODELS

Better research instruments are needed to confirm and quantify
the presence in urban air of certain reactive chemical intermediates
that could affect significantly the state of polluted air. These include
hydroxyl radicals, perhydroxyl radicals, excited states of atomic and
molecular oxygen, and many organic free radicals. Presumably these
chemical intermediates occur in concentrations of about 0.1 part per
billion or less. Some possible methods that might be developed to
detect such minute amounts include

1. Very-long-path infrared absorption, using tuned lasers for
emission sources;
2. Selective chemiluminescence;
3. Stimulated emission, using tuned lasers;
4. Photoelectron spectroscopy (electron spectroscopy chemical
analysis) and/or mass spectroscopy, probably with elaborate molec-
ular beam-sampling techniques.

Better field instruments are required for more exact specification
of the state of urban air and to permit better prognosis of the relative
benefits of alternative control strategies, particularly when urban
crisis episodes are to be modeled. Crisis episodes are associated with
prolonged periods of low winds and stable air. The Gaussian-plume
assumptions employed by most air-quality models are not adequate.
Instead, winds are diurnally controlled and greatly influenced by
local topography. Because inversions dominate, information on in-
version stability and breakup is essential to model-assisted prognoses.
Near plumes, mixing (rather than chemical kinetics) often controls
net rates of chemical change.
The Panel specifically suggests that

1. Remote sensors be deployed to obtain inversion profiles.
[Acoustic probes, radiometers (for carbon dioxide near 15 μm or
oxygen in the millimeter band], and lidar probes (for low-level dust)
are all obvious possibilities.]
2. Concentration ratios, of reactive to inert constituents, be
emphasized near plumes. Measurements must be made with sufficient
time and space resolution to permit the separation of concentration
fluctuations from gross chemical rates.

3. Particle size and composition distribution be measured routinely, including aerosols of sizes less than 0.1 μm.

4. Meteorologists develop criteria for locating instruments, and optimum sampling plumbing be developed and standardized.

Control logistics depend entirely on a presumed relationship between the composition of the atmosphere and the emission of substances to it. Only when these models are realistic will control measures be optimized. Clearly, realistic models will require that data of high quality be obtained under circumstances dictated by both meteorological and chemical aspects of the overall problem.

B. Stratospheric Composition *

The stratosphere presents special problems because of its slow rate of mixing, small mass, and immunity to scavenging by the precipitation process. Primarily because of its exposure to shortwave solar radiation, it is the home of many natural, chemically active trace constituents, such as ozone.

Currently, the nation is engaged in a "crash" program to understand the effect of engine emissions from supersonic transports (SST's) on the stratosphere, especially on the concentration of ozone. Basic questions must be answered and crucial decisions made in too short a time. The Panel agrees that under the circumstances this program is necessary and is being handled adequately. However, this kind of situation should be avoided in the future, if at all possible, through programs of coordinated research with long-range applications. ·

Regardless of the outcome of the SST controversy, the question of stratospheric contamination and alteration is likely to continue indefinitely. Other types of high-flying aircraft will probably be proposed; penetration by rocket and satellite vehicles probably will increase. Transport of trace constituents (for example, sulfur dioxide, methane, carbon monoxide, and nitrous oxide) upward through the tropopause from sources below is poorly understood. The stratosphere contains, in addition to ozone, layers of relatively large particles, whose origin, distribution in space and time, and geophysical effects are not adequately understood.

*Additional detail and documentation appear in Appendixes A and B.

Therefore,

THE PANEL RECOMMENDS A STRONG AND CONTINUING RESEARCH
PROGRAM ON THE COMPOSITION OF THE STRATOSPHERE, INCLUDING
THE FOLLOWING, IN ORDER OF PRIORITY*:
    1. DETERMINATION OF THE NATURAL AMBIENT CONCENTRA-
TIONS OF SUCH TRACE CONSTITUENTS OF THE STRATOSPHERE AS
NO, NO_2, N_2O, NO_3, N_2O_5, HNO_3, H_2, CH_4, and OH;
    2. ACHIEVEMENT OF A MORE DETAILED UNDERSTANDING OF
THE ROLE OF ATMOSPHERIC TRANSPORT PROCESSES IN THE DISTRI-
BUTION OF OZONE;
    3. MORE DEFINITIVE LABORATORY MEASUREMENTS OF RE-
ACTION RATES INVOLVING THE NITROGEN OXIDES, WATER, AND
ODD OXYGEN;
    4. LONG-TERM MONITORING OF STRATOSPHERIC OZONE, WATER,
AND OTHER CHEMICALLY AND PHYSICALLY IMPORTANT CONSTIT-
UENTS;
    5. CONTINUING STUDY OF THE FORMATION, COMPOSITION, AND
LOSS OF STRATOSPHERIC AEROSOL AND OF ITS EFFECT ON ATMO-
SPHERIC RADIATION AND HEAT BALANCE. (The study should include the
sampling of volcanic plumes that penetrate the stratosphere.)

The DOT's CIAP includes a large stratospheric research effort,
the objective of which is the solution of many of these problems. If
this Program terminates in 1975, many vital problems of strato-
spheric pollution probably will remain unsolved. The CIAP has pro-
vided a research base and trained manpower with which to continue
an attack on these problems.

THE PANEL RECOMMENDS CONTINUING FEDERAL SUPPORT AND
COORDINATION OF THIS EFFORT AT A LEVEL COMMENSURATE WITH
THE REMAINING PROBLEMS.

Only recently have U.S. scientists and public administrators become
aware of the necessity of obtaining further information on trace
constituents of the atmosphere and on the complex nature of the
chemical, dynamic, and radiative processes occurring in the strato-
sphere that involve trace constituents. Despite this growing need for
more definitive information on trace constituents in the stratosphere,
the number of aircraft (WB-57F's) formerly utilized for stratospheric
sampling activities have been significantly reduced. The DOD in past
years has made a strong effort to provide adequate aircraft and num-
bers of flying hours to accomplish a major portion of the U.S. sam-

*As summarized from the detailed discussion in Appendix A.

pling program as determined by other agencies. This agency, however, has now phased the WB-57F out of its aircraft inventory. Other federal agencies having either operational or scientific needs or both have had to develop other plans. The Panel is pleased to learn that NASA has made arrangements with ERDA and DOT (CIAP) for the use of one of its WB-57F's for the stratospheric sampling requirements of these agencies.

The Panel considers it absolutely essential that a strong stratospheric sampling program be maintained by the United States for both operational and scientific objectives. The WB-57F aircraft, or its equivalent, should be available in adequate numbers for this purpose. In view of the requirement for support and operational funds now needed by several federal agencies for participating in a stratospheric sampling program,

THE PANEL RECOMMENDS THAT, THE FEDERAL GOVERNMENT ESTABLISH A PERMANENT TASK GROUP TO REVIEW ANNUALLY THE MERIT AND PRIORITIES OF THE ELEMENTS OF THE NATIONAL SAMPLING EFFORT TO ASSURE THAT A STRONG AND VIABLE U.S. PROGRAM IS MAINTAINED AND THAT AGENCIES ARE PROVIDED SUFFICIENT FUNDS TO MEET THEIR ADDITIONAL OPERATIONAL COSTS.

C. Migration and Fate of Atmospheric Trace Substances *

When natural and human sources inject gases and particles into the atmosphere, these substances are transported by winds and transformed by chemical reactions. As a result of these processes a wide variety of trace substances is present in the atmosphere and there is a continuous flux of material between the atmosphere, the hydrosphere, and the lithosphere. In the context of this problem, an entire city or complex of closely spaced cities would constitute a source. Building a higher smokestack, or placing it downwind of a particular city, could ease the immediate urban problem but would not affect the contribution of this source to the large-scale global problem.

Many of the compounds have marked effects either in the atmosphere or at the removal site. For example, sulfur dioxide emitted into the atmosphere is converted into other forms, including sulfuric acid. This strong acid is eventually removed by rain, which is slightly acidified in the process. An impressive body of data suggests the transport of sulfur compounds over distances of 1000 km or more.

*For additional detail and documentation, see Appendixes C, F, G, and H.

Studies in Scandinavia indicate that this mildly acidic water has cumulative and adverse effects on fish propagation in lakes and rivers, on soil nutrients and forest growth, and on exposed materials, especially calcareous statues, buildings, and metal structures.

Carbon dioxide in the atmosphere is slowly increasing because of the consumption of fossil fuels and a limited absorption rate by the oceans. The increase of this compound in the atmosphere causes an increase in the absorption of infrared radiation, which affects the temperature of the earth.

Nitrogen compounds such as nitrous oxide and ammonia are produced in abundance from the decay of vegetation, proteins, amino acids, and animal wastes. From this source they eventually reach the stratosphere, where they may have important chemical consequences.

Metals such as mercury and vanadium are transported through the atmosphere and may be processed and concentrated in the food chains of various ecosystems. Complex organic molecules, many of human origin, such as polychlorinated biphenyls (PCB's) and pesticides, are similarly transported and concentrated in food chains. Pesticide residues might be responsible for the inability of some species of wild birds to produce adequate eggshells.

Since almost all trace materials in the atmosphere are part of a global cycle, there is need for a systematic study of the nature of cycles, including sources, residence times, atmospheric transport processes, removal processes, and trends in atmospheric composition as a result of natural or human sources. Therefore,

THE PANEL RECOMMENDS STUDIES OF BOTH NATURAL AND HUMAN SOURCES OF TRACE CONSTITUENTS TO ASCERTAIN THE CONTRIBUTION AND ROLE OF HUMAN ACTIVITIES TO GLOBAL CYCLES OF THESE CONSTITUENTS.

To detect and monitor any possible long-term trends in atmospheric composition,

THE PANEL FURTHER RECOMMENDS THE ESTABLISHMENT OF A GLOBAL NETWORK OF CHEMICAL SAMPLING STATIONS, SUPPLEMENTED BY SAMPLING AND OBSERVATION FROM AIRCRAFT.

The Panel notes, and encourages implementation of, the plans of the World Meteorological Organization to establish a global network of such stations and of the U.S. National Oceanic and Atmospheric

Administration to maintain five such stations. Initially, a small number of stations should be established in key locations to estimate global average levels and secular trends of substances and to aid in estimating the number of such stations that ultimately will be needed to understand the chemical cycle for any substance. Both atmospheric and hydrometeor composition should be measured. In addition, rain composition measurements should be made at about 100 sites in the United States to permit comparison with data currently available in other countries.

Atmospheric chemical cycles and biological processes often are closely linked. The biosphere can serve as a source or sink in a given cycle. Further, adverse effects on plant and animal life are of major concern in connection with many cycles. Recognizing that there is far too little communication between atmospheric and biological scientists on many common research problems, the Panel strongly encourages the development of more cooperative endeavors drawing on the expertise of these two disciplines.

D. Chemical Aspects of Climatic Change*

A problem rapidly achieving scientific prominence is man's impact on climate. There are many reasons for concern about climatic change on a time scale of 100 years or less, for example, rapid glacial advances or shifts in average temperature leading to crop failures. The overall problem of climatic change is broader than atmospheric chemistry, encompassing also many problems of atmospheric dynamics and atmosphere-ocean interaction. Atmospheric chemists can, however, make major contributions to a better understanding of climate.

Current knowledge of the causes of climate and climatic change is incomplete. Various models of climate have been formulated. Studies employing these models imply that large-scale emissions of pollutants, including carbon dioxide and particulate matter, might cause instabilities that could produce an extreme climate such as an ice age or a "global greenhouse" similar to the atmosphere of Venus. Such models, constructed on incomplete knowledge, are subject to the criticism that the results depend strongly on the initial assumptions. There is pressing need for studies of the nature and types of instabilities that occur, the manner in which climatic systems react to

*Additional detail and documentation appears in Appendixes A, H, and I.

them, and the role of chemical processes. Trace atmospheric constituents clearly affect climatic regulatory mechanisms, but definitive data on the nature and magnitude of their effects are yet to be obtained.

Forecasts of future trends can be no more accurate than the data used in their formulation. Clearly, better data are needed on

1. Optical properties of particles and gases and their temporal and spatial distribution. These optical properties are closely related to chemical composition of the atmosphere, notably the molecular character. Scattering and absorption properties of stratospheric and tropospheric particulate matter of varied composition critically affect incoming solar radiation and terrestrial infrared emissions.

2. Properties of nuclei or of materials emitted by natural and human processes that might lead to changes in hydrometeor size distributions, location of clouds, or the amounts of cloud. Any of these changes can affect the global albedo, to which such data must be related.

3. Secular trends in any of these properties, especially those resulting from human activity. In addition, better knowledge is needed of the possible effects on these quantities of potential changes in human activities.

In light of these circumstances,

THE PANEL RECOMMENDS FEDERAL SUPPORT OF RESEARCH ON OPTICAL PROPERTIES OF ATMOSPHERIC PARTICLES AND ON CLOUD NUCLEATION MECHANISMS.

[The Panel's recommendation for a global network of chemical sampling and monitoring stations (see preceding section) is reinforced by the need for data on factors in climate change.]

Understanding of the formation of atmospheric aerosols, in both the troposphere and the stratosphere, is also a matter of importance. In particular, many gaseous trace substances in the atmosphere can form aerosol by atmospheric chemical reactions that are not yet well understood. That gaseous sulfur compounds, oxides of nitrogen, ammonia, terpenes, and high-molecular-weight olefinic hydrocarbons form atmospheric aerosols already is recognized. Therefore,

THE PANEL ALSO RECOMMENDS FEDERAL SUPPORT OF RESEARCH ON MECHANISMS OF GAS-TO-PARTICLE CONVERSIONS AND STUDIES

OF THE ATMOSPHERIC PORTIONS OF GLOBAL CYCLES THAT INVOLVE THE COMPOUNDS PARTICIPATING IN SUCH REACTIONS.

(These studies also will benefit from the results of global background monitoring.)

A number of interdisciplinary studies to which geological, atmospheric, chemical, and biological sciences have contributed form a basis for understanding the nature of climate. In each of these disciplines, many specific studies are taking place at various institutions, in many cases under the direction of outstanding scientists. The Panel recognizes and commends these much needed efforts and

THE PANEL RECOMMENDS FURTHER THE CONTINUED FEDERAL SUPPORT OF RESEARCH IN
    1. THE PHYSICS AND CHEMISTRY OF THE EARTH'S CRUST AND UPPER MANTLE;
    2. THE ORIGIN AND EVOLUTION OF THE EARTH'S ATMOSPHERE; AND
    3. THE CHEMISTRY AND DYNAMICS OF PLANETARY ATMOSPHERES.

III. CONTINUING REVIEW OF RESEARCH PRIORITIES

The Panel believes that problems and priorities in atmospheric chemistry should be reviewed periodically. New technological developments will have other and different impacts from those currently recognized. In addition, increased research could reveal effects still too subtle for present detection capabilities. As the life sciences, atmospheric sciences, and other disciplines move toward a greater degree of coordination, an increased understanding of interactions between the biosphere and the atmosphere could lead to recognition of new problems demanding high priority in atmospheric chemistry research. Therefore, as a continuing basis for review and coordination,

THE PANEL RECOMMENDS THAT THOSE FEDERAL AGENCIES CHARGED WITH SPECIFIC AIR-RESOURCE MANAGEMENT RESPONSIBILITIES STRENGTHEN THEIR LIAISON WITH UNIVERSITY-BASED ATMOSPHERIC CHEMISTS AND ENCOURAGE RESEARCH EFFORTS DIRECTED TO UNDERSTANDING AND SOLVING LONG-RANGE ENVIRONMENTAL PROBLEMS, AND

ATMOSPHERIC CHEMISTS OUTSIDE GOVERNMENT ACQUAINT THEMSELVES MORE FULLY WITH NATIONAL NEEDS AND GOALS TO WHICH

ATMOSPHERIC CHEMISTRY CAN CONTRIBUTE IN ORDER TO RENDER
MORE EFFECTIVE ASSISTANCE IN NATIONAL PROGRAMS.

These objectives could be accomplished by

1. Appointment of advisory committees to bring government
agencies into closer contact with research results of possible practical
usefulness as well as to inform nongovernment scientists of major
national programs;
2. Visiting scientist arrangements between government and pri-
vate organizations to broaden the perspectives of atmospheric chem-
ists in regard to short- and long-term national needs;
3. Expanded contract-and-grant research programs as an integral
part of atmospheric research missions of federal agencies; and
4. Extension of informal collaboration among atmospheric
chemists through professional society meetings, workshops, and per-
sonal informal information exchange.

In addition, the Panel sees the need for formal periodic reviews
of problems and priorities in atmospheric chemistry related to envi-
ronmental problems. Therefore,

THE PANEL RECOMMENDS THAT BETWEEN 1977 AND 1979 THE
NATIONAL SCIENCE FOUNDATION PROVIDE FOR A REVIEW OF PROB-
LEMS AND PRIORITIES IN ATMOSPHERIC CHEMISTRY RELATED TO
ENVIRONMENTAL PROBLEMS.

IV. EDUCATIONAL PROGRAMS

In order to solve the critical and challenging problems of the atmo-
spheric environment, the United States will need additional scientists
who are educated to deal with the interaction of chemical processes
and atmospheric motions. As with any relatively new subject that
cuts across traditional disciplines, the exact nature of the optimum
education is difficult to specify. In fact, it should not be defined too
rigidly, for problems such as urban air quality and climatic impact
require different types of expertise.

What is needed in many cases is more flexibility and options in
the programs of individual students. It is unrealistic to expect a
student to satisfy all the typical requirements for a PhD degree in
chemistry and at the same time learn a substantial amount of meteo-
rology or vice versa. Departments or universities interested in provid-
ing educational opportunities in atmospheric chemistry must look

for alternatives. Some departments of meteorology might find it acceptable to relax traditional requirements to permit a substantial minor in chemistry. Chemistry departments might do the same in regard to meteorology. Other universities may wish to establish an interdepartmental degree program or even organize new departments of atmospheric chemistry.

Recognizing that choice among these and other alternatives will vary with institutional constraints and objectives, the Panel does not recommend a particular course of action. However,

THE PANEL DOES RECOMMEND THAT DEPARTMENTS OF ATMO-SPHERIC SCIENCES, CHEMISTRY, AND OTHER RELATED DISCIPLINES, INDIVIDUALLY OR JOINTLY, EXAMINE PROMPTLY THE PROBLEM OF ADEQUATE, WELL-BALANCED TRAINING IN ATMOSPHERIC CHEM-ISTRY, PARTICULARLY IN PhD PROGRAMS.

Such educational programs will be developed more rapidly and will be more effective at institutions having faculty and research programs that deal with atmospheric chemistry. The Panel believes that not enough such people are currently available to provide the initial impetus for the development of atmospheric chemistry train-ing programs. Positive action is required to stimulate initial efforts toward development of what should become a self-sustaining pro-gram. Therefore,

THE PANEL RECOMMENDS THAT LIMITED-TERM POSTDOCTORAL PRO-GRAMS BE ESTABLISHED TO ENABLE PhD's IN CHEMISTRY TO STUDY IN METEOROLOGY DEPARTMENTS AND PhD's IN METEOROLOGY TO STUDY IN CHEMISTRY DEPARTMENTS FOR 1 TO 2 YEARS EACH. SUCH POSTDOCTORAL OPPORTUNITIES SHOULD BE LINKED TO ON-GOING RESEARCH PROGRAMS IN ATMOSPHERIC CHEMISTRY AT THE UNIVER-SITIES.

In making this recommendation, the Panel has in mind post-doctoral training of some five to ten students per year for a period of approximately five years. This modest plan, as noted above, is in-tended to provide a nucleus of young scientists that will be prepared to establish additional research and educational programs in the years ahead.

V. CONCLUSION

The Panel has pointed out that the United States currently is spending about $34.5 million annually on the total atmospheric

chemistry program. About $7.7 million of this is devoted to problems of the high-altitude ionized atmosphere and about $26.8 million to the neutral atmosphere, generally below some 80 km. Approximately $13.8 million is allocated to university research, of which approximately $10.1 million supports work in the neutral atmosphere.

Studies of the four high-priority problem areas that the Panel has identified should be pursued with great urgency, and they must be conducted separately from programs dealing with current problems. However, to rely solely on basic research would be a serious mistake. Although a strong, continuing, basic-research program is indispensable, it cannot by its nature provide the broad overview, completeness, and coordination that are needed.

An example of the type of coordination that the Panel proposes is the DOT's Climatic Impact Assessment Program (CIAP), with suitable modifications for longer-term objectives. This program has provided for broad-based scientific input to the identification of problems and planning of solutions through survey conferences and monographs. It has marshalled and coordinated the efforts of government, university, and industrial scientists toward a common goal. It has provided timely information about related efforts through newsletters and technical abstract reports. In short, it has accomplished in this limited area many of the actions recommended by the Panel. Similar programs with longer-range objectives could proceed at a more deliberate pace and should include research efforts requiring longer lead times.

Estimating the ultimate costs of the Panel's recommendations is greatly complicated by problems of definition, semantics, and assignment of specific investigations to specific programs—for example, allocation of aircraft costs for continued *in situ* stratospheric measurements and allocation of satellite costs for stratospheric monitoring. Further, some recommendations duplicate those made by other study groups; for example, the Panel's strong recommendation for global monitoring duplicates recommendation D.1 of the recent report of the NRC Committee on Atmospheric Sciences, *Weather and Climate Modification: Problems and Progress* (National Academy of Sciences, Washington, D.C., 1973, p. 30), and the Panel's recommendations on stratospheric composition are part of a more comprehensive program as described in *Research in the Stratosphere*, an interagency document by the Interdepartmental Committee on Atmospheric Sciences.

The most costly aspect of all the Panel's recommendations will be large-scale atmospheric observations, whether from aircraft, satellites, global monitoring stations, or urban and regional deployment of appropriate measuring devices. Currently, the basic background knowledge is insufficient to specify with absolute assurance what will ultimately have to be measured, to what degree of accuracy, where, and how often.

To avoid the pitfalls of detailed cost analyses in the face of these uncertainties, the Panel suggests that many of its recommendations would be satisfied for the next few years by the following actions:

1. Vigorous pursuit of the St. Louis studies (see Appendix D) as a coordinated effort on the problem of urban air quality;

2. Continuation of the national stratospheric research program at approximately the present level of funding, including continued aircraft measurements; and

3. Full implementation of the national and international plans for global monitoring.

Other recommendations, however, would not necessarily be satisfied by those programs. These include:

1. Development of improved instrumentation for air chemistry measurements;

2. Expanded studies of *natural* sources of atmospheric contaminants;

3. Studies of optical properties of atmospheric particles, cloud nucleation mechanisms, and gas-to-particle conversions in the atmosphere; and

4. Encouragement of a modest program of PhD and postdoctoral education in atmospheric chemistry.

To achieve these latter four goals the Panel estimates that the federal budget for atmospheric chemistry of the neutral atmosphere below 80 km should be increased by from $1 million to $2 million per year over and above inflationary costs in each of the next five years, for a real total five-year increase of $5 million to $10 million.

If these actions are taken, the Panel believes that in about three years a follow-up review of the state of the art in atmospheric chemistry and of the problem areas the Panel has identified will permit a better assessment of the actions required to protect the atmospheric environment and the costs associated with these actions.

4
Epilogue

Since the Panel last met formally and prepared this document about two years ago, a number of situations have changed that are of sufficient importance and concern to us to warrant mention.

Both experimental and theoretical areas of atmospheric chemistry have experienced a period of high activity and of discovery. The Climatic Impact Assessment Program (CIAP) is nearly complete and has produced significant improvements in our understanding of stratospheric processes. Notable was the confirmation of the importance of NO_x in ozone photochemistry. The Environmental Protection Agency's Regional Air Pollution Study (RAPS) has just begun in St. Louis and has absorbed much attention from experimental atmospheric chemists. The recent discoveries that atmospheric halocarbons such as CCl_2F_2 and CCl_3F are increasing and may influence stratospheric ozone poses questions for atmospheric chemists, for control officials, and for economists associated with the use of such materials, e.g., as refrigerants and as aerosol propellants.

The past two years have also been characterized by a continuation of crisis orientation among a large segment of the atmospheric chemistry community. We continue to believe that it is preferable to maintain a steady effort over a continuing period aimed at developing a sound basis for solving problems as they arise.

Costs relating to air-pollution control of automobiles alone are estimated by an NAS study* to be between $5 billion and $8 billion per year, with some of the burden of decision to control or not to control such pollution sources riding on the shoulders of atmospheric chemists. Even though the number of atmospheric chemists has not grown significantly during the past two years, the level of responsibility, measured in dollars, has increased.

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*Report by the coordinating committee on Air Quality Studies, NAS/NAE, prepared for U.S. Senate Committee on Public Works re. S. Res. 135, Sept. 1974, Vol. 1, p. 2.

At the same time, we note that the National Center for Atmospheric Research has dismissed over half of its staff in the area of atmospheric chemistry and has de-emphasized this program. Similarly, the National Science Foundation has diminished its expenditure for long-term atmospheric measurement programs. This de-emphasis has resulted in a net decrease in the field activities of some atmospheric chemical programs; for example, the studies of atmospheric CO_2, even though an attempt has been made by the National Oceanic and Atmospheric Administration to institutionalize several of these measurement efforts. The Environmental Protection Agency has canceled its program of Air Pollution Training grants. This program had been a major source of support for graduate students in atmospheric chemistry and for equipment in university laboratories. It appears, therefore, that in spite of increased responsibilities, support of the basic scientific efforts in atmospheric chemistry is suffering important setbacks.

Looking toward the future, especially toward increased utilization of sulfur-containing coal and oil for energy, it would seem that there is still an urgent need for more and better trained people and more effort aimed at the basic understanding of atmospheric chemical processes. As was pointed out in our report, attempts to control air pollution without adequate scientific basis will likely lead to nonoptimum schemes and either costly overcontrol or hazardous and costly undercontrol. An example of this occurred recently when it was discovered that the catalytic control devices for automobiles produce sulfuric acid aerosol while controlling CO and hydrocarbons.* The decision to utilize the catalyst was made without adequate knowledge of its total impact on atmospheric composition.

Atmospheric chemists may have only a minor role to play in such decisions regarding specific air-pollution control devices; however, the factual basis they are able to provide is essential. On the other hand, there are other important areas emphasized in the report that will take a longer period of time before they reach a stage of application comparable with some areas in the air-pollution field.

We believe, at this time, that new conclusions or new recommendations regarding the issues underlying the situations described above are not required. The events of the past two years as noted confirm our confidence that they remain correct, realistic, and valid.

*Science 182: 368–371 (Oct. 1973).

II
Scientific Reviews
on Problems of
Atmospheric Chemistry

Appendix A
Stratospheric Chemistry
and Transport

RICHARD A. CRAIG AND JAMES P. FRIEND

I. INTRODUCTION

The composition of the stratosphere, including a large variety of trace constituents, constitutes a special and important problem in atmospheric chemistry.

It is separable from chemical problems of the troposphere for a number of reasons. The stratosphere, being stably stratified, mixes relatively slowly. It is also essentially immune to the rainout process that plays an important scavenging role in the troposphere. Thus, trace constituents deposited in the stratosphere, whether by volcanoes or by nuclear tests or by high-flying jet aircraft, have a considerably longer lifetime than those deposited in the troposphere. Moreover, there is the possibility that some of these might affect the abundance of ozone, which is present naturally in the stratosphere. Ozone is an extremely important trace constituent because of its intense absorption of ultraviolet radiation. This absorption not only affects the thermal structure of the stratosphere itself but also shields the earth's surface from potentially dangerous ultraviolet radiation. Therefore, any possibility of decreasing ozone by upsetting the natural chemical balance must be viewed with alarm.

The composition of the stratosphere, especially the lower stratosphere, depends at least as much on meteorological transport processes as it does on chemical processes. The chemical lifetimes of many constituents (for example, odd oxygen*) are very long. The distribution in latitude and altitude of these constituents depends critically on transport processes. Interchange with the troposphere, which may serve as a sink in some cases and a source in others, is a

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*"Odd oxygen" is a term used to denote $O + O_3$.

complicated phenomenon, taking place impulsively in certain meteo-
rological situations that are most common in middle latitudes during
winter and early spring.

Ozone and radionuclides from atmospheric testing of nuclear
weapons have been the most extensively and intensively studied trace
materials in the lower stratosphere. Systematic global-scale sampling
programs coupled with meteorological measurements and knowledge
have provided considerable insight into stratospheric air motions and
the consequent transport phenomena. At the beginning of these
large-scale programs it was hoped that the observations of the distri-
butions of the substances, since they are quasi-conservative in the
lower stratosphere, would permit determination of the air motions.
Chemists believed that they could interpret the tracer data so as to
reveal the behavior of the atmosphere. Almost everyone who has
worked in the field now realizes that tracers mainly serve to verify or
refute meteorological theories of the air motions in the lower strato-
sphere. In and of themselves, observations of tracers do not permit
deduction of detailed atmospheric motions. The reason for this is not
theoretical, it is practical. So far, and probably so into the foresee-
able future, it has not been possible to mount a sampling and analysis
program extensive enough to permit the reliable determination of
fluxes of the trace materials. This means that wind velocity and
tracer concentrations must be measured simultaneously in a sus-
tained global program.

The observations of stratospheric radioactivity have led to the
development of various parameterized models that permit estimates
of fallout distributions, stratospheric burdens, and approximate
stratospheric concentration patterns to be made for given initial con-
ditions. These are all two-dimensional models. Box models in which
first-order kinetics are presumed to prevail (the transfer constants are
the parameters) can successfully reproduce various integrated quan-
tities, hemispheric stratospheric burdens and hemispheric cumulative
fallout, for example. These can be used for prediction for tests with
injections mainly in the stratosphere. For higher-altitude injections
there appears to be uncertainty as to how *a priori* to partition the
materials between hemispheres.

There are at least three versions of model based on a two-
dimensional representation of advection and turbulent diffusion
(particle settling is part of the vertical component of velocity in the
advection portion) plus a scheme for removal by rainout or dry

deposition on the surface. Basically the models consist of finite-difference forms of the diffusion equation in the meridional plane. The eddy-diffusion coefficients (K's) are parameters. Although it is not widely appreciated, the velocity components in the meridional plane are also parameters. The reason for this is that two-dimensional representations cannot represent meridional transport by standing eddies in an explicit manner, so their effects are embodied in the eddy-diffusion coefficients and in the mean velocity components. The foregoing ideas and concepts have been discussed by Feely *et al.* (1971).

II. RADIOACTIVITY

The models discussed above generally give a fair accountability of the distribution and fallout of radionuclides from an *ensemble* of injections (a test series). There have been numerous observations in the Energy Research and Development Administration [formerly the Atomic Energy Commission (AEC)] and the Department of Defense (DOD) sampling programs of debris from single detonations that show behavior markedly different from that "predicted" by the models. Generally, these can be ascribed to meridional and zonal motions, which depart significantly from the average motions. In light of this knowledge, it seems that intensive and extensive spatial and temporal sampling of an ensemble of injections would be required to provide further data for refining of the models. The prospect for this appears to be quite remote.

Natural radioactivity is present in the stratosphere in the forms of several nuclides, including ^{3}H, ^{14}C, ^{7}Be, ^{22}Na, ^{32}P, ^{33}P, ^{35}S, ^{210}Pb, and ^{210}Po. All of these have been measured to some extent during the various sampling programs. The first two nuclides listed are created in large amounts in nuclear fusion explosions. Tritium, ^{3}H, is difficult to treat in simple models because part of it is associated with atmospheric water vapor (with its complex behavior) and part is associated with hydrogen gas. Carbon-14 has been measured extensively, but its observed distributions have not been used in model studies. It seems possible that a currently available model with its stratospheric parameters could be employed to simulate ^{14}C behavior while parameterizing the surface removel conditions. This procedure could aid in understanding the global CO_2 sea-air exchange problem.

The nuclides ^{22}Na, ^{32}P, ^{33}P, and ^{35}S are products of cosmic-ray spallation of atmospheric Ar, while ^{7}Be comes from Ar, O, and N. The source strength for each of these nuclides has been worked out by Lal and Peters (1962) for each point in the meridional plume. Removal is by radioactive decay and by the same physical processes as for fission-product nuclides. Since the source is continuous and quite uniform zonally, the behavior of these nuclides should conform closest of all materials to that given by the two-dimensional models. Unfortunately, the measurements have been sparse in temporal coverage, so that reliable zonal averages are not available for comparison with the model. Another and possibly bigger problem is that of finding suitable particle settling-velocities in the polar regions above 30 km where the source strength is the largest.

The nuclides ^{210}Pb and ^{210}Po are daughter products of radon (^{222}Ra). Radon enters the stratosphere from the troposphere and there decays ultimately to form ^{210}Pb and ^{210}Po. Direct transport of ^{210}Pb and ^{210}Po from the troposphere into the stratosphere also occurs. These processes are being studied by Feely (1972), who is analyzing ^{210}Pb in portions of stratospheric samples from the past DOD and AEC programs. From such studies, the rates of injection of tropospheric materials into the lower stratosphere may become known and applied to problems connected with such materials of tropospheric origin as NH_3, NO_x, SO_2, and CO.

III. STRATOSPHERIC AEROSOLS

Measurements of composition of aerosols collected in the stratosphere have shown the presence of sulfate (or persulfate) in all samples. No other anion has been found in a quantity approaching that of sulfate. Lazrus and co-workers (1971) have found nitrate in filter samples, but they think it is from gaseous HNO_3, which absorbs in the filter material. Most investigations have found NH_4^+ to be present, though the filter samples generally contained less NH_4^+ than needed for the stoichiometry to form $(NH_4)_2SO_4$. Presumably the remaining sulfate was in the form of H_2SO_4. The particles may exist in the stratosphere in mixtures ranging between 100% H_2SO_4, 0% $(NH_4)_2SO_4$ and 100% $(NH_4)_2SO_4$, 0% H_2SO_4. Water may or may not be associated with the particles.

The size distributions of the stratospheric aerosol have been determined on impactor samples by Mossop (1965) and by Friend (1966), using electron microscopic examination. Using their

methods, they could not have observed H_2SO_4 particles if such were present. Various optical measurements have been made in attempts to determine size distribution functions. DeBary and Rössler (1970) using balloons and rockets measured scattered light at two angles. From Mie theory and using various model distribution functions, they concluded that their observations could be explained with the "wedge-shaped" function similar to that found by Friend for the large particles (peak radius of 0.30 μm) combined with a large δ-function-type peak for Aitken nuclei (0.3 μm < r < 0.05 μm). Rosen (1968, 1969) using a balloonborne dark-field microscope measured particle concentrations and also obtained size distribution assuming the functional form of the integral distribution to be $N(r) = ar^{-b}$. Other investigators had made this assumption (Junge and Manson, 1961; Newkirk and Eddy, 1964). This assumption precludes obtaining agreement with the results of Mossop and Friend. Rosen's results were that great numbers of particles were "found" in the size range r < 0.1 μm. This may be substantially in agreement with DeBary and Rössler, setting aside Rosen's assumption about the size distribution function. However, the matter bears further investigation.

The origin of stratospheric sulfate aerosols is still in question. Friend has estimated that about 10 percent of average annual volcanic SO_2 emissions would be enough to account for the pre-Agung sulfate in the stratosphere. He also suggested that most if not all of the stratospheric sulfate comes from volcanic sulfur emissions, mainly as SO_2. The origin of NH_4^+ is presumably from NH_3 from decayed biological materials, including animal urine.

Recently, a laboratory study of aerosol formation from all-gaseous components led Friend *et al.* (1973) to propose a model for stratospheric sulfate aerosol formation. The model suggests that SO_2 is oxidized initially via the three-body reaction

$$SO_2 + O + M \rightarrow SO_3 + M.$$

The resulting SO_3 combines with water to form sulfuric acid, which subsequently combines with several water molecules to form an embryonic nucleus. In the absence of any other chemical processes, the embryonic nuclei would grow by coagulation to form an aerosol of sulfuric acid–water with a particle size distribution approaching the "self-preserving" form for an equilibrium in coagulation. The model of Friend *et al.* (1973) further indicates that if ammonia is present, then the acid nuclei would be neutralized to form "salt

nuclei" consisting of ammonium sulfate and ammonium bisulfate mixtures. These salt nuclei could then be centers for rapid oxidation of SO_2 by a rapid heteromolecular mechanism requiring fluxes of SO_2, NH_3, and H_2O to the growing particles. The mechanism of this heteromolecular oxidation is unknown and may be related to the well-known solution oxidation of SO_2 (whose exact mechanism is also unknown). The work of Friend *et al.* (1973) suggests that stratospheric Aitken nuclei are largely composed of $H_2SO_4 - H_2O$ mixtures. Stratospheric large particles might consist of $H_2SO_4 - H_2O$ mixtures or ammonium sulfate or any composition given by mixing various proportions of the two, depending on the amounts of NH_3 available at the time of formation. The finding of persulfate ($S_2O_8^-$) in some stratospheric samples (Friend, 1966) is not explained by the above model and may be evidence of the involvement of such species as H_2O_2, HO_2, or O_3.

The flurry of excitement over the supersonic transport (SST) has focused attention on the lower stratosphere. It was estimated in the SCEP report (1970) that the sulfate added to the stratosphere by the SST would be modest compared with that present in the post-Agung period. Nonetheless, because the particles constitute a background that interacts with radiation and affects climate, it is important to understand their physical and chemical properties in detail. To accomplish this, the following, which are not now being done, need to be done:

1. Routinely monitor concentrations of sulfate and ammonium. Chloride and nitrate could be done on the same samples at little extra cost. The program should provide good coverage of the meridional plane up to 30 km, using aircraft and balloons. If we are to understand short-term variations of concentrations, at least monthly coverage of the network would be required. The program should last at least two years. This is admittedly expensive, but there appears to be no alternative. Lidar cannot solve the problem of composition and concentration.

2. Obtain many more direct samples by impaction for very careful electron microscopic and electron diffraction measurements. Shadowing techniques should be used to help identify H_2SO_4 particles. This task should be done in conjunction with lidar measurements.

3. Make lidar soundings in conjunction with all direct sampling.

4. Collect and determine number concentration, size, and composition of stratospheric particles including Aitken particles. Clearly, this is a field (Aitken) in which little or nothing is known. New methods will have to be employed because the old ones cannot accomplish the task.

5. Sample volcanic plumes and the stratosphere in the vicinity of volcanic eruptions. Measurements of SO_2, NH_3, NH_4^+, $SO_4^=$, H_2O, and optical mixing ratios should be made. Impactor samples should also be obtained for electron microscopic studies.

6. Measure NH_3 and SO_2 concentrations in the lower stratosphere and upper troposphere. Again, new methods must be found to perform this task.

IV. OZONE AND RELATED SUBSTANCES

About ten years ago, it appeared that the stratospheric ozone problem was "solved." The oxygen-only photochemistry of Chapman (1930), as applied by a number of workers using the latest available data on solar flux, rate coefficients, and absorption coefficients, seemed to give a good account of the observed ozone distribution between 30 and 50 km. Below 25–30 km, it was assumed that atmospheric transport processes predominated over chemistry, in view of the very long chemical lifetime of ozone. The picture was one of net ozone formation in a production region at 30 ± 5 km in low latitudes (and in middle and high latitudes in summer), of ozone transport by the atmosphere to lower levels and higher latitudes, and of an ultimate ozone sink in the troposphere and at the ground.

Now, serious questions have been raised about the details of the chemistry and about the relative importance of chemistry and transport in the lower stratosphere. The problem has taken on great practical significance since the suggestion by Johnston (1971) that SST emission of nitrogen oxides at 20 km might seriously deplete the ozone shield with unfavorable biological effects.

Newer laboratory data have cast doubt on the sufficiency of the simple chemistry suggested by Chapman (1930). It appears now that the rate coefficient for the $(O + O_3)$ reaction, which is the principal mechanism for destruction of odd oxygen in the Chapman scheme, is considerably smaller than used in early calculations [for example, by Craig (1950)]. Just as important, but not generally mentioned, absorption coefficients for both O_3 and O_2 in the "window" region

near 2100 A are now assigned smaller values than before. These two factors cause more recent calculations to predict too much ozone in comparison with observations.

Various ideas have been offered to explain the discrepancies between the calculations and the observations. It was first suggested (Hunt, 1966) that hydrogen compounds (OH, HO_2) might play an important role in destroying odd oxygen. The latest suggestion (Crutzen, 1971; Johnston, 1971) is that nitrogen oxides (NO, NO_2) might play this role. Considerable uncertainty remains, partly because we find ourselves in the uncomfortable position of not knowing very accurately how much OH, HO_2, NO, NO_2, and other related trace constituents occur naturally in the terrestrial stratosphere.

Ozone is not formed *in situ* at low altitudes. This is because the radiation that dissociates O_2, thus producing atomic oxygen, which in turn leads to ozone formation, does not penetrate to low altitudes in significant amounts; its level of maximum absorption is in the upper stratosphere. The height below which significant ozone production ceases depends on the absorption coefficients of O_2 and O_3 in the window region around 2100 Å and on the zenith angle of the sun. With an overhead sun and accepted values of these coefficients, little ozone is produced below 20–25 km. Certainly there is no significant production of ozone in the lower stratosphere at high latitudes in winter, when the sun is near or below the horizon.

However, it is an observed fact that the largest ozone densities found anywhere in the atmosphere occur in the lower stratosphere (between 10–20 km) at high latitudes in late winter and early spring. This fact attests to the importance of transport processes in the lower stratosphere. The atmosphere transports ozone (from lower latitudes and higher altitudes) into this region where it accumulates during the winter. The ozone removed from the source region is replaced by the usual photochemical production processes. In the high-latitude, low-altitude accumulation region, the ozone (once it is transported there) suffers no significant chemical destruction; although photodissociation of ozone may still occur (by absorption in the 3000–3400 Å bands and in the visible), the oxygen atom released in the photodissociation goes quickly back into ozone by three-body association with O_2, which is a very fast reaction at such relatively high densities. Destruction of odd oxygen, by the $(O + O_3)$ reaction in the Chapman scheme, is relatively slow.

The ozone transported into the high-latitude lower stratosphere during the winter is eventually transported into the troposphere. Since the ozone maximum is usually reached in February or March, it appears that at this time the loss across the tropopause begins to exceed the gain from the winter stratospheric transport processes. Once in the troposphere, ozone is more rapidly mixed in the vertical, as shown by observations that the vertical variation of ozone mixing ratio in the troposphere is very much less than in the lower stratosphere. Ozone is destroyed at the ground, as shown by the diurnal variation of ozone density near the ground. There may also be other chemical sinks in the troposphere.

Although we do not understand the transport processes well enough to make definitive calculations at the present time, we can infer several things from their observed effects. The transport of ozone poleward is much more rapid during the winter months than during the summer, since high-latitude ozone decreases during the summer despite the return of the sun. The transport occurs along surfaces that slope downward toward the pole; observations show that these surfaces are roughly parallel to surfaces of constant potential vorticity (Hering, 1966). Transport through the tropopause occurs preferentially in late winter and early spring and in middle to high latitudes. Incidentally, all of these statements are verified by the observed transport of radioactive material deposited in the stratosphere from nuclear explosions.

We also know that synoptic-scale, meteorological conditions in the stratosphere change drastically with season and latitude. In low latitudes, the flow is nearly zonal and horizontal at all times of the year. The same is true of middle and high latitudes in late spring, summer, and early fall. However, the middle- and high-latitude winter stratosphere is very active meteorologically with well-developed troughs and ridges and significant large-scale vertical motions. To most meteorologists, it seems clear that the poleward and downward transports of radioactive material and of ozone in winter is connected with these synoptic-scale circulations and not with sub-synoptic-scale eddy diffusion represented by a Fickian-type formulation. Furthermore, the preferred time and place for transport from stratosphere to troposphere corresponds to the preferred time and place for direct interchange between the two regions along frontal surfaces and stable laminae (Danielson, 1959, 1968).

In view of the situation described above, there are several areas of measurement and research that are required for a satisfactory resolution of the ozone problem.

1. The highest priority is to determine the natural ambient concentrations of trace constituents of the stratosphere, such as NO, NO_2, N_2O, NO_3, N_2O_5, HNO_3, H_2, HO_2, CH_4, and OH. This is necessary to help determine the relative importance of various suggested chemical reactions and should be accomplished as soon as possible to provide baseline data prior to any era of substantial pollution.

2. Next in importance is to achieve an understanding of the role of atmospheric transport processes in the distribution of ozone, as a function of latitude, altitude, and season.

3. More definitive laboratory measurements are needed of reaction rates involving the nitrogen oxides, water, and odd oxygen.

4. Any doubts about the magnitude and spectral distribution of extraterrestrial solar flux in the critical region of 2000–2400 Å (and its possible variability) should be cleared up.

5. In view of the possibility of substantial future pollution, the long-term monitoring of ozone, water, and other chemically important constituents should be planned for comparison with what we know or can soon find out about the "natural stratosphere" (see 1 above). Although in situ measurements from balloons and aircraft are needed now, their prohibitive cost for long-term global measurements suggests satellite methods such as limb measurements of infrared emissions.

V. OTHER SUBSTANCES

Methane has been measured in the lower stratosphere in a limited program by the National Center for Atmospheric Research (NCAR) group (see Ehhalt and Heidt, 1973; and Bainbridge and Heidt, 1966). They found suggestions of decreasing mixing ratio with increasing height. Scholz et al. (1970) found no methane in an air sample taken from the vicinity of the stratosphere. The intriguing notion that a significant proportion of water vapor in the upper atmosphere may come from the oxidation of methane has been put forth by these investigators. Investigations of this idea are of importance in understanding planetary atmospheres and may be relevant to the evolution of the earth's atmosphere.

Carbon monoxide has been determined in limited sampling of aircraft-based measurements by Seiler and Junge (1970). Rapid decrease of CO concentrations above the tropopause have led to the notion that OH in the stratosphere reacts with CO to make the stratosphere a major sink for CO. This concept must be approached with caution in light of recent findings of volcanic sources of CO and bacteriological sinks at the surface. Furthermore, computations of mixing involving only the vertical dimension are possibly too crude to determine that chemical reactions may occur in the lower stratosphere. Study of CO in the lower stratosphere should be coupled with tropospheric and surface CO observational programs. Unless CO represents a significant sink for OH, it has relatively little effect on the stratospheric environment.

No measurements have been made in the lower stratosphere of concentrations of NH_3, SO_2, and H_2S. Their concentrations are undoubtedly very low (mixing ratios of the order of 10^{-4} ppm or less). They are probably important in the formation of stratospheric aerosols and because of that should be measured.

Measurements of concentrations of CO_2 in the lower stratosphere were made in conjunction with ^{14}C and the AEC and DOD high-altitude sampling programs. The results showed that average abundances closely paralleled those in the troposphere. Small fluctuations in abundance presumably reflected larger fluctuations in the troposphere. Though sampling and analysis are not difficult or very expensive, it does not appear worthwhile to use CO_2 as a tracer for stratospheric motions. From a geochemical point of view, the amount of CO_2 in the stratosphere is a small fraction of atmospheric CO_2. Assessment of the long-term effects on atmospheric radiation of CO_2 abundances may be quite closely determined from the tropospheric measurement programs. Short-term fluctuations of the order of 10–20 ppm (out of ~320 ppm) will have insignificant effects on the cooling of the stratosphere through net emission of long-wave radiation.

VI. SAMPLING AND ANALYSIS

A. Equipment

Existing balloons and RB-57F aircraft can adequately perform the missions involving air-filter sampling. The aircraft sampling hatch may require modification to prevent seepage of tropospheric air with

much higher concentrations of trace materials. The polystyrene filters made by NCAR appear to have acceptably low background amounts of the trace substances of interest.

Balloonborne cascade impactors offer the best chance of obtaining particulate samples from which adequate size distribution spectra can be obtained. At least a backup filter sample will provide opportunity for the determination of the chemical composition of Aitken nuclei. The RB-57F aircraft have the capability of carrying the body-type impaction probes used in the past and recently by Cadle. These probes are not efficient for particles with radius < 0.15 μm. Also these probes are uncalibrated. Extensive use in a sampling program would necessitate a wind tunnel calibration test using standard aerosols.

Side-looking balloonborne lidar and scattering measurements similar to those of DeBary and Rössler can provide meaningful information on the temporal and spatial (vertical) variations in optical mixing ratio. Concurrent sampling and optical measurements may reveal significant interrelationships so that optical soundings can generally give useful information on aerosol concentrations.

The concentrations of SO_2, NH_3, and NO_x are so low that methods of measurement employed in the past are ineffective in providing useful data. Specialized tunable laser spectroscopic techniques may provide acceptable results. A sophisticated mass spectrometric system may be the best means for obtaining high-quality, reliable data concerning the above gases. Certainly, the payload is a problem, but it is not insurmountable. Even measurements in the upper troposphere can provide useful information.

B.   Programs

As pointed out earlier, the monitoring of natural background concentrations of ozone and particulate matter in the lower stratosphere can provide adequate understanding of the environment only if undertaken on a suitable time and space scale. Estimates suggest that approximately monthly coverage of a global scale (or hemispheric scale) network over a two- to three-year period would be reasonably adequate. The program would involve aircraft and balloons. Other measurements such as SO_2 and NH_3 require a much less intensive effort.

Finally, sampling of volcanic plumes is important, and there should be created some means by which men and equipment can be quickly dispatched to the sites of active volcanoes of sufficient size.

Appendix B
Upper Atmospheric Dynamics and Chemistry

JOHN E. GEISLER and DONALD M. HUNTEN

I. INTRODUCTION

An active and growing area in dynamical meteorology is global modeling of the circulation of the lower atmosphere. Some of these general circulation models (GCM's, as they are now called) extend up into the stratosphere. Knowing sources and sinks, scientists today can use a GCM to calculate the global distribution of trace gases in the troposphere and in some cases the lower stratosphere (e.g., Hunt, 1969). There is considerable demand to push the ceiling of existing GCM's to greater heights. What the ultimate ceiling will be cannot be stated. What can be said is that above about 30 km (that is, in the upper half of the stratosphere and beyond) there is a strong interaction between chemistry, radiation, and the motion field. Before a GCM can be extended upward into this region, and thus be used to study the effect of motions on trace gases, a great deal more than is now known about this interaction will have to be learned. Furthermore, there is little descriptive knowledge of the motion field above about 30 km against which we could check the output of a GCM. There seems no way of confronting this latter difficulty except by increased synoptic data coverage.

This paper considers what is known about atmospheric motions and chemistry in the 30- to 100-km altitude range. For purposes of discussion, three types of motion systems are distinguished: global circulations in the zonally averaged flow (meridional cells), planetary waves, and small-scale motions. The global circulations are driven by *in situ* radiative sources and sinks. These are primarily absorption of solar radiation by ozone and infrared cooling by carbon dioxide. Planetary waves are forced in the troposphere, and their propagation into the upper atmosphere is influenced by radiative and photochemical damping. The small-scale processes are internal gravity waves and

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turbulence. Gravity waves are forced in the troposphere and so far as is known are not subjected to photochemical damping. Turbulence develops in the large shears associated with these waves at high altitudes. At present, it is not known which of these three types of motion fields is most effective in transporting chemical constituents in the vertical. Also, there exists a good deal of controversy between aeronomers and meteorologists as to which of these motion systems provides a transport that can be parameterized as eddy diffusion.

II. GLOBAL CIRCULATIONS

Documentation of the synoptic-scale motion pattern above about 30 km is by the regular observations of the meteorological rocket network, providing synoptic maps up to about 55 km, but only over North America and Western Europe is the density of observing sites barely adequate. Elsewhere and at higher altitudes, data are sparse. Data averaged zonally (that is, around a latitude circle) and seasonally reveal a broad current system with a maximum in middle latitudes at an altitude of about 60 km. The flow is from the west in winter and from the east in summer.

Models of these circumpolar currents were constructed by Leovy (1964b). To force the motion, Leovy (1964a) calculated zonally averaged heating by ozone absorption of solar radiation and zonally averaged cooling by carbon dioxide radiation in the infrared. As in an earlier calculation of this type (Murgatroyd and Singleton, 1961) his heating calculations show a net heating (cooling) between 30 and 70 km in high latitudes in the summer (winter) hemisphere. This is the basic radiative source–sink pattern. In his dynamical model, net radiative heating and cooling are primarily balanced by adiabatic cooling and heating by vertical motion, giving a meridional circulation extending from pole to pole. The action of Coriolis torque on the upper branch of this cell gives the broad circumpolar currents. The results are sensitive to a parameterized horizontal eddy heat flux and to the amount of radiative and photochemical damping inserted in the theory. The nature of the damping is described below in Section III.

This first-order picture of the dynamics of the seasonally reversing pole-to-pole meridional circulation and the associated circumpolar currents has not been improved on. Considered next is the state of knowledge regarding the sources and sinks for this circulation. Carbon dioxide is distributed with constant mixing ratio up to about 90 km (Hays and Olivero, 1970), and its concentration as a function

of altitude is therefore well known. The subject of radiative transfer by carbon dioxide has been developed to a high degree of precision. The current calculation of radiative cooling in this region (Kuhn and London, 1969) is believed to be accurate enough for any dynamical calculations in the near future. The situation is different with the heating rate. Unlike carbon dioxide, ozone is not uniformly mixed. A considerable effort, both observationally and in photochemical calculations, should be made to establish the distribution of ozone over the globe and in altitude. The situation is not so bad as it could be, since above about 40 km the lifetime of an ozone molecule is sufficiently short that large-scale motions do not affect its distribution and photochemical theory is appropriate. (The status of such photochemical theory is reviewed in Appendix E.) However, heating rates for calculations of the global circulation in the 30- to 70-km region are not well known because of lack of knowledge of the global distribution of ozone.

Between 70 and 100 km, infrared cooling by carbon dioxide continues to function as the heat sink, but absorption of solar radiation by molecular oxygen takes over as the heat source. Molecular oxygen is distributed with constant mixing ratio up to about 100 km, but the calculation of heating rates as a function of latitude is rendered uncertain by the fact that the solar spectrum depends on the amount of molecular oxygen above this level. Heating rates have been calculated by Johnson and Gottlieb (1970). Subtracting carbon dioxide cooling rates, they obtain the zonally averaged net sources and sinks of thermal radiation in the 70- to 100-km region. On the assumption that these are balanced by adiabatic heating and cooling, they deduce a vertical motion pattern that is downward over the polar cap in the winter hemisphere and upward over the polar cap in the summer hemisphere. The implied meridional circulation is crucial in determining the amount of molecular oxygen above 100 km as a function of latitude. That, as noted above, is what screens the solar energy, providing the heating that drives the circulation. Thus, there is a genuine coupling problem here, made much more difficult by the presence of small-scale motions that may provide much of the vertical oxygen transport.

III. PLANETARY WAVES

Large-scale waves are operationally defined by Fourier analysis of the height field of a constant-pressure surface around a latitude circle. These waves can propagate zonally and vertically in the zonally

averaged (that is, wavenumber zero) wind field. The very longest waves (wavenumber one and two) are referred to as planetary waves. These are quasi-stationary in character and probably owe their existence to the distribution of continents and surface heating. Under certain conditions, they can propagate well up into the 30- to 100-km region.

Planetary waves are strongly refracted and reflected by the circumpolar currents as described earlier in Section II. Charney and Drazin (1961), using a tangent plane coordinate system and considering only the vertical structure of the current, showed that upward propagation takes place when these are moderate westerlies. When the circumpolar current is easterly (summer) or strong westerly (midwinter) the waves are reflected downward. Dickinson (1968b) and Matsuno (1970) treated the problem of upward propagation of planetary waves on a sphere. They showed that there is refraction into a high-latitude "polar waveguide" by westerly currents, so that substantial upward propagation occurs even in strong westerly flow. The predictions are in agreement with observations up to the highest level at which synoptic maps can be drawn. These show an undisturbed easterly regime in summer and a highly disturbed westerly regime in winter (Finger et al., 1965).

These waves are of enormous potential signficance to upper-atmosphere phenomena, simply because so much energy resides in them. Results of a recent calculation by Matsuno (1971) illustrate the point. The most dramatic meteorological event in the stratosphere is the well-documented "sudden warming" in which over a period of some days the winter circumpolar current breaks up and reverses into a steady easterly current. The associated temperature field changes from a cold polar cap to a warm one (relative to lower latitudes). Matsuno assumes a surge of energy into the wavenumber one and two height field in the troposphere with an amplitude consistent with observed data. The waves propagate upward in his model and interact with his westerly current system, breaking it down and replacing it with an easterly system on a ten-day time scale.

As noted, planetary waves are present to the highest level at which synoptic maps are drawn (55 km). Their detection at higher altitudes awaits the development of a program designed to isolate quasi-stationary variations of any observable quantity along a latitude circle. There is some evidence for their appearance at these heights. The quasi-stationary wavenumber one component in winter, the so-called Aleutian high, is visible in rocket grenade winds to 70

km (Nordberg *et al.*, 1965). Ionospheric absorption data show a systematic difference between Europe and North America (Thomas, 1962). Some indication of planetary waves in meteor wind data up to the 100-km level was reported by Newell and Dickinson (1967).

Apart from the lack of definitive global observations, the most important factor influencing our inability to demonstrate the relevance of planetary waves to atmospheric processes in the 30- to 100-km region is their susceptibility to radiative and photochemical damping. The relevant chemistry has been described by Leovy (1964b), and dynamical calculations with damping included have been presented by Lindzen (1966) and Dickinson (1968a). Radiative and photochemical damping dissipate the temperature field associated with the wave, planetary waves being particularly vulnerable because of their long time scales. Radiative damping is provided by CO_2: in the high-temperature part of the wavefield, infrared cooling rates are enhanced. Photochemical damping is provided by O_3. Over most of this region of the atmosphere, O_3 is in photochemical equilibrium. Temperature sensitivity of the rate coefficient for the reaction that destroys O_3 by combination with O leads to an equilibrium concentration that increases with decreasing temperature. In the low-temperature part of the wavefield, the increased O_3 absorbs more solar radiation, giving a heating wave that is out of phase with the temperature wave and thus acting to damp the planetary wave.

Uncertainty in radiative damping by CO_2 arises only near and above 90 km, where it may depart from a well-mixed distribution. But, as noted earlier, ozone is not well mixed, and there is a great uncertainty in its average distribution in the vertical, let alone its variability in space and time. It may well be that ozone variability governs the depth of penetration of planetary waves into the 30- to 100-km region.

To the extent that planetary waves do propagate into the region, they will have an influence on the distribution of many minor chemical constituents. Over the altitude range where it has a long lifetime, a particular constituent will be subject to quasi-horizontal transport by the wavefield in much the same way as ozone and other trace substances in the troposphere and lower stratosphere. Even where lifetimes are relatively short, transport by the vertical motion field of the wave will affect the vertical distribution of the constituent; the temperature field of the wave will be manifest in temperature-sensitive reactions.

IV. SMALL-SCALE PROCESSES

Motions on the space and time scale of internal gravity waves are found in the troposphere in fluctuating wind systems and in the vicinity of convective clouds and small-scale topography. These waves can propagate to great heights and are, in fact, observed up to the 100-km level. When the energy density of such a wave remains constant with altitude, its amplitude grows exponentially because of the decrease of density. Very large horizontal shears result and (particularly in combination with shears in the wind field of the atmospheric tides) are thought to be the origin of the turbulence that is observed up to about 100 km. Both the wavefields and the turbulence can produce vertical transport of chemical constituents. Current theory parameterizes these processes by assuming that the vertical flux is proportional to the gradient of mixing ratio for the constituent in question with a constant of proportionality K, the diffusion constant.

This scheme has been successfully applied to a number of minor constituents in the 80- to 110-km region. A description in terms of eddy diffusion seems particularly appropriate here, because the motion field, as observed by the spreading of artificial trails, appears turbulent. However, eddy coefficients determined from trails refer to the horizontal direction and are much too large to be acceptable for vertical transport. The approach has therefore been to search for tracers from which an effective value of K can be deduced. The first attempts to do this were made by Johnson and Wilkins (1965) and Colegrove et al. (1965, 1966); the principal tracers were, respectively, heat and atomic oxygen. Because the oxygen observations of the time were defective, the K's found were much too large. The eddy coefficient can also be obtained from the gravitational separation of argon, and von Zahn (1967) showed that a K somewhat under 10^6 cm^2 sec^{-1} would give the best account. Only recently have reliable oxygen measurements been obtained (Offermann and von Zahn, 1971). Both tracers now give eddy coefficients of (5–10) $\times$ 10^5 cm^2 sec^{-1}. Another potential tracer is NO; Strobel (1972) suggests that it, too, may have a behavior consistent with the low K.

Johnson and Gottlieb (1970) have revised the earlier treatment of eddy heat conduction. As noted earlier in Section II, they calculated the net radiative heating above about 60 km and derived a vertical motion field that would correct global imbalances. There remains a net globally averaged heating at all levels. This necessitates

a global downward heat flux into a sink somewhere below 60 km. They assume the heat flux is proportional to the vertical gradient of potential temperature (everywhere positive in a statically stable atmosphere). This determines K, which enters the proportionality constant. It is necessary to be cautious about accepting such a result, which gives the large K of 3×10^6 cm^2 at 100 km. It is derived from the difference between estimated heating and cooling rates, each subject to uncertainty. Moreover, heat is not an inert tracer: it causes buoyancy effects that can profoundly affect the motions being traced. Thus, the eddy-conduction coefficient can be expected to differ from the eddy-diffusion coefficient, although sometimes by less than a factor of 2.

V. PARAMETERIZING TRANSPORT PROCESSES AS EDDY DIFFUSION

Although eddy diffusion is by no means adequate for a full description of vertical transport of trace constituents, it is still useful if its limitations are kept in mind. Several investigators (e.g., Wofsy *et al.*, 1972) have applied it to lower atmospheric layers. There are examples of atmospheric layers that are fairly well mixed in the horizontal but nearly isolated from their vertical neighbors. Probably the best known is the lower stratosphere, 15-25 km, with its ozone, radioactive debris, and sulfate layer. Departures from horizontal uniformity are important, too, especially for radioactivity with its localized sources. Nevertheless, eddy diffusion gives a useful approximation to the vertical transport. Junge (1962) has shown that a similar description works very well for tropospheric ozone. It must be remembered that the "eddies" do not need to be of small scale for "eddy mixing" to be valid. It is only necessary for horizontal motions in each layer to be rapid enough to maintain stratification to the required degree of approximation. An uplift somewhere must be accompanied by a subsidence elsewhere, and the combination may be thought of as just another, very large, eddy.

The "layers" that can be dealt with in the above manner are about a scale height thick. The boundary layer at the surface is a different matter; here the description must be local and time-variable.

Apart from the boundary layer, Junge (1962) finds K to be close to 10^5 cm^2 sec^{-1} in the troposphere. There is an abrupt drop at the

tropopause, which can be studied by means of the tracers O_3, N_2O, CO, and CH_4 (Bates and Hays, 1967). The stratospheric K seems to be 10^3 to 10^4 cm^2 sec^{-1}; the corresponding residence times L^2/K are 1–10 years for a scale L of 5 km.

Little information is available for the mesosphere and upper stratosphere. The existence of a temperature inversion up to 50 km suggests that K should stay low and then perhaps increase at greater heights. It may be that most of the vertical transport occurs during the polar nights, when the thermal structure is quite different and motions are strong. The only chemical tracer at present is hydrogen, free and combined. There is an upward flux of about 10^8 cm^{-2} sec^{-1}, leading eventually to Jeans escape, and the mixing ratio of total hydrogen does not decrease much between 30 and 100 km. The corresponding lower limits on K (cm^2 sec^{-1}) may be shown to be 5 $\times$ 10^3 at 50 km, 5 $\times$ 10^4 at 70 km, and 5 $\times$ 10^5 at 90 km. These are close to what would have been obtained by a simple interpolation for the 50- to 90-km region. Currently, considerable attention is turning to this difficult region, and improvement in both data and analysis can be expected soon. A start has been made by Anderson (1971) with his dayglow measurements of OH.

Attempts to describe and understand vertical transport on the earth have been stimulated by work on the other planets. On Mars, rapid communication between the ionosphere and the surface seems necessary to keep the high-altitude oxygen and CO from building up above observed amounts. McElroy and McConnell (1971) require a K of 5 $\times$ 10^8 cm^2 sec^{-1}. Dickinson (1971) suggests a large-scale diurnal circulation as an alternative, but it has not been worked out in detail. Venus is an enigma; there are a few hints of relatively slow transport, but as on Mars, it appears that CO and O must be rapidly removed from the ionosphere. For Jupiter, H may be used as a tracer, as O is on the earth. Hunten (1969) has interpreted the Lyman albedo of the planet to give a K of 5 $\times$ 10^6 cm^2 sec^{-1} near the mesopause.

Appendix C
Sources, Sinks, and Budgets of
Atmospheric Trace Constituents

JOHN W. WINCHESTER

I. THE PROBLEM (See Section II.A)

A major objective in monitoring chemical contaminants of the atmosphere is to assess the impact of anthropogenic sources on air quality and indirectly on contamination of freshwater, soils, and the ocean. Yet much of the effort that has been expended in the United States on air-pollution monitoring of trace substances has been without detailed reference to the chemical characteristics of their sources. Consequently, for some substances the dominant role of large-scale natural sources has been overlooked in all but the most polluted areas, and for others we have been unable to assess the extent of long-range transport from localized sources for want of good estimates of natural atmospheric levels. Such ignorance of atmospheric chemistry leads to misguided pollution-monitoring design strategy and misjudgment of the extent of our damage to air quality. It is important, therefore, to upgrade our understanding of sources and transport of atmospheric trace substances so that such mistakes can be avoided.

Evaluation of long-range transport depends on determining the strengths of natural large-scale area sources as well as of localized anthropogenic sources. Many substances, which are regarded as pollutants if they occur at unnaturally high concentrations, are also naturally occurring substances, but the true degree of pollutant transport through the atmosphere has been difficult to assess because of poor estimates of natural sources. In addition, estimates of source strengths for these substances are restricted to a few cases, although this information is essential in order to evaluate dispersion and removal during transport from the source area. Therefore, a program is

needed to determine source strengths of important gaseous and par-
ticulate components of air pollution, at both their anthropogenic
sources and at any natural sources for these substances that may be
significant.

A. The Ocean as a Source or Sink (See Section II.B)

Many urban communities are located near the sea. The air composi-
tion in these areas may be determined in part by substances emanat-
ing from the sea, such as sea-salt aerosols or certain trace gases, and
conversely the composition of the nearby sea may be affected by
fallout of urban or industrial air pollutants. Sea-to-air transfer mech-
anisms are poorly understood, especially for trace substances that
may be concentrated by surface slicks and may become airborne with
spray. Phosphate is known to be enriched several hundredfold in
droplets from bursting bubbles, and organic matter in general is
greatly enriched in aerosol droplets generated at the sea surface.
Certain bacteria may be thousands of times more concentrated in
spray droplets than in the bulk aqueous phase. Sea slicks are known
to have higher concentrations of some trace metals than does sea-
water, although it is not yet determined whether the sea can be
considered a net source or a net sink for these elements.

Fallout of lead has been shown to increase lead concentrations
significantly in surface ocean water, especially near coastal cities. On
the other hand, mercury, which was once suspected to contaminate
the ocean above natural levels, is now considered to be at its natural
concentration in seawater, sediments, and marine organisms, except
for the immediate environs of certain pollution sources. Had we had
a proper understanding of natural and anthropogenic mercury source
strengths on a global scale, especially to the atmosphere through
which long-range transport to the open ocean can occur, we might
have averted recent public alarm when it was claimed that certain
marine fish were unnaturally contaminated by mercury from the sea
and their consumption as food should therefore be curtailed. Present
evidence indicates that their mercury content is not greater than it
was a century ago.

Transfer of other substances to the ocean through the atmo-
sphere certainly occurs, although quantitative estimates are still few.
It is particularly important that improved atmospheric flux determi-
nations for hydrocarbons and other organic compounds be made so

that a better strategy can be designed for the control of these marine contaminants.

It has only recently become apparent that CO has large natural sources—in the sea-surface layers, on land, and within the atmosphere—and the occurrence of atmospheric CO in regions remote from automotive sources is not to be taken as evidence of long-range transport of pollution. At present, our knowledge of its atmospheric chemistry is weak, particularly in the assessment of its natural source strengths and processes and its atmospheric residence time and mode of destruction or removal. It is unfortunate that such fundamental information concerning the atmospheric chemistry of this important trace constituent is not yet fully available, at a time when we are on the threshold of major national policy moves for the control of air pollution. We cannot afford to be mistaken about any of the facts concerning the occurrence or origin of CO in the atmosphere if we are to recommend possibly costly measures to regulate its atmospheric concentration, e.g., by restricting its emission from automobiles.

The recent discoveries concerning CO have led to a realization that the sea-surface layers may also be significant sources of other atmospheric trace gases, e.g., nitrogen oxides. This information suggests that photochemical and other reaction mechanisms of urban air pollution may be appreciably influenced by proximity to the sea, but a careful examination of this possibility does not appear to exist in the scientific literature. Quite clearly, good estimates of the importance of oceanic sources of trace gases and substances occurring in particles are necessary before we can define regional or global budgets and transport paths of air contaminants or before we can be sure of the most effective plan for the management of urban air quality, particularly in cities near the sea.

B.   The Land as a Source or Sink (See Section II.C)

Although the importance of oceanic sources and the role of the ocean as a sink of anthropogenic air contaminants are now recognized, though not perfectly understood, the importance of the land as a source or a sink has not recevied the attention it deserves. A large part of the reported chemical analyses for atmospheric constituents near the ground are made in cities, and the data in themselves do not give a clear indication of the sources of these constituents. We now have estimates for the contribution of major urban sources of

the important pollution gases, but the task of detailed interpretation of observations in terms of source strengths, atmospheric chemical reactions, and air motions still lies ahead of us in our efforts to develop air-pollution models. For the inorganic chemical components of particulate matter, present estimates of urban sources are still preliminary, and for organic components, even more so. It may be that air-pollution concerns of the future will include the health effects of heavy metals and toxic organic compounds, as well as pollution gases, and good assessment of the sources of these substances is a prerequisite to the design of a strategy for their control. Such source assessment must include both primary sources and secondary sources, for example, recycling of dust from pollution fallout or chemical conversion of primary pollutants in the atmosphere.

Numerous atmospheric constituents, such as trace gases, organic vapors, and the inorganic and organic components of particulate matter, are generated continuously at the land surface by natural processes. From the standpoint of evaluating the extent of man's impact on the composition of the atmosphere, it is no less necessary to understand these natural processes than it is to understand processes occurring at anthropogenic sources. Trace substances may arise from soil dust by mechanical action; from biological material, such as the organic vapors of forests or trace gases through microbiological activity in soils; and from freshwater surfaces, through natural wind action, evaporation, or deliberate aeration in water treatment. In order to decide the relative importance of any particular pollution source to overall air quality, we must compare it with the aggregate of all sources, both natural and anthropogenic. As our air-quality concerns extend to exotic substances, we will find it far from a trivial matter to evaluate natural sources, particularly on land, where the variety of possibly important source processes is considerable. Basic research in this area is very much needed.

The land and water surfaces of the earth act as sinks of atmospheric trace substances, and their efficiencies determine atmospheric residence times. Contaminants of the middle and upper troposphere, e.g., radioactivity from nuclear weapons detonations, are brought down effectively by precipitation scavenging, and considerable research has been directed to the investigation of the cleansing of the atmosphere by rain and snow. It cannot be assumed, however, that trace gaseous and particulate matter that enters the atmosphere at the earth's surface is returned mainly with precipitation; except for a few substances, the dominant mechanism operating in clear air is not

really known. We believe that CO_2 is absorbed mainly by surface seawater, but it was only recently that we learned that the sea-air flux of CO is in the opposite direction. In land areas, O_3 appears to be destroyed near the earth's surface, but which of several possible mechanisms is most important is not known. Sea salt, which penetrates over continents, appears to be removed from the atmosphere to a greater extent than can be accounted for by precipitation alone, suggesting that clear-air deposition by impaction, sedimentation, or other processes is also important. Empirical clear-air deposition velocities (the ratio of surface area deposition rates to overlying air concentrations) of millimeters per second to centimeters per second have been measured for several trace gaseous and particulate materials, indicating effective removal rates with less dependence on particle size or gaseous state than simple theory predicts. Before air-pollution models can include removal processes, research on the details of these processes should be extended substantially.

More thorough study of the fates of pollutants whose health effects may be of future concern is essential. Reactive trace elements such as bromine, selenium, and arsenic, toxic metals such as lead and cadmium, and organic compounds of a wide range of types should be investigated to determine their lifetimes in the atmosphere and to predict the effect of one urban area on the air quality of another.

C. The Atmosphere as a Source or Sink (See Section II.D)

Within the atmosphere occur some of the key chemical reactions that govern the transport and fate of trace components. On an urban scale it is generally recognized that chemical transformations among gaseous compounds of oxygen, nitrogen, sulfur, and carbon can occur with rates comparable to air motions, so that short-term variations in meteorological conditions and details in the locations of primary air-pollution sources play an important role in regulating pollution gas concentrations and their changes during the course of a day. Yet, at present, we understand only in a general sense the dependence of chemical reactions on meteorology. Through close interaction between experts in chemistry and meteorology in coordinated research on the interplay of chemical and dynamic aspects of urban air-pollution transformations and transport, substantial improvement in the ability to predict air-pollution concentration levels could be achieved.

An area of great importance in air-pollution research is the inter-relation between trace gases and suspended particulate matter. Organic gases may react with particle surfaces and may add to the mass of particulate matter. Inorganic substances may be reactive and liberate volatile components. Both gases and particles may interact with water droplets under certain conditions, leading to accelerated removal from the atmosphere. The mission of much of the current U.S. air-quality measurement effort is the monitoring of gases and of particulate matter in relatively disconnected programs, with little high-precision specification of the particulate chemical composition. If this measurement effort were revised by more centralized planning of air-pollution research and monitoring, more rapid progress would be realized in understanding and predicting the behavior of both gases and particulate matter.

Because human activities may have far-reaching impact on the composition of the atmosphere, research on the interactions of trace gases and particles in remote regions and in the stratosphere has become of considerable importance. As an example, when it was proposed to fly large numbers of supersonic transport (SST) aircraft in the stratosphere, our lack of knowledge was exposed concerning the interdependence of ozone and nitrogen oxides at high altitudes and the possible effect of the SST emissions on their chemical balance. Another example is our recognition of sulfur compounds as important constituents of stratospheric dust, but even now we still lack measurement of sulfur gas concentrations and comprehensive analytical data on particle composition at this altitude. Without such information it is difficult to account with certainty for the occurrence of particulate sulfur and the possible importance of man's activities on the stratospheric aerosol. These effects are problems in the dynamics as well as the chemistry of the stratosphere and are illustrative of the need for interdisciplinary research in atmospheric chemistry.

D.   Special Cases of Unnatural Pollutants (See Section II.E)

Certain substances have been found to have important anthropogenic sources but no detectable natural sources, e.g., synthetic chlorinated hydrocarbon pesticides, such as DDT, and industrial chemicals, such as the PCB's. Their occurrence in the air and sea and on land is taken as evidence of their transport from anthropogenic sources, but we do not have a desirable level of understanding of transport pathways and

manner of degradation or disappearance in the environment. For example, we have not yet fully evaluated to what degree these substances are recycled from the sea back into the air by sea spray or volatilization and how this may compete with removal from the sea through incorporation into organic or inorganic sedimentary matter. In order to estimate a time constant for disappearance from the exchangeable reservoirs of our environment we need better information on the extent of atmospheric recycling.

A problem of a different sort arises for inert synthetic gases added to the atmosphere, such as SF_6 and the chlorofluoromethanes (e.g., Freons). If water solubility is the main limitation on their eventual dissolution in the sea, the rate of uptake may depend on the dynamics of circulation in the upper layers of the ocean. This problem has not been examined in depth except for fossil fuel CO_2 uptake, but its solution may have to await further advances in physical oceanography. At the same time, a coupling of research on circulation of the oceans with the problem of oceanic absorption of artificial trace-gas pollutants could provide an opportunity for rapid progress in both subjects.

The occurrence of anthropogenic substances widely dispersed in the atmosphere and its adjoining oceanic and terrestrial exchange reservoirs reveals our need for better understanding of pollution sources, sinks, and budgets. At the same time, this occurrence presents us with an attractive opportunity to learn more about the fundamental processes of atmospheric chemistry and for future management of air quality.

II. ANNOTATED BIBLIOGRAPHY

A. Interest in the possibility of long-range transport of air pollution was highlighted by the report *Air Pollution Across National Boundaries: The Impact on the Environment of Sulfur in Air and Precipitation* (Bolin, 1971) and its subsequent discussion at the United Nations Conference on Human Environment in Stockholm in June 1972. The evidence indicates that transport of SO_2 originating in Western Europe can significantly increase the acidity of rainfall over Sweden and cause ecological damage by acidification of lakes and leaching of nutrients from soils. Typical of questions now being raised in the press is the report of Pothier (1972) reporting the findings of H. P. Gerrish of the University of Miami that air pollution originating in the northeastern United States can be transported

southward and under certain atmospheric conditions extend over Florida.

B. Baylor *et al.* (1962) showed that phosphate occurs at higher concentrations in sea-surface water and bubble spray than in average seawater, a discovery of considerable significance in marine ecology. Experiments by MacIntyre and Winchester (1969) showed that the enrichment of phosphate in aerosols generated by bubble bursting may be several hundredfold and suggested that the mechanism may involve attraction from solution to a sea-air boundary layer and skimming during bubble bursting to enrich the aerosol in the surface active material. Blanchard (1967) reported that organic matter is generally abundant in sea spray compared with seawater, and Blanchard and Syzdek (1972) found that some bacteria may be several thousandfold enriched in aerosols generated by bubble bursting. It may be that many substances are added efficiently to the atmosphere from water surfaces by similar mechanisms, although quantitative studies are still few. A report by Duce *et al.* (1972), indicating enrichments of several heavy metals and organic compounds in a sea-surface microlayer sampled directly, suggests that trace metal enrichment in aerosols may also occur.

Far-reaching pollution of surface seawater by lead was demonstrated by Tatsumoto and Patterson (1963) and attributed to the combustion products of leaded automotive fuel, transported to the ocean either through the atmosphere or by runoff from the land. Chow *et al.* (1969) were able to show that the atmosphere over the central Pacific Ocean has greater lead concentrations than can be explained by processes other than atmospheric transport of air-pollution particulate matter from continental areas. Gillette and Winchester (1972) found that the particle size distribution of lead aerosol in clear air near the ground is quite invariant in space and time and therefore may be expected to travel great distances. Patterson (1965) summarized evidence that man and his atmospheric environment may already be appreciably contaminated by lead dispersed through man's activities.

Recent reports from Asia, Europe, and North America of high mercury levels in fish from freshwater and nearshore oceanic areas sparked interest in the possibility of global contamination by mercury. Weiss *et al.* (1971) showed that recent ice layers in Greenland contain higher mercury levels than older ice, suggesting a recent increase in the mobilization of this element by man and its transport

through the atmosphere, but no specific source type of the additional mercury could be identified. Barber *et al.* (1972) report mercury analyses of recent ocean fish and similar specimens from a century ago and conclude that there is no measurable increase over this time span, implying that the concentrations are still at natural levels. However, discussions by Saperstein *et al.* (1973) and Barber *et al.* (1972) illustrate that interest in the question of mercury pollution of the marine environment is still keen.

Publication of a paper by Swinnerton *et al.* (1969) surprised many by demonstrating that surface waters of the oceans are supersaturated in carbon monoxide, though not in methane, and that the ocean must be a source, not a sink, of CO. Seiler and Junge (1970) have confirmed this finding and have stimulated research on the role of the oceans in regulating the trace-gas composition of the atmosphere. Careful work by Stevens *et al.* (1972), reviewed by Maugh (1972), on the isotopic composition of atmospheric CO pointed to several different source processes for CO, many of which must be natural and some of which may occur within the atmosphere. Weinstock and Niki (1972) suggest mechanisms for the generation of CO naturally in the atmosphere, and Stewart *et al.* (1972) show that man may generate considerable amounts of CO under certain conditions of physiological stress. Once regarded as a relatively stable atmospheric contaminant without significant natural sources, CO has now become recognized as a trace gas with complex atmospheric chemical behavior.

C. The lack of quantitative estimates of source strengths of trace elements in urban air-pollution particulate matter was pointed out by Winchester and Nifong (1971), and estimates were made for Chicago using data on expected composition of emissions from several major sources and data on their total particulate emissions. Although the estimates were only approximate, they were useful in accounting for pollution contributions to the amounts measured by Harrison *et al.* (1971). Correlations among these trace-element concentrations could then be used by Dams *et al.* (1971) to distinguish essentially natural levels from those strongly influenced by pollution. Loucks and Winchester (1969) attempted to calculate pollution contributions of automotive fuel combustion to the halogen content of average aerosol over the United States and concluded that the bromine content may be largely pollution-derived. Rahn (1971) discovered, in aerosols collected near the ground in remote regions of Canada, that

several trace elements are at concentrations far higher than can be accounted for by assuming soil dust as a principal source. Before pollution sources can be assumed, however, more research is needed on possible processes for natural enrichment of the atmosphere at the soil–air interface.

Mechanisms for cleansing of the atmosphere by precipitation have been thoroughly reviewed in a collection of papers, *Precipitation Scavenging* (1970). Not so thoroughly studied are mechanisms for deposition in clear air. Eriksson (1959, 1960) reasoned that sea-salt particles are deposited over continental areas from clear air at twice the rate as during precipitation, at an apparent deposition velocity of about 1 cm/sec. Chamberlain (1959) measured the deposition of ^{131}I vapors from a nuclear reactor accident and found an apparent velocity of 0.3–0.4 cm/sec. This and other evidence indicate that the clear-air deposition rate is not so strongly dependent on particle size or gaseous state as simple gravitational settling theory may suggest and is quite great for trace materials originating near the ground.

D. The occurrence of lead, chlorine, and bromine in pollution aerosols illustrates the need to consider gas–particle interactions in the atmosphere. Lininger *et al.* (1966) found that the bromine content of Cambridge, Massachusetts, aerosols is probably derived substantially from pollution in spite of the proximity to a strong natural source at the sea coast. An inland city, Fairbanks, Alaska, was found by Winchester *et al.* (1967) also to be heavily polluted in bromine, and in both instances the primary pollutant was assumed to be the lead halide aerosol produced during the burning of leaded automotive fuel. However, the bromine content relative to lead was substantially below that of the fuel, and it was believed that considerable loss of gaseous forms of bromine to the atmosphere occurred during or after exhausts were emitted. Robbins and Snitz (1972) showed that the loss of bromine from the aerosol is gradual over the course of hours and appears to be controlled by chemical reactions with other atmospheric gases. Whether the released bromine subsequently enters into additional chemical reactions has not been investigated.

E. The attention of the oceanographic and atmospheric chemistry community has been directed strongly since 1970 to the occurrence

of chlorinated hydrocarbons in the marine environment as contaminants far from their points of origin. A series of conferences has been organized and encouraged by E. D. Goldberg, and the results have been issued as the reports *Chlorinated Hydrocarbons in the Marine Environment* (1970), *Marine Environmental Quality* (1971), and *Baseline Studies of Pollutants in the Marine Environment* (1972). At this time, the level of understanding of this complex subject is increasing rapidly, and additional reports and publications are expected.

Appendix D
Urban Air Chemistry
Measurements

ROBERT J. CHARLSON

I. INTRODUCTION

One of the most important tasks of atmospheric chemists is to provide data on the composition of air in cities and urban areas. The need for such data is clear when, for example, pollution-control devices costing millions of dollars are required of an industry by an air-pollution control agency that bases its requirements on air-composition measurements. The objectives of air-quality surveillance by public agencies published by the Environmental Protection Agency (1971) are

1. To judge compliance with and/or progress made toward meeting ambient air quality standards.
2. To activate emergency control procedures to prevent air pollution episodes.
3. To observe pollution trends throughout the region including the nonurban areas. (Information on the nonurban areas is needed to evaluate whether air quality in the cleaner portions of a region is deteriorating significantly and to gain knowledge about background levels.)
4. To provide a data base for application in evaluation of effects; urban, land use, and transportation planning; development and evaluation of abatement strategies; and development and validation of diffusion models.

In addition to these operational applications, data from routine observations and from specialized measurement programs are used for a variety of other purposes, largely in research. Studies of photochemical processes and atmospheric reaction rates have utilized air-composition data (Eschenroeder, 1971). Research on the effects of air pollution on health, especially epidemiological studies, requires large quantities of data on a variety of toxic or irritating substances (see, for example, McCarroll et al., 1967). Urban measurements have

also been used to infer causal relationships with a variety of other air-pollution effects including corrosion, loss of visibility, soiling of clothing, plant damage, and rubber cracking. At this point the application of data merges with item 4 above. Indeed, it is possible to consider all research requiring air-composition data as included in item 4; however, there exist differences in the way data are used in research and the way they are used in pollution-control operations. These sometimes subtle differences often necessitate different types of data of different accuracy.

As might be expected from the diversity of chemical compounds produced by man and introduced into the atmosphere, a large number of elemental, ionic, or molecular species are or have been the subject of measurement programs. Due largely to differing chemical mixtures in different cities, and to different air-pollution laws, the substances measured vary from city to city and state to state. A more or less "basic" set of specific gaseous pollutants is measured in many locations: carbon monoxide, sulfur dioxide, nitrogen oxides (NO, NO_2, or the total of both), nonmethane hydrocarbons, and ozone (or total oxidants). Besides these, a variety of other gases are occasionally measured, such as hydrogen sulfide, polycyclic aromatic compounds, and mercaptans.

Particulate matter (often called aerosol) is monitored widely and in most cases reported as total suspended particulate matter (TSP) in micrograms per cubic meter. Samples of filterable material are analyzed for a large number of elements, ions, and molecules, including

benzene soluble organics	cobalt
gross beta activity	copper
nitrate ion	iron
sulfate ion	lead
ammonium ion	manganese
antimony	molybdenum
arsenic	nickel
beryllium	tin
bismuth	titanium
cadmium	vanadium
chromium	zinc

This list of both gaseous and particulate substances changes with time and can be expected to grow, particularly in the analysis of

specific organic molecules and the molecular nature of the inorganic substances.

Several coordinated studies of urban air chemistry, meteorology, and aerosol physics and their interrelationships are in progress. These studies will utilize urban air-composition data and a variety of other measurements to elucidate the nature of chemical and physical-chemical processes in city air. The Los Angeles study of 1969 (Whitby *et al.*, 1972) was followed in 1972 by a series of studies in several locations in California aimed at mapping the spatial and temporal distribution of trace atmospheric constituents, at characterizing the aerosol in photochemical smog, at defining the background aerosol, and at studying the impact of the automobile as a source of pollution. Two major studies are under way in St. Louis. Metromex (Metropolitan Meteorological Experiment) (Chagnon, 1971) deals mainly with the impact of a city on meteorological processes, including thermal (heat island) and precipitation (condensation and freezing nucleus) effects. The EPA-sponsored Regional Air Pollution Study (RAPS) has a variety of purposes, some of which are concerned with the need for better operational schemes for air-quality surveillance and for better knowledge of the chemical processes that occur in urban air. Both basic science aspects and operational details are included in the goals that are directed in part toward providing a scientifically sound basis for developing least-cost control strategies. There is specific interest in quantifying the effects of air pollution and in a quantitative understanding of physical-chemical processes in the atmosphere. It is hoped that predictive models of air pollution will result.

It is in studies such as these that the needs for high-quality data are most stringent. As a result, workers in all of these studies have found it necessary to institute measurement programs for their own purposes in addition to the routine monitoring data taken by the local air-pollution agencies. In some cases, the routine monitoring data are useful adjuncts to the special measurements, while in others they will not be used at all.

The fact that much monitoring data are unacceptable for air chemistry research is one of the important problems that must be faced in the future. It is hoped that the intensive studies mentioned above will generate monitoring schemes that produce more data of quality acceptable for research purposes as well as for air-pollution abatement. This goal can be justified if the research produces information that more clearly delineates cause/effect relationships and

thus leads to more effective control strategies. Scientists in EPA are well aware of these problems and plan to incorporate the results of the intensive studies in future monitoring programs.

The purpose of this review of urban air-chemistry measurement procedures is to identify strengths and weaknesses and to provide a basis for judging how well these measurements meet needs, both
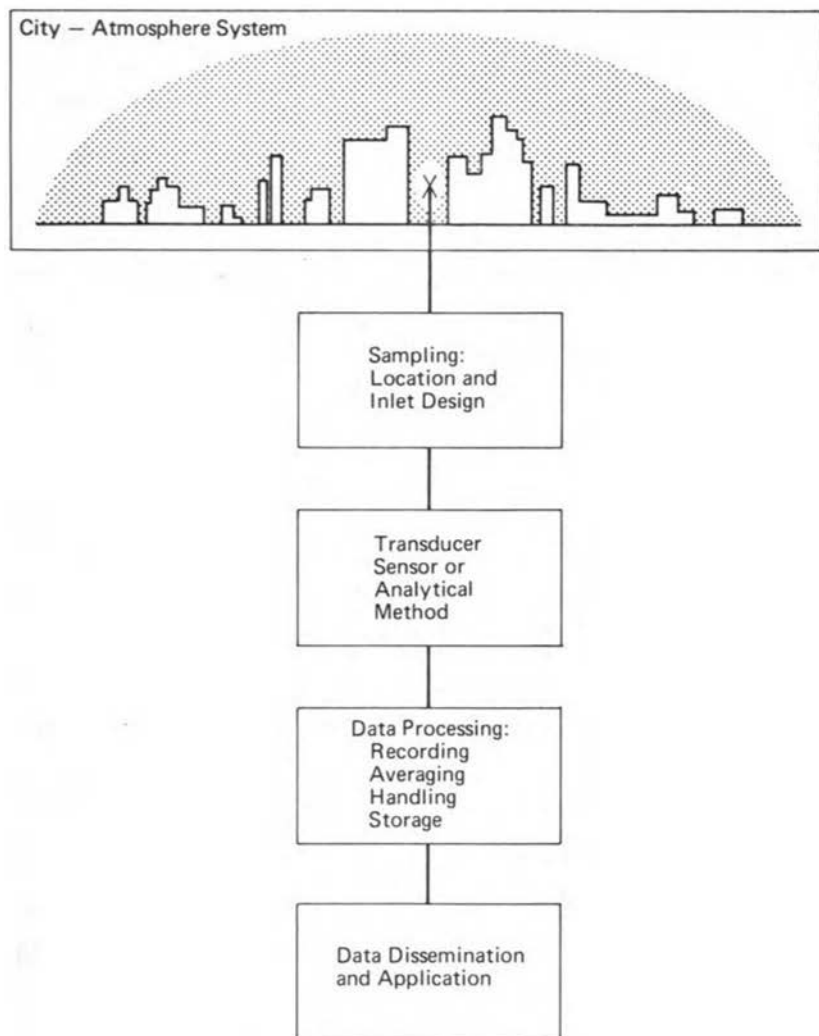

FIGURE D.1 Urban air-chemistry measurement system.

basic and applied. It is not possible in the available space to review fine details, such as analytical methods for the wide variety of substances measured. Rather, it is hoped that the urban air-chemistry measurements can be thought of as a simple system comprising a sampling component, transducers, a data recording system, and data disseminators. Figure D.1 illustrates this system concept. It is important to realize that the data produced by the system are limited by the transducer (or analytical method) *and* the sampling component. Each part has to function properly if the data are to be successfully applied. Before considering details of the urban measurement system, it is useful to assess the nature of the air sample that is subjected to measurement.

II. SAMPLING

The location and number of sampling devices and the design of inlet pipes are the major parts common to all sampling activities. Besides these, the extraction or removal method is included for those measurement methods that do not sense an atmospheric constituent *in situ*.

A. Location of Monitoring Stations

The usual practices in siting are based on fairly obvious considerations, mainly on the overall station purpose. Among the purposes that are often intended are the following (Morgan and Ozolins, 1970):

1. Surveillance of specific sources, source categories, or demographic areas of a city, especially areas known or thought to represent pollution maxima;
2. Monitoring of "general" or "representative" air quality in population centers;
3. Establishment of the background levels of trace constituents in air entering the urban area;
4. Verification of models on which control decisions and enforcement actions are based. (To some extent, the first three are all involved in the fourth purpose.)

Few published data exist from which guidelines can be derived for the location of monitoring stations or that provide insight into

the significance of existing locations. Current urban practices are often dominated by the availability of a building at low rent rather than some technical consideration. Studies of the spatial distribution of pollutants in cities are rare, so it is difficult to judge whether adequate numbers of stations exist or whether their location, height above ground, proximity to buildings, trees, and sources (e.g., roads or chimneys) is appropriate for the purposes of the station. No measurements are routinely made over water even though most of the large urban areas of the country are on bodies of water and even though the water quality may be affected by the air quality.

Siting practices presumably affect the character of data and their interpretation; however, few experimental studies have been performed to confirm or refute such conjectures. Ruff (1971) showed that the relocation of a sampling site by a few city blocks to an apparently similar site changed the nature of the CO record. In view of the lack of uniformity of location with respect to streets, buildings, small sources, height above ground, etc. as shown by Yamada (1970), the comparability of data from site to site is certainly questionable.

In some cities, e.g., New York, the three-dimensional extent of man-made (and man-occupied) topography and of emissions is so complex that a representative site for monitoring probably does not exist.

Meteorological models or calculations are sometimes used as an aid to siting, for instance, in surveillance of single sources. Such calculations are usually done by air-pollution agency staff personnel using handbook values for dispersion parameters such as those developed by Turner (1969). There are usually only limited meteorological data available for such effort.

Some studies aimed at the siting problem have been done using multiple-source diffusion models, which have had extensive development (Stern, 1970). Craw (1970) did one such study for Buffalo, New York, with sampler location as the specific goal of the effort.

It is anticipated that the several large urban measurement programs currently in progress will lead to a better understanding of the problems of location of air-chemistry measurement systems. Such experimental results should lead to guidelines for siting that are useful to both pollution control and research. Since these studies will utilize both fixed and moving instrument systems (e.g., aircraft), the relationship of single sites to the whole spatial distribution should be obtained.

B. Air-Sampling Methods

Just as there is necessarily a wide variation in the nature of sampling locations, sampling practices vary from location to location and city to city. Yamada (1970) showed that there exists a wide variety of practices in design of the means for delivery of air from the atmosphere to the transducers, most of which are indoors. The material, length, diameter, and flow rate (and hence residence time and diffusive losses) are extremely variable from site to site and sometimes from instrument to instrument at the same site. For example, one common practice involves a separate sampling line for O_3 (or oxidant), another one for a paper-tape sampler for particulate matter, and a third one for the other gas transducers (CO, NO_x, SO_2, etc.). The high-volume air sampler for particulate matter is always located outside, usually on a flat roof. Materials used for sampling lines vary and include stainless steel, glass, aluminum, Teflon, and various other kinds of plastic. Residence times range from seconds to minutes because of variations in both the flow rate and cross-sectional area of the pipes.

Several kinds of problem occur in sampling lines that should be considered in many urban measurements:

1. Reactions with the tube walls (or with materials on the walls);
2. Reactions between substances in air caused by the passage of the sample from the atmosphere into the different environment of the tubing;
3. Delays (in the case of very long lines).

There is interest in predicting with accuracy the effects of interactions with tubing walls on gas composition. Yamada and Charlson (1969) showed that based on diffusion theory, sampling lines can grossly affect the composition *if* the tubing wall is a sink. The lack of definitive information regarding the sink properties of tubing materials (especially the surface of a tube coated with urban particulate matter) precludes accurate error estimates. Many urban measurements are made with small-diameter, dirty tubing, possibly leading to major errors. Clean glass tube, and possibly some plastics (e.g., Teflon) will work if properly maintained, but there is some evidence that current practices do not assure a chemically clean surface. Some agencies place a plug of glass wool in the intake line "to keep the tubing clean" not realizing the effects that the dirty glass wool might have.

The second sort of problem—that of reaction in the sampling system due to change in the physical environment—is typified by the $NO-O_3-NO_2$ system. Butcher and Ruff (1971) show that large errors (50 percent or higher at times) can occur when this system is removed from sunlight. The reaction $NO + O_3 \rightarrow NO_2 + O_2$ is very fast, and the cessation of photodissociation

$$NO_2 + h \rightarrow NO + O$$
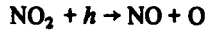
in the dark interior of the sampling line produces major shifts in the composition. This change in composition leads, of course, to data that are not representative of the atmosphere and that cannot be used to relate to photochemical models. Such data may be misleading when used for control strategy development.

The specific location of high-volume air samplers is almost always 1 m above a flat roof surface. Such surfaces are known to be sources of dust that depend on wind and recent precipitation history. This location has been criticized by Whitby and Liu (1970) and probably should be studied carefully in order to determine the magnitude of systematic effect that exists in historical data.

There is currently considerable interest in the efficiency of sampling of large ($5 < r < 50 \, \mu m$) particles, which depends in a complex way on the wind velocity and orientation of the sampler housing or inlet tube. The lack of standardization of inlet geometrics is another topic that should be studied. In addition, the loss of particles in tape sampler inlet lines produces unknown effects.

One solution to the tubing problem is to use a large duct (10–15 cm diameter) to minimize diffusive losses. Laminar flow conditions in larger pipes (for which diffusive loss is easily calculated) yield smaller errors from reactions at the wall because of the short distances over which molecular diffusion is effective. When turbulent flow is used, eddy diffusion will increase the losses, but when properly designed, this sort of larger duct minimizes losses to the walls. Also because of the very short residence times that can be achieved in such pipes, the errors due to reactions between constituents in the air sample are held to a minimum.

In summary, there are four air-sampling problems that need the attention of the research community:

1. Until adequate spatial information for ground-station siting is available, sites should be considered preliminary. Spatial information

should be developed, for example, from intensive urban studies that can be used to formulate location guidelines. It is especially important to use data on and models for the spatial scales of pollutant concentrations.

2. The use of routine mobile or airborne sampling should be expanded, including areas over both land and water. Research is needed to delineate the utility of such means for pollutant mapping.

3. Sampling errors for particulate matter should be assessed and research undertaken to develop improved methods. Location criteria for such samplers should be developed, tested, and promulgated. Effects of specific locations should be assessed to aid in interpreting historical data.

4. Research is needed to establish an optimal design for intake plumbing for gas samplers as well as for samplers for particulate matter. This research should lead to guidelines, and perhaps standards, for the sampling procedures.

III. TRANSDUCERS AND ANALYTICAL METHODS

A highly developed part of the urban air-chemistry measurement system includes the large variety of automatic and manual techniques for analyzing an air sample. In comparison with the sampling methodology, most of the analytical approaches have received attention from scientists. Most methods for gases use a flow of air in a tube such as that discussed in the preceding section, while particulate matter is sampled directly for postanalysis.

Considerable amounts of research have dealt with gas sensing in recent years (United States Department of Health, Education, and Welfare, 1970). This effort has resulted in a variety of gas sensors that are reliable, specific, and well suited for the urban measurement system. Examples—all recently developed—are the chemiluminescent devices for O_3 and NO and the flame photometric device for gaseous sulfur compounds. References to large numbers of specific methods are readily available in journals, textbooks, and reference books.

Compared with gas sensing, aerosol sensing and analysis have lagged. No continuous sensors are available for aerosol composition, and most data are taken over a 24 hour or longer period with the high-volume sampler. This sampling period in itself is so long that it is difficult to utilize the data in conjunction with meteorological data. Some real-time sensors exist for aerosol properties such as size

distribution (optical particle counters, mobility analyzers, etc.), extinction coefficient (integrating nephelometer) or soiling index, sometimes called COH or coefficient of haze (paper-tape or filter sampler) that do not provide chemical information.

The postanalysis normally used for high-volume filter samples is accomplished in centralized laboratories, usually within a few months of the actual sampling. In almost all cases the analysis done for the National Air Sampling Network samples accounts for less than 50 percent of the *sampled* material, usually less than 25–30 percent (Wagman, 1970). Since some of the material on the filters is volatile, the analyses often miss more than they include. In addition, chemical changes during filter handling may alter the nature of the sample. For example, H_2SO_4 reacts quickly in the presence of NH_3 in laboratory air to yield $(NH_4)_2SO_4$, so there is no way to ascertain whether H_2SO_4 existed even though it is strongly suspected of health effects. Although there is need for molecular information to relate to toxicity or solubility and other properties, virtually all the analyses are for ions or atomic species.

In most public agencies, the only aerosol analysis or detection is accomplished with the high-volume and paper-tape samplers. The heavy dependence on these two devices seems to be a particularly significant weakness, since the kind of information obtained (especially with the tape sampler) is inadequate for chemical studies. Mass budgets, for example, cannot be ascertained with a tape sampler, and possibly not with a high-volume sampler.

Data acquired from the stain on a filter paper tape have not been related via optical theory to any recognizable physical or chemical property of the aerosol and can, therefore, only be used empirically. This constraint requires that comparisons between locations can only be made if all the controlling variables are nearly identical. Because of changes in light-absorbing properties of the particulate matter from city to city, or with time in a given city, the empirical relationship to mass concentration presumably changes. This precludes the use of such data for deducing an increase or decrease in aerosol content or for saying that one city has more or less particulate matter than another.

It seems clear that there is a basic need for measurement of physically and chemically definable aerosol properties rather than quantities that are limited to empirical correlation. There is also a need to avoid methods that depend on the particular embodiment and operation of an instrument and to seek methods that can be

reproduced in the future by other workers with different tools.

Another problem results from recent rapid changes in gas and aerosol sensors. Many public agencies (federal, state, and local) have spend large sums in the past 5 to 10 years to purchase instrumentation that is already obsolete. Examples of obsolescence are (1) the use of wet chemistry when newer devices use gas-phase reactions, (2) the nonspecificity of many wet chemical methods such as the iodometric O_3 method, or (3) high maintenance when newer devices are designed for low maintenance. The agencies are now committed heavily to maintaining these instruments, even though data from them are faulty. The cost of buying the newer, more accurate, and reliable devices is too high to permit conversion to them.

The "standardization" on some of the older methods, which have important systematic errors, is sometimes considered necessary because of the cost and the desire for continuity. Many of the older wet chemical methods exhibit serious interferences from molecular species not present in the clean laboratory setting in which they were developed. One danger of maintaining old methods is a freezing of methodology that is in many cases inadequate. One often hears the suggestion that an archaic method should be used so the data can be compared with a body of existing data, even though the method may be quite inadequate and undesirable. For example, many data exist for "oxidant" determined iodometrically. Oxidant in photochemical smog is thought to be largely O_3 for which specific measurement techniques are now available. At the same time, when a changeover occurs from one sensor to another, the comparison of data from both methods is necessary if a relationship to historical records is to be maintained, for example, with regard to health effects of pollutants.

Still another problem exists as a result of the high cost of the newer gas and aerosol sensors, typically several thousands of dollars each.

There seem to be three major problems with regard to transducers:

1. Ways to provide better instrumentation at much lower cost are needed. Perhaps mass production of a few of the newer devices would bring the unit cost down to acceptable levels.

2. Agency awareness of rapid changes in technology and the availability of new devices should be ensured.

3. The development of aerosol sensing apparatus should be encouraged, especially in the direction of real-time sensing of aerosol molecular composition and physically definable properties.

IV. DATA REDUCTION, HANDLING, AND STORAGE

The Environmental Protection Agency has established the National Aerometric Data Information Service (NADIS), which serves as a data bank for all urban areas in the United States. State and local agencies are expected to submit their data to NADIS voluntarily. A coding system—Storage and Retrieval of Aerometric Data, SAROAD—has been developed for data submitted to NADIS.

This data-handling system seems functionally adequate in most respects, with the exception that most air-chemistry measurements today involve manual analysis or manual reduction of data from strip charts. These data are usually digitized and then handled by modern computer methods. Because of the current heavy dependence on old, wet chemical sensing methods and manual data reduction from strip charts, there is quite a mismatch of technology.

Conversely, there is a tendency to accept numbers produced by a computer without questioning the transducer.

Another weakness in the data-handling area is the usual partitioning of jobs within agencies. Chemists take the data, but meteorologists analyze them. This is generally true at federal, state, and local levels. Since the meteorologist is often unaware of the transducer limitations, interferences, etc., the data processing does not properly match the data quality. We see, for example, far too many significant figures attached to contaminant concentration or a lack of error bands on data.

V. CONCLUSION

Air-quality surveillance guidelines and technologies are presently aimed at limited goals and are not always adequate for basic research needs. Yet, basic air-chemistry information is a necessary part of formulating effective control strategies, for example, for photochemical smog. Wherever possible, data should be sought that can be used not only for the judgment of compliance, etc., but also for establishing a fundamental understanding of air chemistry. At times

it may be necessary to establish a special measurement program to obtain data for basic research in air chemistry.

The advent of a more sophisticated technology in urban air measurements will likely demand a shift of the type of training or background of people employed to make such measurements. This is true for all parts of the system described above. Education and training programs for personnel engaged in all phases of the measurement system should keep pace with technological requirements.

Appendix E
Chemical Reactions and
the Dynamics of the Troposphere

HALSTEAD HARRISON

I. INTRODUCTION

The traffic of air chemistry with atmospheric motions flows along a two-way street, but with unequal authority. Tropospheric circulations strongly influence the chemistry, but the chemistry affects the circulations only slightly, locally, and infrequently. This follows because air is relatively inert. Even for oxygen, reactions that break the molecular bond energy of 118 kcal/mole require activation by 10 percent or so of this energy from thermal or electronic degrees of freedom. At tropospheric temperatures, kT amounts to only half a kcal/mole, and consequently kinetic Boltzmann factors discourage even exothermic and sterically favored reactions by factors of 10^8 to 10^9. This fortunate circumstance simultaneously permits the kinetic stability of protoplasm and restricts the scope of tropospheric chemistry to atypical interactions of the atmosphere's minor constituents. Of these, the most reactive rarely exceed mixing fractions of 10^{-6}; the most exothermic rarely exceed "flame" temperatures ($-\Delta H/C_p$) of 10^3 deg; thus direct contributions to tropospheric heating and convection from reaction enthalpies in dispersed air chemistry are negligible. On the local scale, however, forest fires and urban-centered combustion of fossil fuels produce heat islands that do affect advection, and photothermal interactions of absorbing molecules (NO_2) and aerosols do affect temperature profiles and thus convective stabilities.

Conversely, tropospheric circulations profoundly affect the air's chemistry. This follows because most of the atmosphere's reactive constituents have inhomogeneous source loci, in both space and time, and because molecules must move close to one another before they can interact. Dispersion effects usually outweigh intrinsic

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kinetic rate coefficients in determining net rates of concentration changes in the troposphere. *An understanding of mixing is a necessary concursor to an understanding of atmospheric chemical rates.*

In these circumstances, the risks are considerable that erroneous interpretations may be made of expensive and therefore necessarily sparse field data. Diurnal variations of measured concentrations of the dilute reacting atmospheric constituents may often with seemingly equal plausibility be ascribed either to a changing sun's effect upon the photochemistry or to its influence upon the diurnal microclimate and thereby the mixing. Additional confusions follow easily from the prevalence of parent–daughter reaction sequences. First sources and ultimate sinks for several species may be several steps removed from, and multiply interconnected with, the temporal histories of those intermediate species whose measurement may be emphasized by experimental convenience or by social demand. In short, hidden variables abound. Additionally, postulated reaction schemes, though plausible and even possibly correct, are often intrinsically not determinable from currently possible measurements. Exotic and evanescent species [OH, HO_2, $O(^1D)$, $O_2(^1\Delta)$] are believed to have crucial influences at dilutions several magnitudes beyond our detection limits, a circumstance of high challenge or placid reassurance, depending on from which of several vantage points these constructions are viewed. A strong and revealing parallel can be drawn between today's high ratio of conjecture to experiment in this facet of the atmospheric sciences and that similar ratio experienced in the superterrestrial disciplines that flourished during the space decade. It now seems possible that increasing experimental efforts will shortly be made toward unscrambling some of the many uncertainties in air chemistry. Therefore, it also seems desirable to pause and briefly to survey a few of these uncertainties, and from them to suggest general methods and strategies toward the sensible and economic amelioration of our larger ignorances. The following sections discuss selected aspects of the interrelated air chemistries of the nitrogen and carbon oxides and tropospheric ozone, of sulfur dioxide and its oxidation to sulfate aerosols, and of the mixing dynamics as they affect these chemistries and are affected by them. This discussion is not intended as a learned review but rather as background material to support the Panel's opinions on desirable priorities.

II. NITROGEN AND CARBON OXIDES AND TROPOSPHERIC OZONE

Much work and more speculation have been stimulated by urban, ground-level observations, typified by Figure E.1. These curves display at least two obvious puzzles: after the apparent injection of NO by a morning traffic pulse, how does it get oxidized "so quickly" to NO_2? Then where does the NO_2 go?

The obvious reaction is too slow to answer the first query:

$$NO + NO + O_2 \rightarrow 2NO_2. \tag{E.1}$$
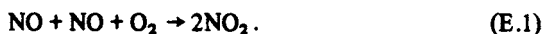
Heicklen *et al.* (1971) suggest

$$NO + HO_2 \rightarrow NO_2 + OH, \tag{E.2}$$

where the hydroperoxyl radical is produced by

$$OH + CO \rightarrow CO_2 + H, \tag{E.3}$$
$$H + O_2 + M \rightarrow HO_2 + M. \tag{E.4}$$

Smog chamber simulations support this mechanism (Westberg *et al.*, 1971) and also suggest that

$$HO_2 + NO_2 \rightarrow HNO_2 + O_2, \tag{E.5}$$
$$HNO_2 + h\nu \rightarrow OH + NO \tag{E.6}$$

partially reverses the chain oxidation of NO by CO. Quasi-equilibrium concentrations of HO_2 and OH consistent with these reactions and with Figure E.1 are about 5×10^9 and 10^8 molecules/cm^3 (0.25 and 0.005 ppb), respectively.

It is well established that ozone reacts rapidly with nitric oxide,

$$O_3 + NO \rightarrow O_2 + NO_2, \tag{E.7}$$

and this reaction almost certainly accounts for the lag in the rise of ozone until the nitric oxide is essentially depleted, as shown in Figure E.1.
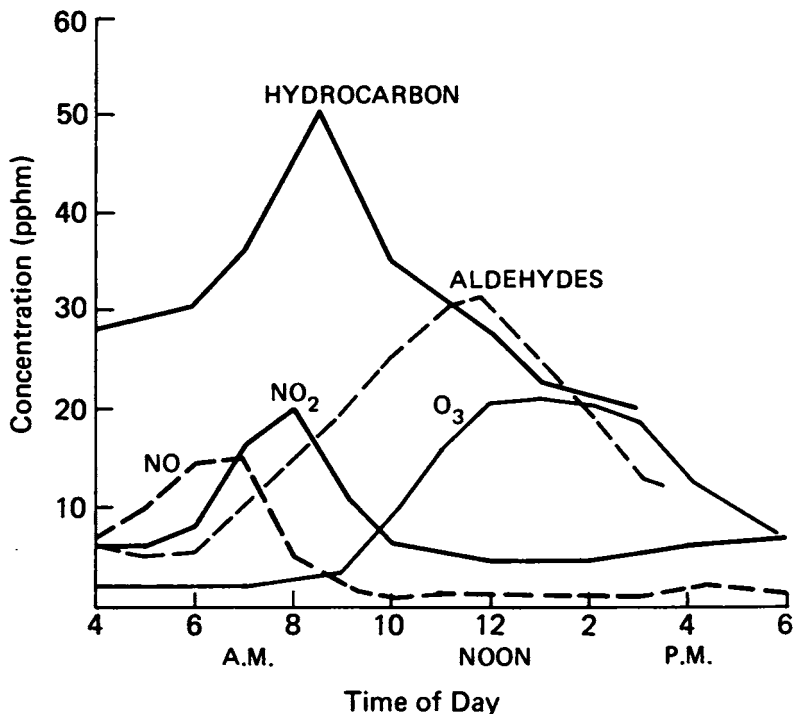
FIGURE E.1   Surface concentrations of various atmospheric species or func-
tions of time of day. (Taken from R. D. Cadle and E. R. Allen, 1970: *Science*,
167, 243.)

An advective explanation for the rapid change from NO to NO_2
is at hand if we postulate a layer aloft of NO_2 leftover from the
previous day, which is brought to the observing site by the onset of
vertical motion due to insolation. The true explanation is very
possibly a combination of chemical and meteorological processes.

Nitrogen dioxide is the principal synthesizing catalyst for ozone,
via

$$h\nu + NO_2 \rightarrow NO + O, \qquad (E.8)$$
$$O + O_2 + M \rightarrow O_3 + M. \qquad (E.9)$$

More conjectural are possible tropospheric reactions initiated by
$O(^1D)$ and $O_2(^1\Delta)$ from ozone's photodissociation

$$h\nu + O_3 \xrightarrow{\lambda \leq 3400 \text{ Å}} O_2(^3\Sigma) + O(^1D),$$
$$h\nu + O_3 \xrightarrow{\lambda \leq 3100 \text{ Å}} O_2(^1\Delta) + O(^1D). \qquad (E.10)$$

These include

$$O(^1D) + H_2O \rightarrow 2OH \qquad (E.11)$$
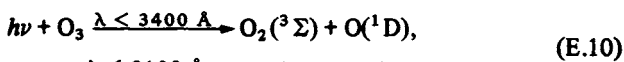
as a chain initiating step for nitric oxide's oxidation cycle (Westberg *et al.*, 1971; Levy, 1971; Donovan and Husain, 1970) and for possible oxidation of methane to formaldehyde via methoxy, methyperoxyl, and methyl radicals, Reaction (E.3):

$$OH + CH_4 \rightarrow CH_3 + H_2O, \qquad (E.12)$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M, \qquad (E.13)$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2, \qquad (E.14)$$
$$CH_3O + O_2 \rightarrow H_2CO + HO_2. \qquad (E.15)$$
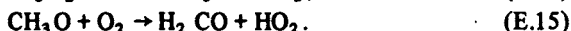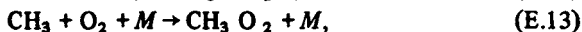
In rural environments, far from crowds of commuting cars, $O(^1D)$ may significantly contribute to measured syntheses of NO from N_2O (Donovan and Husain, 1970), which as with CH_4 is a metabolic product and is present in the troposphere at mixing fractions near 10^{-6}.

$$O(^1D) + N_2O \rightarrow 2NO. \qquad (E.16)$$

Molecular $O_2(^1\Delta)$ has been suggested to affect olefin attack:

$$
O_2(^1\Delta) + R\text{-}\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}\text{-}R^1 \rightarrow R\text{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-}\overset{\overset{\displaystyle OH}{|}}{C}=C\text{-} \qquad (E.17)
$$
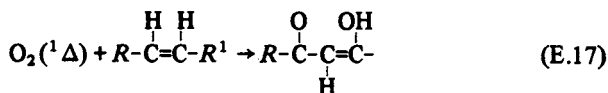
Still more conjectural, and in this case probably wrong, is an often suggested chain consisting of reactions (E.10) and (E.11) and

$$OH + O_3 \rightarrow HO_2 + O_2, \qquad (E.18)$$
$$HO_2 + O_3 \rightarrow OH + 2O_2. \qquad (E.19)$$

The evidence cited to support this is that with slow photolysis of concentrated ozone mixtures, added water vapor greatly increases the quantum yield for ozone's photodecomposition. Recent opinion (Langley and McGrath, 1971), however, supported by flash photolysis experiments, is that reaction (E.18) must be very slow and that

vibrationally excited hydroxyl radicals are likely (in a still contro-
versial way) involved in the laboratory photolysis experiments. In
dilute ozone mixtures such as the troposphere, however, vibra-
tionally excited hydroxyl radicals would certainly quench in prefer-
ence to chain propagation.

Returning again to Figure E.1, we asked earlier where the NO_2
went, more or less coincidentally with the delayed rise in O_3. A
currently favored suggestion is that most of the fixed nitrogen pauses
temporarily as organic nitrates such as peroxyacetylnitrate. This now
popular constituent, first detected by long-path infrared absorption,
is routinely measured with great sensitivity by gas chromatography
with electron attachment detection. Total organic nitrates have been
shown upon occasion to display a near mass balance with total earlier
NO_2, and other obvious nitrate sinks, such as ammonium nitrate and
nitric acid aerosols, do not seem to appear in sufficient quantity.
However, the reaction sequences for nitration and the ultimate
removal of NO_2, which almost certainly involve heterogeneous chem-
istry upon aerosol coagulates, is today only sketchily understood.
Again, many postulates involve transitory and reactive intermediates.

Clearly, detection of some of the many intermediates of the
postulated photochemical stew would encourage us that some of our
guesses are qualitatively correct. Clearly also, this will be a formi-
dable job. We recognize that verifying postulated intermediates is an
old problem theme in chemical kinetics, and that the old solution
theme has been to test hypothetical reaction mechanisms by explor-
ing the effects of concentration and temperature variations. We
observe that this approach is not generally available in the atmo-
sphere, and we believe that close laboratory modeling is not generally
possible. Consequently, actual detection of at least some of the many
intermediates seems to us to be relatively more important to con-
fident progress in air chemistry than it has been, for example, with
combustion kinetics. On the other hand, this detection may be facil-
itated in the atmosphere, as compared with laboratory conditions, by
the availability of long paths, low surface-to-volume ratios, and large
sample volumes. Additionally, new technology, for example ultra-
high-resolution optical absorption spectroscopy using tuned lasers, is
now becoming feasible. Efforts to develop and employ new detection
skills should be encouraged. Real progress in understanding air chem-
istry cannot be expected from repetitious deployment of present
instrumentation.

III. SULFUR DIOXIDE AND ITS OXIDATION TO SULFATE AEROSOLS

While on a global scale the relative magnitudes of artificial to natural sulfur injections are still somewhat controversial, on both urban and continental scales the principal sources of atmospheric SO_2 are usually anthropogenic and arise mainly from fuel combustion and sulfide ore reduction (Robinson and Robbins, 1968). The sink mechanism for sulfur oxides appears principally to involve precipitation scavenging of atmospheric sulfates and sulfuric acid aerosols. Between source and sink occurs a confusing competition between alternate oxidation paths that display measured rates varying over nearly four magnitudes (Urone and Schroeder, 1969).

Among the reactants that have been shown strongly to affect the (presumably, but not always demonstrated) homogeneous oxidation rates are NO and NO_2, olefins, water vapor, and ammonia. In aqueous solution most transition metal ions (such as are copiously emitted both by smelting and coal combustion) are also catalytic. In natural aerosols, oxidation in differing circumstances may be plausibly rate-limited by gas diffusion to surfaces, adsorption isotherms, and by bulk diffusion and pH.

Laboratory studies attempt and sometimes succeed in isolating effects of one or a few variables upon the oxidation rates, but laboratory measurements rarely approximate field conditions, which display rates differing greatly from both those of the laboratory and other field measurements at other sites or times. Field campaigns are typically underparameterized, even for the chemical effects, and the unscrambling of relative SO_2 decays due to plume dilution and to oxidation is probably beyond the power of *a priori* models for plume dispersion (Tsang, 1969). Near stacks this can be, but too often is not, ameliorated by estimating dilution relative to another more inert stack gas, such as CO_2 or CO. Even so, density fluctuations in the plume may strongly affect observed mean rates, especially when reactions are of kinetic order greater than one. Far from the stack, too few have bothered to report even relative humidities or concurrent aerosol properties.

It is essential that continuing and future field measurements be vastly upgraded in sophistication. To parameterize the problem properly it is necessary to know which parameters govern on which

occasions. In the near field, the plume must be specified by measurement not by models alone. In the far field, concentrations of other minor atmospheric gases, such as the nitrogen oxides and olefins, may dominate. In both near and far fields, heterogeneous chemistry probably governs, and so size and composition parameters of the aerosol phase must be specified. Therefore, it is necessary that field networks be established to measure many parameters around and above major sulfur plumes. Of special interest also are related problems of washout kinetics affecting the sulfate aerosols once formed and of subsequent soil chemistry affected by rain with systematically lowered pH, such as that falling in Western Europe (Bolin, 1971).

IV. SOME REMARKS ABOUT THE RELEVANCE OF CURRENT AIR-QUALITY DATA BANKS

In Appendix D, questions are raised about the adequacy of instrumentation, sampling procedures, and data reduction now employed by EPA-sponsored air-quality-control districts. There are strong doubts that measurements contributing to research insights will result from these networks, where the originating motivation is to document trends in certain canonical indices of air quality. There is some concern that the existence of these monitoring networks may be used to argue against apparently duplicating measuring campaigns motivated by research needs. Occasional task force expeditions should be sponsored to study intensely certain explicit scientific questions. The highly successful 1969 cooperative Los Angeles Smog Project, which involved investigators from the Universities of Minnesota and Washington, the California Institute of Technology, and the California Departments of Health and Air Pollution Research, could well serve as a model for such studies.

Appendix F
Comments on Transport of Trace Constituents in the Atmosphere

JOOST A. BUSINGER

I. THE TURBULENT TRANSFER COEFFICIENT

To evaluate transport characteristics of the atmosphere, the complexities of atmospheric motions have been simplified by introducing the concept of a mean overall turbulence, sufficiently homogeneous that it may be characterized by turbulent-transfer coefficients. The flux, F_s, of any atmospheric constituent, s, may then be simply described by the product of the eddy transfer coefficient, K, and the negative gradient of the concentration of the constituent $-\nabla s$, i.e.,

$$\vec{F}_s = -K\nabla s. \tag{F.1}$$

The research is directed toward establishing values for K under various conditions. It turns out that K is dependent on space, time, and the stratification of the atmosphere in complicated ways (Lumley and Panofsky, 1964; Hinze, 1959).

This complexity is such that Equation (F.1) is not always meaningful and may lead to serious misconceptions when applied to vertical fluxes. The type of error that one may encounter is illustrated by the following classical example: The long-term average temperature of the air just above the earth's surface is higher than the average surface temperature, yet the average heat flux is from the surface to the atmosphere, contrary to what the concept of an eddy-transfer coefficient would predict, unless we accept negative coefficients.

The values of K may differ for different properties that are being transferred. It is therefore important that transfer coefficients be used only in situations where their validity has been tested.

In some cases it is possible to use the concept of eddy transfer in an indirect way by using similarity arguments. If the behavior of one trace element is fairly well known, other trace elements may be related to this, assuming that their behavior is similar. An example of how this method may be used successfully is given in the next section.

II. THE EARTH'S SURFACE AS A SINK AND A SOURCE FOR TRACE ELEMENTS

The turbulent transfer in the atmospheric boundary layer and particularly in the surface layer (the lowest 20 m) has been extensively studied for momentum, heat, and water vapor (e.g., Businger et al., 1971; Dyer, 1965, 1967; Swinbank, 1964, 1968; Webb, 1970). Some of this knowledge can readily be applied to other atmospheric constituents. The characteristics of the water-vapor flux at the surface are probably most relevant for the transfer of other gases. In this section a simple outline of the procedure is presented together with a few comments on how to refine it.

Near the surface, if uniform and with only small heat fluxes, the logarithmic wind profile is a good approximation:

$$u = \frac{u_*}{k} \ln \frac{z}{z_0},$$
(F.2)

where u is the mean wind speed, u_* is the friction velocity $= (\tau/\rho)^{1/2}$, k is von Karman's constant $\simeq 0.4$, z_0 is the roughness length.

Since the friction velocity is approximately independent of height (in the lowest 20 m or so) we have also

$$u_*^2 = K_m \frac{\partial u}{\partial z}$$
(F.3)

(where K_m is the eddy-transfer coefficient of momentum) and therefore

$$K_m = k u_* z.$$
(F.4)

This eddy-transfer coefficient of momentum may be used as a first-order approximation for the transfer of other quantities such as O_3 or SO_2. Therefore, the flux F_s of a constituent with average density $s(z)$ near the ground may be given by

$$F_s = -K_m \frac{\partial s}{\partial z}.$$
(F.5)

This means that similarity between the u and s profiles has been assumed. Substituting Eq. (F. 3) into Eq. (F. 4) and integrating yields an expression similar to Eq. (F.1):

$$s - s_0 = \frac{F_s}{ku_*} \ln \frac{z}{z_0},$$
(F.6)

where s_0 is the density at the surface, where the wind speed vanishes.

In order to determine s_0 and F_s, it is usually necessary to make observations at two heights, z_2 and z_1 of both wind speed and s. We have then the following set of equations:

$$\frac{u_*^2}{F_s} = \frac{u_2 - u_1}{s_2 - s_1}$$
(F.7)

or [using Eq. (F.1)]

$$F_s = \frac{k^2 (u_2 - u_1)}{(\ln z_2 / z_1)^2} (s_2 - s_1);$$
(F.8)

also

$$s_0 = s_2 - u_2 \frac{s_2 - s_1}{u_2 - u_1};$$
(F.9)

and, finally,

$$\frac{F_s}{s_0} = \frac{k^2 (u_2 - u_1)^2 (s_2 - s_1)}{\left(\ln \frac{z_2}{z_1}\right)^2 \left[s_2 (u_2 - u_1) - u_2 (s_2 - s_1)\right]}.$$
(F.10)

Now, if there is reason to believe that s_0 should be 0 at the surface because the surface acts as a sink, the fact that $s_0 \neq 0$ when computed from Eq. (F.8), which is an extrapolation of s to the surface, indicates that there is a surface resistance that is not accounted for by the logarithmic profile or, better, by the turbulent transfer in the surface layer. The quantity $s_0/F_s = r_s$ may be interpreted in this case as a surface resistance.

It is desirable that such resistances be determined for a number of constituents. In some cases it may be difficult to determine $s_2 - s_1$; particularly, when the resistance, r_s, is very large this quantity may be very small and a different technique to determine r_s should be used. A mass balance technique, if possible, could be useful.

The conditions of a neutral atmosphere and similarity between the u and s profiles are not often fulfilled. A substantial heat flux may cause a significant correction to the wind profile, resulting in dissimilar wind and temperature profiles (Businger *et al.*, 1971). There is no good reason to assume that under nonneutral conditions the profiles of trace elements would be similar to the wind profile. It is therefore useful to try to find a passive scalar quantity that is fairly well known and relatively easy to measure and for which similarity with trace elements may be assumed. Such a quantity is water vapor. Water vapor behaves in many respects as an atmospheric trace element with a source at the surface. A considerable amount of research has been carried out on evaporation in agricultural areas and in air–sea interaction. This knowledge can more or less readily be applied to problems in atmospheric chemistry.

When the surface is wet, the surface concentration of water vapor is saturated, and water vapor is readily transferred into the atmosphere. Similarity between temperature and water-vapor profiles has often been assumed and sometimes verified (Dyer, 1967). If the surface is relatively dry, the water vapor encounters a barrier between the wet soil at some depth below the surface and the surface. The resistance in this case may be given in an expression similar to Eq. (F.9). In the case that this resistance is very large, $q_2 - q_1$ (the difference in specific humidity at two heights) may become very small and reference is then made to the energy budget equation to obtain F_E and r_E (Tanner and Fuchs, 1968; Wilson and Rouse, 1972).

In general, using water vapor and a knowledge of the vapor flux F_E, we can develop an equation similar to Eq. (F.7) but more accurate as follows:

$$F_s = \frac{F_E}{\rho} \frac{s_2 - s_1}{q_2 - q_1}, \qquad \text{(F.11)}$$

where ρ is the density of air and q is the specific humidity.

Similarity between water vapor and the trace element may also be used in situations where change of terrain occurs. The problems become quickly complex but are still capable of numerical solution.

Two conclusions based on this discussion are

1. Detailed knowledge of the turbulent transfer processes near the earth's surface, whether water or land, is needed to evaluate the surface as a source or sink of trace elements. This type of information may be provided by micrometeorologists, experts in air–sea interaction, and agricultural meteorologists.

2. The study of the transfer of water vapor near the surface may be especially useful as a similarity model for other trace elements. Similarity with water-vapor transfer is much more likely to be valid than similarity with heat or momentum transfer.

III. DIFFUSION MODELS

Most diffusion models make use of turbulent-transfer coefficients and assume that the diffusion of matter is a random process. Consequently, the concentration distribution in, e.g., smoke plumes, is Gaussian. Predictions of concentration with the use of these models are usually satisfactory. Therefore, in general the diffusion models are adequate to describe the dispersion of trace elements in the atmosphere under various conditions of stability. Difficulties are still encountered when complicated boundary conditions prevail, for example, complex source distributions in complicated terrain. With the aid of numerical techniques these problems can be solved with reasonable accuracy.

However, there are situations when these models are inadequate. These occur primarily when the winds are light and when the concentration levels become exceptionally high.

Of special interest is the case of *fumigation*. During the night a reservoir of pollutants is collected from various sources in the stable layers at and slightly above the stack heights. During the morning hours heating of the lower atmosphere causes vertical mixing. When

this mixing reaches the reservoir of polluted air, relatively high concentrations of pollutants may be carried down to the surface. This process is called fumigation. The prediction of the levels as well as the time and place where the maximum concentrations due to fumigation occur is still difficult. It is important that this aspect be studied in sufficient detail because dangerously high levels of concentration of certain trace elements may occur.

The reason why difficulties are encountered under light winds is that the turbulence diminishes and the air to a large extent loses its dispersive qualities. The statistical approach of turbulence becomes inadequate, and a detailed analysis of the mesoscale circulations is required.

Another problem that deserves special attention is related to reaction rates as a function of fluctuations of concentrations. If the fluctuations in concentrations are known, corrections may be made if the reactions are not linear with concentration. The prediction of the fluctuations is often more difficult than the prediction of the concentrations themselves. Here again it depends on how well the atmospheric condition can be approximated by homogeneous turbulence. In the case of light winds, spuriously high concentrations may lead to significant corrections in the anticipated reaction rates between various trace constituents. (See also Appendix E.)

Two conclusions from this discussion are

1. Maximum concentrations that result from fumigation should be analyzed in more detail as a basis for more adequate predictions.

2. Fluctuations of concentrations in plumes should be studied to allow corrections for chemical reaction rates when the reactions are not linear with concentration.

Appendix G
Hydrometeor Composition

ROBERT J. CHARLSON

I. INTRODUCTION

There are several basic facts about the chemistry of cloud and precipitation water that are useful starting points for this discussion.

1. Precipitation is probably the most important single sink for many trace atmospheric constituents, both natural and anthropogenic (Junge, 1963).

2. In the case of many substances that are cycled through the atmosphere (sulfur and nitrogen compounds, for example), an understanding of the role of precipitation is necessary if the cycle is to be understood (Kellogg *et al.*, 1972).

3. Precipitation water is not now and never was pure H_2O but changes composition because of both natural and human influences (Bolin, 1971).

4. Compared with other countries, the effort devoted to the study of precipitation chemistry in the United States is miniscule.

5. The composition of precipitation is important to the biosphere. In the natural environment, there is a complex balance among substances in rain. Human activities have been shown in specific cases to change dramatically the composition of precipitation, with attendant changes in the hydrosphere and lithosphere (Bolin, 1971).

6. While precipitation composition cannot be used in any simple way to reflect local, short-term air-pollution levels, it is useful for following long-term trends in air composition.

This report reviews briefly the state of knowledge in this field, delineates the major problems, and suggests needed actions.

Few quantitative and general methods exist for predicting the effectiveness of precipitation in scavenging trace materials from air or

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for estimating the amounts of a substance thus removed. Indeed, it is often easier to determine the removal of both gases and particles from air by change of composition of rain rather than by diminution in air. There is extensive literature on the microphysical aspects of the transfer of gases and particles to falling raindrops—often called washout. Another area—historically called rainout (or snowout)—involving in-cloud scavenging processes also has received attention. Englemann and Slinn (1970) summarized the state of knowledge in these microphysical areas. Most models of precipitation scavenging depend largely on empirical coefficients, with most attention given to the removal of particles.

There can be little doubt that large, water-soluble particles such as $(NH_4)_2 SO_4$ act as condensation nuclei and are eventually removed in rain. Since $(NH_4)_2 SO_4$ is probably an end product of SO_2 oxidation, SO_2 is removed by the process. SO_2 and other water-soluble gases are also removed if they dissolve in cloud or rain drops. The removal process is complicated by the existence of both dissolved and gaseous forms of substances (e.g., $H_2 SO_3$, its dissociation products in the aqueous phase and gaseous SO_2). The existence of chemical processes between several phases (gaseous, liquid, and solid) has precluded a general approach.

Gases that do not react in water, or are not soluble, do not seem to be much affected by the presence of condensed water in the atmosphere. Methane and other low-molecular-weight alkanes fall into this category, as possibly does carbon monoxide. A report of a high CO level in rain (Swinnerton *et al.*, 1971) complicates this simple partitioning.

The most extensive measurements of the composition of precipitation water have been made in Europe, particularly in Scandinavia; some data have also been collected in the United States. Although these data are convincing evidence of the interaction of atmospheric gases and aerosols with cloud and precipitation water, there are few extensive studies of the relationship of gas, rain, and cloud or fog compositions.

One U.S. study (Hales *et al.*, 1971) explored the washout of SO_2 from a power plant plume. It showed that the washout rate depends on both the initial composition of the rain and the gas composition below the plume. However, the authors were careful to limit their conclusions to a single case, and no general results were produced that might be applied to cases not involving SO_2 plumes.

II. CURRENT RESEARCH IN HYDROMETEOR CHEMISTRY

The center of activity in precipitation chemistry is Europe, especially in the Scandinavian countries. Sweden probably has the strongest position in the field, with two major institutes devoting substantial resources to this area. The Meteorological Institute of Stockholm University started research in precipitation chemistry in about 1955 under the guidance of C. G. Rossby. At that time, a network for collection of precipitation water was established and was subsequently extended throughout Europe. Today over 100 stations cover Western Europe, Great Britain, Iceland, and Scandinavia. Samples are also taken in the Eastern European countries and the Soviet Union.

Although some differences in analytical methods exist from country to country, extensive data have been collected on the following ions and properties: $SO_4^=$, Cl^-, NO_3^-, NH_3, Na^+, K^+, Mg^{2+}, Ca^{2+}, H^+ (usually from pH), HCO_3^-, electrical conductivity, and amount of precipitation. Less extensive data exist for trace elements, including Hg, Mn, Pb, Al, and Br.

Of these data, those on acidity and sulfate have shown marked geographical variations and systematic changes in time, with both acidity and sulfate increasing in some areas, especially in Scandinavia. Bolin (1971) summarized these studies, along with an appraisal of the effects of the acidic water on soils, fish, forests, and materials. This comprehensive report, which includes economic and policy studies, is the result of a team effort of scholars from several disciplines working together on one environmental problem. This Swedish team concluded that the increased sulfate and acid is from fossil fuel combustion in Germany, Holland, Belgium, Great Britain, and elsewhere, and that it has significant biospheric effects. The most notable ones attributable to the increased acidity are decreases in the pH of lakes and rivers and leaching of calcium from forest soils. The pH has become sufficiently low in some lakes to cause some fish to disappear. The thin forest soils show important changes in nutrient balance, and there is some evidence of decreases in growth rate of trees.

Thus, this study of precipitation chemistry has expanded beyond the usual bounds of scientific research and has been applied directly to human problems. The summary report (Bolin, 1971) was submitted to the United Nations for policy discussion.

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It must be emphasized that this study was based on only 15 years of data, and that the statistical significance of the suggested trends and effects is not so good as is desired. The acquisition of another decade or two of data will help to identify real effects more positively. These sorts of problems require continuous data over several decades and over large geographical areas.

While there has been some study of hydrometeor chemistry in the United States in the past decade, it has been by comparison with the European efforts highly fragmented, sporadic, and unfocused. There has been no network established that could provide data for comparison with the European results. Until recently there has been no long-term sampling effort (i.e., several decades' duration). In 1971, the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA) began a small data-collection program with ten stations:

Bishop, California	Atlantic City, New Jersey
Alamosa, Colorado	Raleigh, North Carolina
Salem, Illinois	Pendleton, Oregon
Caribou, Maine	Huron, South Dakota
Meridian, Mississippi	Victoria, Texas

These sites will coordinate their activities with the World Meteorological Organization (WMO) efforts in precipitation composition. The samples will be analyzed by the EPA laboratories for pH conductivity residue, acidity, SO_4^-, NO_3^-, NH_4^+, F^-, Cl^-, As, Be, Cd, Ni, Zn, Cn, Fe, Mn, Pb, V, Na, K, Ca, Mg, and Hg.

No determinations are planned for HCO_3^-, asbestos, pesticides, PCB's, or other exotic molecules. The lack of carbonate/bicarbonate data precludes comparison with the European data.

This effort is smaller by about a factor of 10 than that in Europe and hence provides little spatial resolution. It is not adequate, for example, for studies of the sulfur budget.

There are some efforts on a small scale, including studies on the composition of cloud or fog water (Lazrus et al., 1970). Some studies of precipitation composition also have been made by or for agronomists and foresters (see, e.g., Feth, 1964).

Of course, extensive measurements of radioisotopes in precipitation water have also been made, and a network exists for studies of ^{137}Cs, ^{90}Si, ^{3}H, and other materials in dry fallout and in rain and washout processes. This activity is sponsored by the Health and

Safety Laboratory (HASL) of the Energy Research and Development Administration, which also supports much basic research in precipitation scavenging. Other countries maintain extensive radionuclide monitoring activities as well (see, e.g., Szalay and Csongor, 1968). The use of isotopes for tracing condensed water in air is another major area of activity (Dansgaard, 1964; Ehhalt and Östlund, 1970; Schell *et al.*, 1970). This work is being carried into surface and subterranean hydrological studies.

A U.S. precipitation chemistry network (in addition to the radiochemistry network) was started in about 1956 'by C. E. Junge. Lodge *et al.* (1968) at the Public Health Service and subsequently the National Center for Atmospheric Research (NCAR) carried the network activities from 1962 to their conclusion in 1966. Data were continuous only from 1962 to 1966, largely because of changes in personnel and sponsorship.

III. TECHNICAL PROBLEMS IN STUDIES OF HYDROMETEOR CHEMISTRY

The high cost of doing wet chemical analysis by traditional methods retarded U.S. hydrometeor chemistry studies. There are no automated systems for recording precipitation composition. There is a need for simultaneous, automatic analysis of many properties and ions, a capability that can be achieved at modest cost with modern analytical systems. Automatic samplers are available at ~$500, so the initial cost of a network is small. There may be chemical properties that will prove to be important at some future date that are not yet recognized.

There is a need for standardization of methods on a global scale if comparison with data in other countries is to be made. Sampling must be standardized, including location and collection method. It is essential, for example, to be sure that all rain collectors are covered to eliminate dry fallout and that some automatic means is used to open and close the collector (Lodge, 1972).

Another technical problem arises in continuity of data collection. The chemical properties of precipitation show large, complex fluctuations requiring clever statistical treatment of the data. As is the case with all noisy signals, appropriate averaging periods are necessary if significant variations and trends are to be detected. Data must therefore be acquired on a regular basis, without interruption, if they are intended to show secular changes.

Yet another technical problem lies in the handling and storage of samples. Biological activity in the water may change their composition, and certain substances react, decompose, interact with the container, volatilize, or are otherwise modified. Prompt analysis, preferably instantaneous, is desirable.

IV. CONCLUSION

Based on the importance of precipitation as a sink, as a part of chemical cycles, and as a major element of the hydrologic cycle providing water and its dissolved substances to the biosphere, the primary need is clearly to establish an appropriate precipitation chemistry sampling and analysis network. If this need is to be met, a spatially adequate network (~100 stations) should be established soon under the sponsorship of an appropriate governmental unit or units. This activity must have a continuous program for at least a decade, or preferably longer, so that patterns and trends can be defined. Data from this effort should be used to assist in formulating generally applicable models of precipitation scavenging, to elucidate chemical cycles in the atmosphere, and to provide information relevant to biospheric/ecological problems. Data should be collected outside the United States as needed to delineate chemical cycles more clearly. Data on sulfur are needed in the southern hemisphere, for example. All of these activities should be coordinated with those of other countries because of the proven international nature of this form of atmospheric chemical transport.

Since precipitation composition strongly affects the surface waters of the earth, with a subsequent biospheric impact, it is essential to tie the studies of precipitation composition to those of runoff waters, surface waters of lakes, reservoirs, ponds, and the like. It is also necessary to maintain close connections with studies of the biological and pedological effects of precipitation composition. It appears that organic matter in precipitation water may be important and that biological activity may exist.

The current technical costs of hand analysis are not consistent with current technology. It should be possible to develop an automatic precipitation composition analyzer after suitable study of available approaches.

These suggestions are not new. The American Chemical Society discussed the problems of acidity in rainwater in Scandinavia (Lodge, 1969) and recommended studies of the removal rates of pollutants.

The American Chemical Society (1971) reiterated this discussion and urged high priority to studies of large-scale pollution.

The chemist-meteorologist workshop of 1971 (Reiter *et al.*, 1971) gave high priority to studies of precipitation chemistry including (1) establishment of current levels of substances in precipitation and (2) evaluation of the rate of change of composition.

The SCEP report (1970) pointed out the need for studies of precipitation scavenging of heavy metals, DDT, and other halogenated hydrocarbons and their residues. Their rationale was based on the need for information relevant to biological effects.

Appendix H
Worldwide Air Pollution
and Its Effects

RICHARD D. CADLE AND ROBERT J. CHARLSON

I. INTRODUCTION

It is now widely recognized that the earth and its subsystems—such as the atmosphere, hydrosphere, lithosphere, and biosphere—comprise a closed system, and that human activity is exploiting the substance of these resources. There is an obvious concern that effluvia of human activity might accumulate in some part of the system in quantities sufficient to make life unpleasant or difficult or, worse, to trigger a change that would eradicate life from the earth. The atmosphere as an element of the system is subject to a number of insults, some of which it seems to accommodate easily and others that lead to secular trends. Numerous effects of these trends have been suggested, ranging from local to global. Carbon dioxide is accumulating at an ever-increasing rate in the whole atmosphere because of the burning of fossil fuels, and particulate matter is probably also increasing on a global scale. A lack of measurements of other substances precludes listing further examples even though it is almost certain that large areas of the earth are affected by such long-term compositional trends.

The effects of such regional and global air pollution can adversely affect mankind in several ways. For example, pollutants could influence weather and climate, a subject about which little is known. We do know that carbon dioxide (CO_2) affects the radiation balance of the earth and that increasing the concentration of CO_2 would have a warming effect (all else being equal), but we cannot at present estimate the amount of this effect for a given increase of CO_2.

Fine particles suspended in the atmosphere can affect the weather and climate in many ways. They can serve as condensation and/or freezing nuclei, scatter radiation, and absorb radiation. But

the overall effect on climate of increasing, worldwide, the pollutant-particle concentration is unknown. Also it is important to take into account the fact that many gases emitted into the atmosphere become airborne particles through chemical reactions. There are several ways to investigate the effects of such aerosols on climate. One is to estimate such physical properties of the particles as size distribution, optical properties, and behavior as condensation and freezing nuclei and to develop appropriate numerical models of these properties in conjunction with those on general circulation of the atmosphere.

Another but more naive method for judging the effect of pollution on global climate is to estimate and compare the relative amounts of man's and nature's contribution to each important trace atmospheric constituent, both gaseous and particulate. If man's contribution is much smaller than nature's, his effect on the climate is probably, but not necessarily, small. Much less is known about the strength of natural sources, such as oceans and rain forests, than of human sources. Mean residence times must be known in order to estimate the extent to which material from a given source is distributed worldwide. Expeditions to determine the strengths of natural sources and sinks of trace constituents and the concentrations of trace constituents are often undertaken. Such field work is backed up by laboratory studies to determine the properties of chemical and biological reactions that can serve as sources and sinks and the development of improved analytical techniques.

Monitoring the atmosphere for trace constituents for a number of years, with monitoring stations placed in remote locations, has served to indicate whether the human contribution to atmospheric trace constituents is changing.

Besides climate there are at least two additional ways in which global air pollution may adversely affect man. The air serves as a route through which certain toxic pollutants travel, to the land, streams, lakes, and oceans. Such trace constituents may be relatively harmless in the atmosphere but do considerable damage after their removal. Examples are insecticides and several metals. The other possibility is that jet aircraft, such as supersonic transports, flying in the stratosphere will emit pollutants that decrease ozone concentrations, thereby allowing more harmful ultraviolet radiation to reach the earth's surface, and particles that in other ways affect the radiation balance. The extent to which such emissions will produce important effects, even if there is extensive use of such aircraft, is somewhat controversial at the moment.

II. AIR CHEMISTRY IN WEATHER AND CLIMATE CHANGE

The possibility of climate change caused by air pollutants has largely developed in the last few years as a topic of great potential importance to mankind. The SCEP report (1970) is dedicated largely to this sort of problem, and many strongly worded conclusions and suggestions for study are made. An international meeting, organized by C. Wilson of MIT, was called the Study of Man's Impact on Climate (SMIC, 1971). In addition to re-emphasizing the recommendations of SCEP, SMIC provided a deeper examination of questions of terrestrial climate.

Since the problem of climate is a complex problem, and since the possibility of man's triggering of an instability is real but quite difficult to model or predict, there are major uncertainties about the nature and direction of changes in simple climatological factors, such as temperature. The details of changes in cloud processes, precipitation chemistry, and radiation are even more difficult to predict. Adequate models of such a complex and interrelated system as climate will require major inputs from air chemistry.

The discussion that follows is limited to chemical problems associated with the general climate problem and to the role of chemists in the area of weather and climate change.

A. Instabilities versus Reversible Effects

Among the climatic theoreticians (Rasool and Schneider, 1971; Bryson, 1967; and Budyko, 1969, for example), the key issues today are the effects of CO_2 on earth warming and the complex effects of aerosol on the earth's radiation balance. The theme of many such forecasts is the triggering of various kinds of instability. In this case, an instability might be broadly defined as a self-propagating change. That is, once the change is initiated, weather and climatic processes amplify and continue the trend. An ice age is one of the end products of such an instability. Any nonlinear effect, if positive feedback occurs, may qualify. It is important to point out that some of these instabilities are slow processes requiring hundreds of thousands of years.

Other marginal climate changes, not leading to instability, also can cause unpleasant consequences, which presumably could be reversed. Instabilities illustrating the diverse impact of chemical phenomena are discussed.

Fleagle (1969) lists four instabilities relevant to weather and climate modification:

1. Phase instability of water in the supercooled state;
2. Colloidal instability of cloud particles (both this and 1 are manifest in rainfall);
3. Vertical instability of local regions, manifested in convection cells and cumulus clouds;
4. Horizontal instability associated with temperature gradients, manifested in large-scale storm systems.

Other less clearly delineated and possibly overlapping instabilities include

5. Ice age generating mechanisms;
6. Desert creation by albedo change (Bryson, 1971);
7. Deliquescence causing sudden shifts in optical properties of aerosols (Covert *et al.*, 1972);
8. Events related to systematic shifts in ocean circulation;
9. Arctic sea-ice instability (SMIC, 1971);
10. Salinity–sea-ice instability (SMIC, 1971).

B.   Gas Chemistry Effects

1. CO_2, the Gas Most Likely to Cause Climate Change   The effects of CO_2 on terrestrial climate have dominated atmospheric chemistry research for perhaps a decade. The work of Keeling (1971), Bolin and Bischof (1970), Keeley (1969), and others covers the subject very well. While no definitive statement can be made about the net climatic effect of CO_2 change, it is being studied extensively by chemists and physical climatologists. A first-order result of human activity is the increase of atmospheric CO_2 globally. Present research is aimed at establishing (a) the partitioning of anthropogenic CO_2 between the air, oceans, and biosphere and (b) the climatological consequences of CO_2 increase.

The role of air chemistry is central to this problem. The climatological effects on biospheric CO_2 demand study, as does oceanic CO_2 solubility.

Other aspects of the CO_2 problem also merit study. The effect of high concentrations of CO_2 on the chemistry of precipitation, on the pH of oceans, and on mesoscale radiation balance are examples. The

effect of CO_2 on the shattering of freezing supercooled water drops might deserve further study (Dye and Hobbs, 1966).

There is an outside chance that systematic H_2O vapor changes could occur in the atmosphere leading to changes in the infrared balance. Unlike CO_2, H_2O is controlled by precipitation and other processes of the hydrologic cycle, and hence should be slow to change. Mesoscale phenomena can be expected to appear long before global effects occur.

2. Other Gases Gases that apparently do not produce aerosol (CH_4, CO, and possibly others) are not involved in processes important to climate. The Study of Critical Environmental Problems reached this conclusion, which seems reasonable, although CO and CH_4 are much more reactive than were previously thought (Weinstock and Niki, 1972).

The place where these gases are most apt to be important is in the stratosphere, if there is an involvement in the complex odd oxygen systems reactions. While this possibility might seem remote, there is a chance that CO, hydrogen-producing substances (H_2O, CH_4, or any hydrocarbons), or nitrogen oxides (Johnston, 1971) could have serious effects (see Appendix A).

C. The Role of Aerosol

Figures H.1 and H.2 show the atmosphere as a chemical system with a flow of trace substances from source to sink via a large number of possible routes. Various classes of trace substances or their physical state are shown as separate boxes in the diagrams.

These figures show two basic types of meteorological effect resulting from the presence of specific trace substances in the atmosphere: (1) direct radiative interactions and (2) water in nucleation processes and the like. Nucleation processes are manifest in two general ways:

1. Modification of albedo by changes in clouds, or other changes in radiative processes, including modification of surface albedo by snow accumulation, conversion to desert, and dry soil to wet soil;

2. Hydrometeor modification, including amounts, composition, and optical properties.

It is clear that most current efforts center on direct climatological involvement via albedo changes and modification of other

radiative processes (SCEP, 1970). While a great deal of attention has been given to the study of cloud and nucleation microphysics, little of it has developed to the point at which global or even mesoscale or synoptic-scale effects can be unequivocally explained.

There still are uncertainties about whether increases in atmospheric particulate matter will act to heat or to cool the earth (Atwater, 1970; Charlson and Pilat, 1969; Charlson *et al.*, 1972; Ensor *et al.*, 1971; Mitchell, 1971; Rasool and Schneider, 1971; and others). The uncertainty exists for several reasons. First, there are various approaches to ascertaining the effects of particulate matter even when the physical and chemical properties are known. Unfortunately, in the case of the atmosphere they are not known well enough. It is particularly important to know the sizes, shapes, and indices of refraction of the particles. The complex part of the refractive index is governed by the molecular character of the particles, which is a problem of certain interest to air chemistry.

The following topics represent a partial list of relevant problems for which increased effort seems justified.

1. Rate of conversion of gases to particles and the climatological consequence of the aerosols so created;

2. The possible stabilization of fog or clouds by organic matter;

3. The role of deliquescence in radiative balance of clouds, fog, and haze;

4. Relative importance of reactions in cloud drops to gas phase reactions in 1.

5. Role of nucleation [both cloud condensation nuclei (CCN), and ice nuclei (IN)] in changing albedo of clouds;

6. Role of CCN and IN in changing area covered by clouds or cloud height.

III. CURRENT STATUS OF GLOBAL TRACE CONSTITUENT MEASUREMENTS

Certain minor constituents of the atmosphere have been measured for many generations. However, our knowledge of the sources, sinks, and even the concentrations remains woefully inadequate. Many of the analytical techniques that have been used in the past are highly questionable; a large percentage of the measurements have been made in places where the air is unusually highly contaminated, as in Europe. Global coverage has not yet been achieved and, with only

Primary
Meteorological
Effect

Gaseous, Non-Aerosol
Precursors.

$CO, CO_2, CH_4, \ldots$

Absorption of IR and
Visible (?) Radiation.

Gaseous Aerosol
Precursors

$SO_2, H_2S, NO, NO_2,$
$HC, NH_3, (H_2O)$

Absorption and Backscatter
of Visible Radiation
Absorption of IR
(small?)
Changes in Electric
Conductivity

Low RH Aerosol
$RH < ca. \ 0.7$

High RH Aerosol
$0.7 < RH < 1.0$

Dissolved Reactant

Product

Absorption and Backscatter
of Visible Radiation
Absorption of IR
Fog Formation and
Stabilization

Modification of Clouds

Warm Clouds
$T \ ca. \ -5°C$

Reactant

Product

Absorption (?) and
Backscatter of Visible
Radiation
Absorption of IR
Precipitation
Latent Heat Release

Ice Cloud Modification

Ice Clouds
$T < ca. \ -5°C$

Absorption (?) and
Backscatter of Visible
Radiation
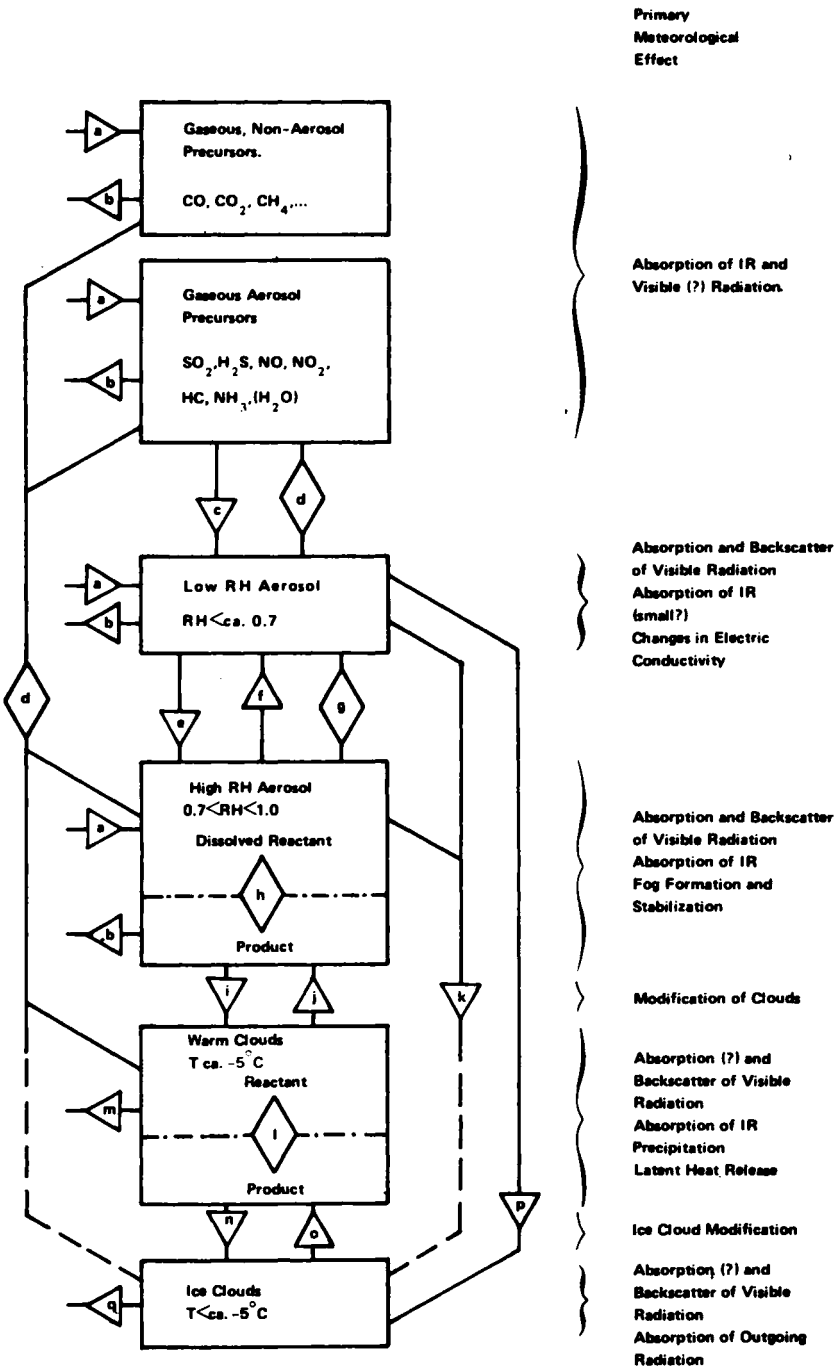Absorption of Outgoing
Radiation

FIGURE H.1   The troposphere as a chemical system. Rectangles are recognizable entities in the atmosphere. Triangles represent processes that have a single direction of material flow, and diamonds (two triangles) represent reversible processes. a, Sources; b, sinks; c, gas-to-particle conversion; d, sorption; e, deliquescence; f, efflorescence; g, Raoult's equilibrium; h, reaction in concentrated solution droplet; i, nucleation and condensation of water; j, evaporation; k, capture of aerosol by cloud drops; l, reaction in dilute solution; m, rain; n, freezing of supercooled drop by ice nucleus; o, melting; p, direct sublimation of ice on ice nucleus; q, precipitation. *Note*: Figures H.1 and H.2 are drawn separately for convenience. It must be realized that exchanges also occur between the stratosphere and troposphere. (From S. S. Butcher and R. J. Charlson, 1972: *Introduction to Air Chemistry*. By permission Academic Press, New York.)

Primary Weather/Climate Effect

Gaseous, Non-Aerosol

Precursors $-CO_2$

a
b

Absorption and Emission of IR

Gaseous Aerosol
Precursors

SO_2,NO_x,HC,...

a
b

Absorption of Visible and IR

c

Aerosols

$SO_4^=$, Soot, Volc. Ash,...

a
b

Contribution to Tropospheric Aerosol

Absorption and Backscatter of
Visible Radiation

Absorption of IR (?)

Changes in Electric Conductivity

H Compounds

H_2,CH_4, HC,...

a
b

Absorption of IR (small)

Emission of IR

d   e

H_2O Vapor

a
b

Absorption of IR

Emission of IR (both up and down)

f   g

H_2O Clouds

(Ice)

a
b

Backscatter of Visible Radiation

Absorption and Emission of IR

Molecules Which
Interact With O_3:

NO, H_2O, CO,...

a
b

Absorption and Emission of IR (small?)

h   i

O_3

j

Absorption of UV
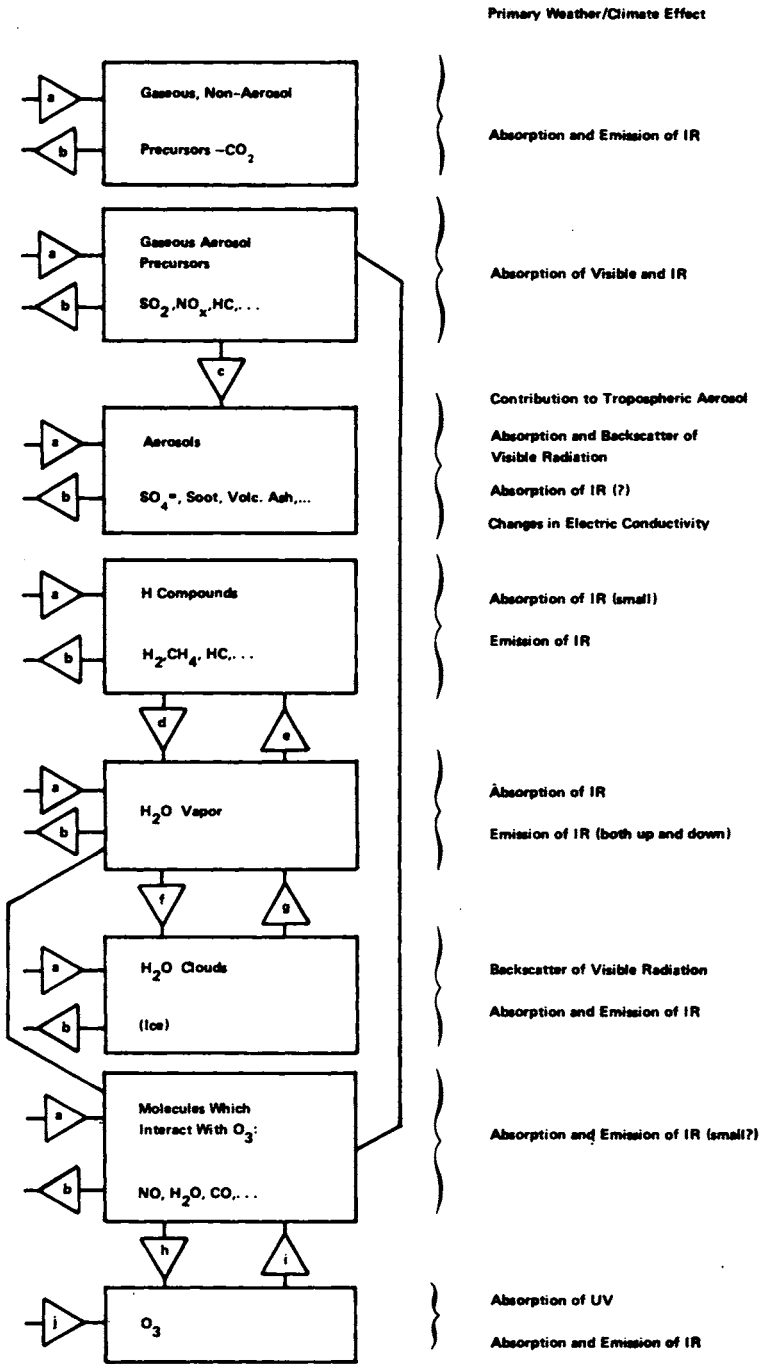
Absorption and Emission of IR

FIGURE H.2   The stratosphere as a chemical system. Symbols convey the same significance as in Figure H.1, with the following processes: a, Sources; b, sinks; c, gas-to-particle conversion; d, oxidation reactions; e, reduction reactions; f, nucleation and deposition of water; g, sublimation; h, ozone-producing reactions; i, ozone-consuming reactions; j, radiation. (From S. S. Butcher and R. J. Charlson, 1972: *Introduction to Air Chemistry*. By permission Academic Press, New York.)

few exceptions, consistent measurements have been over long periods of time. Exceptions are carbon dioxide and ozone, but more complete knowledge of the behavior in the atmosphere of even these substances is badly needed.

Research on atmospheric trace constituents up to about 1963 was reviewed by Junge (1963). More recently, Cadle (1966) has reviewed the subject of atmospheric particles; Rosen (1969), the subject of particles in the stratosphere; and Robinson and Robbins (1968), the sources, sinks, and concentrations of gaseous atmospheric pollutants. The conclusions and recommendations of the SCEP (1970) meeting included evaluations of the impact of global air pollution. Two technical volumes were published in late 1971. Reports on atmospheric chemistry by Cadle (1967, 1971) to the Fourteenth and Fifteenth General Assemblies of the International Union of Geodesy and Geophysics summarize some of the most recent research by U.S. scientists. Papers presented at the Visby, Sweden, Commission on Atmospheric Chemistry and Radioactivity (CACR) Symposium in 1965 and the Heidelberg, Germany, CACR Symposium in 1969, and published in *Tellus* (CACR, 1966) and the *Journal of Geophysical Research* (CACR, 1970), respectively, also describe much of the recent global trace constituent measurements.

IV. GLOBAL MONITORING

Needed research on global trace constituents includes

1.   A global network of atmospheric chemical monitoring stations. These are needed for at least two reasons. First, they can provide "benchmark" data to make it possible, by obtaining measurements over a number of years, to establish whether pollution of the atmosphere from human activities is increasing globally. Second, data obtained at such stations can provide information concerning natural as well as man-made sources and concentrations of minor atmospheric constituents.

Obviously, not every trace constituent that can be measured should be included. The substances to be measured should probably include (a) total particle concentrations, (b) concentrations of those gases and vapors in the atmosphere that react chemically to produce airborne particles, and (c) toxic substances for which the atmosphere provides a route. The stations should also measure atmospheric turbidity and should be provided with simple meteorological instrumentation. Of priority is the collection of rainfall and the measurement

of its trace constituents at each station (see Appendix G). Meteorological data should be taken at these sites.

2. Expeditions to determine the strengths of natural sources and sinks. Such expeditions can use more elaborate procedures and sophisticated techniques than are usually possible at a monitoring station. One of the most important uncertainties is the role of the oceans in supplying or removing trace atmospheric constituents.

3. Increased sampling with aircraft, balloons, and rockets. Useful as is information obtained near the earth's surface, it can be quite misleading unless supplemented by data obtained at greater altitudes. Our misunderstanding of stratospheric chemistry is largely dependent on *in situ* sampling and measurements. We know almost nothing about the nitrogen compound chemistry of this region, which may play an important role in determining the concentrations of stratospheric ozone. Also, more complete studies of the variations of the concentrations and composition of particles in the "sulfate layer" are needed to determine the role volcanoes play in the marked variations in concentrations with time that have been observed. The cooperative use of lidar and aircraft measurements is especially recommended. Such studies also will help in evaluating the impact of SST aircraft on the environment.

4. Research aimed at understanding the role of aerosols in the earth's radiation balance. Whether airborne particles increase or decrease temperatures at and near the earth's surface is not known, although we know that particles from volcanic eruptions have increased stratospheric temperature. Especially needed is a coordinated effort to measure simultaneously radiation fluxes both upward and downward at several altitudes, while collecting particles for chemical analysis and size distribution determination. From such experiments it should be possible to determine the relative importance of absorption and scattering of light by the particles.

This is only a part of what is needed to learn the effect of increasing global air pollution on the earth's climate. We must know the combined effects of pollution on radiation balance, condensation and freezing in clouds, precipitation, and general circulation. Eventually numerical models to show the interactions of these effects must be developed, but they will only be useful for prediction of climate when we have the necessary basic data.

5. The extent to which major metropolitan areas contribute to air pollution on a global scale. The most insidious air pollution on a local scale is almost certainly photochemical smog. It is produced in

tremendous quantities in all major cities, but almost nothing is known concerning the extent to which it contributes to regional and worldwide air pollution. In particular, the extent to which it is removed by chemical reactions in air and by interaction with plants and the soil before becoming widely dispersed is essentially unknown. To partially alleviate this uncertainty, a major coordinated sampling program is being conducted by the National Center for Atmospheric Research (NCAR) and Environmental Protection Agency (EPA) for St. Louis. However, based on the results of this first study, additional studies involving other cities will probably have to be made. Numerical models, including both meteorology and gas-phase chemical reactions, have already been developed to describe the concentrations of pollutants downwind of a couple of cities, but they are highly empirical, since they include large correction factors to make them agree with actual experience. Even so, they are not very satisfactory. An important result of the above studies could be the development of greatly improved methods for the numerical modeling of the fate of the air pollutants from cities.

6. The continued development of greatly improved analytical techniques for undertaking the various types of studies suggested. Several types of improvement are needed, but especially greater sensitivity and specificity. For example, no reliable method existed until recently for determining hydrogen sulfide in relatively unpolluted air. We cannot at present reliably measure sulfur dioxide in the high troposphere and in the stratosphere. Numerous other examples could be cited.

Very sophisticated but very elaborate and expensive analytical techniques are being developed to help fulfill this requirement. A recent example is the Fourier transform infrared spectrometer. There is also a need for simple inexpensive techniques that can be deployed at a large number of field sites and operated by nonprofessional personnel. Power requirements should be low so that they can be battery operated.

7. Laboratory studies of the chemical reactions that occur even in relatively uncontaminated air. Research of this type is being undertaken at a number of laboratories, but many important questions remain unanswered. Until the rate constants for many individual chemical reactions are firmly established, it will be difficult, if not impossible, to predict the impact of increased emissions of pollutants on our environment.

Appendix I
Evolution of Planetary Atmospheres
(Venus, Earth, Mars)

DONALD M. HUNTEN

I. INTRODUCTION

The sun and planets are generally thought to have formed at essentially the same time, 4.5×10^9 years ago, by condensation from a rotating mass of gas and dust—the solar nebula. (For a general discussion, see Jastrow and Cameron, 1963; for a recent model, Cameron, 1973.) The composition of the nebula should have been very like that of the sun. A planet made of this material would resemble Jupiter, with enormous amounts of hydrogen and helium and only a few percent (by mass) of heavier elements. In earth, Venus, and Mars the hydrogen and helium are almost entirely lacking. Loss of the two lightest elements frequently has been attributed to Jeans escape, but as Öpik (1963) has stressed, selective escape of planetary masses of light gas is most unlikely. Instead, one should expect an indiscriminate loss of all gases, or collection of only a little gas in the first place. Indeed, careful examination of earth shows that it lacks nearly all the noble gases by very large factors. (A clear discussion is given by Rasool, 1972.) The exception, ^{40}Ar, is accounted for by the decay of ^{40}K. The underabundances of the noble gases, by factors as large as 10^6, were demonstrated independently in 1949 by H. E. Suess and H. Brown. Brown (1952) concluded that "during the process of earth formation the mechanism was such as to prohibit the retention of an appreciable fraction of any substance that existed at that time in the gaseous state." Presumably the situation was similar for Venus and Mars. It is usually assumed (e.g., Cameron, 1973) that the original, or primary, atmospheres of the terrestrial planets were removed by an enormous solar wind just after the sun began to shine; the same wind is invoked to dissipate the

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remains of the solar nebula. Alternatively, one may suppose that the accretion process worked only for solids and liquids, and that there were no primary atmospheres. The germ of this idea is in the above quotation from Brown, and it has been used with great success recently by Lewis (1972). Presumably small amounts of gases would be trapped by the accreting material; thus, the earth would retain small amounts of CH_4 and NH_3.

The secondary atmospheres were presumably produced during radioactive heating, melting, and differentiation of the planets (cf. Rasool, 1972). A detailed discussion of the evidence is given by Rubey (1951). He concludes that H_2O and CO_2 have probably been released at a fairly uniform rate throughout the history of the earth. The CO_2 is recycled into the ground, mainly as carbonate rocks; the estimated amount would produce a partial pressure of 18 bars, if retained as a gas in the atmosphere. A more recent estimate (Ronov and Yaroshevskiy, 1967) is 72 bars. If only C and CH_4 were retained from the solar nebula, production of CO_2 requires the liberation of oxygen by the escape of H, as discussed below.

Most studies of atmospheric evolution do not take sufficient account of possible secular changes in atmospheric structure and solar input. The loss of hydrogen from the earth is a sensitive function of its particular thermal regime. Models of the sun agree that its output has risen by some 37 percent over geologic time (Sears, 1964; Ezer and Cameron, 1965; Torres-Peimbert *et al.*, 1969). The ultraviolet flux may have varied even more (or less); we have no way of predicting it at present.

II. THE PRESENT SITUATION

Table I.1 summarizes the available information on the atmospheres of the terrestrial planets. Most of it is taken from the recent review by Hunten (1971). The CO_2 abundances are similar for earth and Venus; the much smaller value for Mars suggests that only 0.04 percent of that planet is degassed (if earth is taken as the standard). Alternatively, there may be a great deal of CO_2 in permanent polar deposits. Water is strikingly scarce on Venus. The value given for Mars is the amount that has passed through the atmosphere, if Jeans escape of H has always proceeded at the present rate (Anderson and Hord, 1971; Hunten and McElroy, 1970). Again, possible permanent deposits have been omitted. With this important reservation, it appears that CO_2 and H_2O have been degassed from Mars and earth

TABLE I.1   Some Atmospheric Abundances for Planets[a]

	Earth	Venus	Mars
CO_2	72 kg cm^{-2}	90 kg cm^{-2}	15 g cm^{-2}
H_2O	270 kg cm^{-2}	200 g cm^{-2}	400 g cm^{-2}
N_2	780 g cm^{-2}	$<3 \text{ kg cm}^{-2}$	
O_2	239 g cm^{-2}	$<0.3 \text{ g cm}^{-2}$	7 mg cm^{-2}

[a]The CO_2 amount for earth and the H_2O amount for Mars are estimates of what has passed through in 4.7×10^9 years.

in essentially the same proportion. The O_2 entries for Mars and Venus are based on the results of Carleton and Traub (1972).

Liquid water is necessary if CO_2 is to be recycled back to the crust. The dominance of CO_2 on both Venus and Mars can thus be understood. It is much less clear why Venus should have so little water. Two possibilities stand out, and neither can be refuted at present:

1.   Venus and earth retained the same amount of water, but Venus lost most of it because of the proximity of the sun;

2.   Venus was formed in a warmer part of the solar nebula, where hydrated compounds were much less prevalent (Lewis, 1972).

Although 2 is entirely reasonable, a quantitive discussion is not available at present. Considerable attention has therefore been given to 1, and this work is summarized below.

III. ATMOSPHERIC EVOLUTION

As a secondary atmosphere is degassed from the body of a planet, several processes act to modify its composition. Here we shall concentrate on those that act on major constituents. Recycling of CO_2 back to the crust has already been mentioned. Next in importance may be photolysis of H_2O, followed by escape of hydrogen. We are no longer dealing with planetary masses; Öpik's objections therefore lose their force. CO_2 is a most unlikely compound to be retained from the solar nebula; the expected forms of carbon are C or CH_4. Part of the oxygen from H_2O is probably used in forming CO_2; the fate of the rest is discussed below. Enough solar radiation falls on

Venus to dissociate H_2O at the globally averaged rate of 5×10^{12} cm^{-2} sec^{-1} (McElroy and Hunten, 1969). In principle, this rate could remove 200 km of liquid water. The actual loss is much smaller, because the relevant solar radiation is absorbed by CO_2 and O_2. The rate therefore depends on the details of the mixing of water vapor to high levels and the opposing fallout of condensed phases. (On none of the terrestrial planets is the loss rate of H controlled at the escape level.) Another important detail is the effectiveness of CO_2 and O_2 as shields. For many years, following Urey (1959), it was thought that a very small amount of O_2 (about 10^{-3} of the present terrestrial amount) would give complete shielding, and therefore that H_2O photolysis could not produce more O_2 than this. Berkner and Marshall (1965, 1966) built a far-reaching model of the history of terrestrial oxygen on this base. But a careful examination by Brinkmann (1969) showed that the "Urey shield" is very leaky at longer wavelengths, 1800–2000 A. The absorption by H_2O is weak in this region, but the solar intensity is high, and these abundant photons will be absorbed by a long enough path. At the same time, McElroy and Hunten (1969) showed that shielding by CO_2 is equally poor (though their quantitative results need correction; see Hunten and McElroy, 1970). They also pointed out that the stratosphere of Venus is warm enough to hold a considerable amount of water. Thus, if water had been abundant at some time in the past, a very rapid loss of hydrogen could have occurred. At present the rate is very small; Walker et al. (1970) argue that the present degassing rate of H_2O on Venus must be similarly small and that if Venus ever had a large amount of water, it must have been degassed in a large, early burst. There is some reason to believe that a "runaway greenhouse" would operate with the solar flux incident on Venus (Ingersoll, 1969; Rasool and de Bergh, 1970; Pollack, 1971). Thus, a potential Venus ocean would be entirely evaporated into the atmosphere. Most recently, Smith and Gross (1972) have modeled a pure-H_2O atmosphere for Venus and found that it would indeed dissipate, perhaps so rapidly as to reach the Öpik blow-off state in which the oxygen would be carried away with the hydrogen.

For earth, Brinkmann (1969) finds a dissociation rate for H_2O of 1.6×10^9 cm^{-2} sec^{-1}. The escape rate of H is about 1×10^8 cm^{-2} sec^{-1} (Tinsley, 1971); thus, of the H atoms produced, only about 3 percent escape, and the rest are oxidized back to H_2O. Even so, 2.1 m of liquid water would be lost over the life of the earth, and 190 g

cm^{-2} of O_2 would be left, almost the amount now in the atmosphere. The loss rate is delicately controlled by a "cold trap" that keeps the H_2O content of the stratosphere at 5 ppm (by volume). Thus, loss rates in the past could have been much greater, if the structure and circulation of the atmosphere had been slightly different; a factor of 100 could readily be accommodated.

The photolysis of H_2O on Mars has been studied by Hunten and McElroy (1970). Again it is found that the escaping atoms are about 10 percent of those produced. The production rate is based on spectroscopic determinations of H_2O abundances, and the escape rate on Lyman-α data from Mariners 6 and 7 (Anderson and Hord, 1971). The O_2 produced should have been 350 g/cm^2; the observed amount would be produced in a mere 10^5 years.

O_2 is universally held to a product of photodissociation, but a decision has not been possible between the two possible mechanisms on the earth: escape of hydrogen or photosynthesis followed by burial of free carbon. Photosynthesis is far more popular, but the grounds for rejecting hydrogen escape are very insecure, as we have seen. A major uncertainty is the strength of the sinks for O_2. A budget has been given by Holland (1962). Oxidation of ferrous iron, sulfur, and CO accounts for 1 kg/cm^2; if conversion of C to CO were added, the figure would increase by 20 percent. Holland also includes oxidation of H_2, which is observed in volcanic gases; it could raise the figure by a factor of 3-4. But if the earth accreted out of condensed materials, the hydrogen would already have been in the form of ice. Another figure, which is an extreme upper limit, has been given by Berkner and Marshall (1965); oxidation of the entire crust to a depth of 17.5 km could consume 1350 kg/cm^2. Holland's value of 1 kg/cm^2 will be adopted here; it is a factor of 5 larger than the source estimated above, on the basis of the present escape rate of H. An increased rate in the past could easily meet the requirement and leave enough free O_2 for the present atmosphere.

Photosynthesis is well known to have ample capacity to produce the required O_2. Indeed, the proposal of Berkner and Marshall (1965, 1966) is that successive steps in evolution of life were intimately linked to successive increments in atmospheric oxygen. The idea is very attractive (Cloud, 1968); although one of its bases, the Urey self-regulation mechanism, can no longer be accepted, the picture could still be generally correct. If the carbon were originally free or combined as CH_4, the O_2 would be originally from H_2O,

even if its proximate source were CO_2 through photosynthesis. The delay in the appearance of free O_2 would correspond simply to the time required to oxidize the CH_4. Alternatively, the picture of an early atmosphere nearly devoid of oxygen could be in error (National Academy of Sciences, 1965, especially the paper by C. F. Davidson).

Oparin (1938) and Urey (1952), followed by many others, have argued that the origin of life requires a reducing atmosphere, preferably with considerable methane. Nitrogen would be present as NH_3. The loss of hydrogen needed to reach the present state is a little greater than already suggested, but the requirement is still not excessive.

The hydrogen escape flux from Mars is nearly twice that from the earth, and the O_2 production rates are presumably in the same ratio. Clearly, oxygen must be removed as fast as it is produced. Reaction with surface materials is inhibited by the lack of liquid water and the probable slow rate of exposure of fresh material. An alternative suggestion (McElroy, 1972) is attractive. It is thought that the dominant ion in the upper atmosphere is O_2^+. Recombination of O_2^+ yields enough kinetic energy to permit escape of one of the O atoms. An estimate of the escape rate gives almost exact balance with the rate for H inferred from Mariner data. McElroy argues that a feedback mechanism may exist to enforce this equality. The process does not work for earth or Venus because their escape energies are much greater. Earlier, Brinkmann (1971) proposed a different non-thermal mechanism for loss of Martian N_2; numerically it is much less secure.

If Mars is in an early stage of degassing, it might be expected to be producing CH_4 rather than CO_2. Methane should be rapidly oxidized by OH, which is present as part of the photolytic cycle of H_2O. According to the following comparison, the supply of oxygen is ample. The amount of CO_2 now in the atmosphere requires a mean degassing rate of 1.4×10^6 carbon atoms cm^{-2} sec^{-1}. The hydrogen escape rate implies a water degassing rate of 9×10^7 cm^{-2} sec^{-1}, which would be reduced by about 5 percent if some of the H were coming from CH_4. H_2O is thus in excess by a factor of 16 and can readily provide the oxygen needed to make CO_2.

If oxygen is present at all on Venus, its mixing ratio is much less than on Mars. The escape rate of H is uncertain (cf. Walker *et al.*, 1970) but is probably much smaller. Even this amount may be produced from HCl, rather than H_2O (Prinn, 1971). Chlorine may act as a catalyst to carry hydrogen from the surface or lower atmosphere

to the regions where HC1 is photodissociated. The surface of Venus is so hot, and conditions below it are so uncertain, that one may readily imagine it absorbing vast amounts of oxygen.

On all three planets, the atmospheric O_2 seems to be set by differences between huge production and loss processes. Large fluctuations are to be expected, and the apparent stability of terrestrial O_2 may require a special explanation.

CO_2 also is subject to photolysis, but it seems that rapid mechanisms must operate on both Mars and Venus to recombine the resulting CO and O_2. Details are not clear, but there has been considerable recent discussion (Aeronomy of CO_2 Atmospheres, 1971). Prinn (1971) has suggested that C1 from the photolysis of HC1 may catalyze the process on Venus. For Mars, it appears that H_2O_2, a by-product of H_2O photochemistry, may be the key; its photolysis produced OH, which rapidly oxidizes CO (Parkinson and Hunten, 1972).

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