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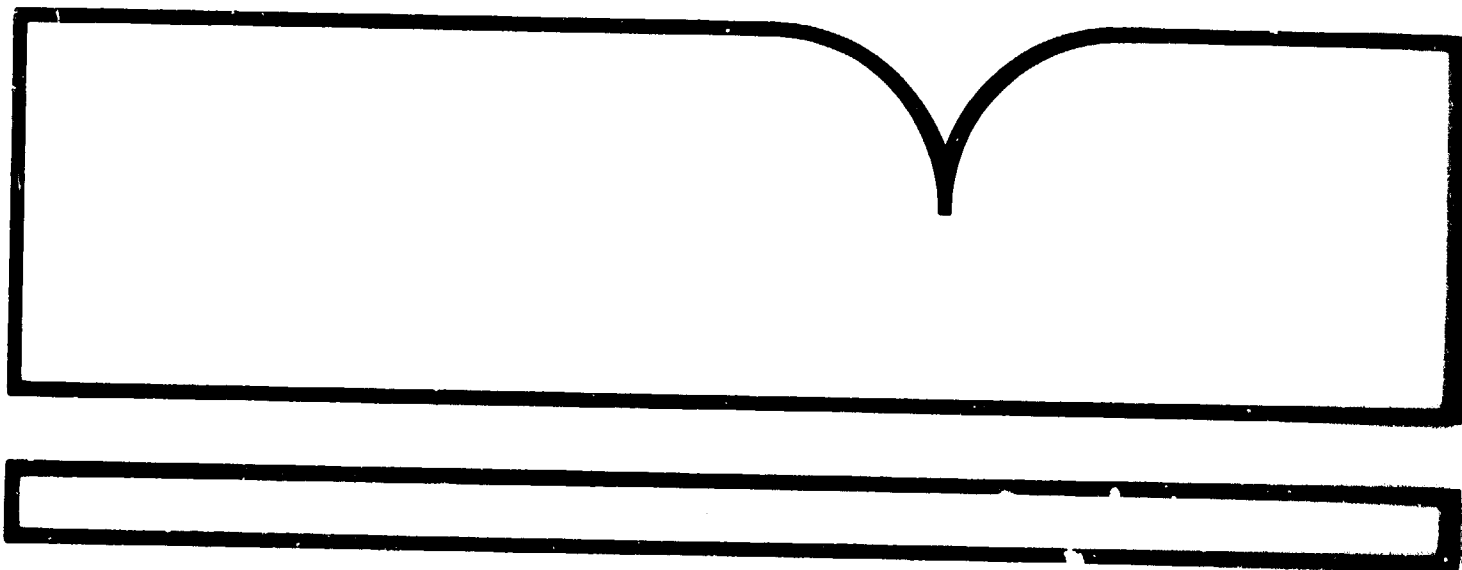
Global Tropospheric Chemistry
Chemical Fluxes in the Global Atmosphere

National Center for Atmospheric Research, Boulder, CO

Prepared for:

National Science Foundation, Washington, DC

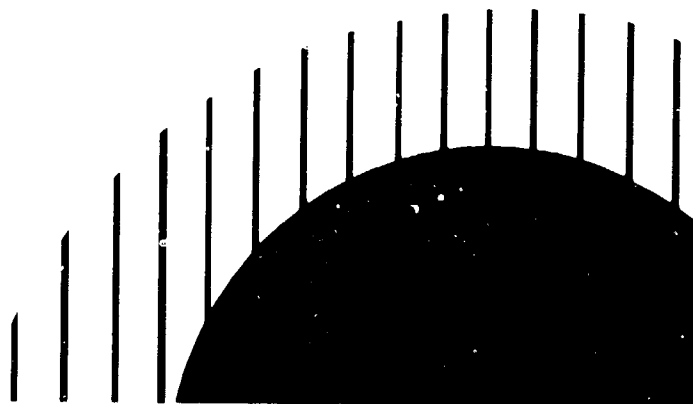
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CHEMICAL FLUXES IN THE GLOBAL ATMOSPHERE



May 1989

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Global Tropospheric Chemistry

CHEMICAL FLUXES IN THE
GLOBAL ATMOSPHERE

Report of the Workshop on Measurements of
Surface Exchange and Flux Divergence of
Chemical Species in the Global Atmosphere

Prepared by the
National Center for Atmospheric Research
P.O. Box 3000, Boulder, Colorado 80307

for

the National Science Foundation,
the National Aeronautics and Space Administration,
and the National Oceanic and Atmospheric Administration

Edited by
Donald H. Lenschow and Bruce B. Hicks

May 1989

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The opinions, findings, conclusions, and recommendations expressed in this workshop report represent those of the authors and workshop participants, and do not necessarily reflect the views of the National Science Foundation, the National Oceanic and Atmospheric Administration, or the National Aeronautics and Space Administration. NCAR is operated by the University Corporation for Atmospheric Research and is sponsored by the National Science Foundation.

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PREFACE

The looming possibility of major changes in the earth's climate system as a direct consequence of increasing concentrations of atmospheric gases has attracted intense interest in both atmospheric science journals and the general press. This "greenhouse gas effect" has joined acid rain and ozone depletion on the list of well-known environmental impacts that can arise from human activities and changing natural conditions, and that may affect the earth on a global scale. Understanding these impacts and their underlying causes well enough to develop effective national and international policies to mitigate and/or to cope with them is one of the major challenges facing the people of the world in the 1990s.

The National Academy of Sciences has recommended a major national program of research under the leadership of NSF, NASA, and NOAA, which have ongoing programs in global tropospheric chemistry, as an essential step in meeting that challenge. One of the most important elements of that program must be the study of the interaction between the atmosphere and the surface of the planet. It is there that gases and particles are introduced into the atmosphere and, usually after chemical transformation, removed from it. Measuring the fluxes of material across the air-surface interface and understanding the myriad processes that give rise to those fluxes is a central problem in atmospheric chemistry.

In October 1987, NSF, NASA, and NOAA jointly sponsored a workshop at Columbia University to assess the experimental tools and analysis procedures in use and under development to measure and understand gas and particle fluxes across this critical air-surface boundary. This report, *Global Tropospheric Chemistry: Chemical Fluxes in the Global Atmosphere*, presents the results of that workshop. It is published to summarize our present understanding of the various measurement techniques that are available, identify promising new technological developments for improved measurements, and stimulate thinking about this important measurement challenge.

The Center for the Study of Global Habitability at Columbia University and the Goddard Institute for Space Studies were local hosts for the workshop. We wish to thank them for their excellent arrangements. We wish also to thank the many scientists who participated in the workshop and contributed their expertise to the preparation of this report. The report was edited by Donald Lenschow and Bruce Hicks, who deserve special thanks for their extensive, careful, and patient efforts in bringing the report together.

Robert J. McNeal
Manager
Tropospheric Chemistry Program
National Aeronautics and Space Administration

Jarvis Moyers
Program Director for Atmospheric Chemistry
National Science Foundation

Vernon E. Derr
Director
Environmental Research Laboratories
National Oceanic and Atmospheric Administration

ORGANIZATION OF WORKSHOP

CHEMICAL SPECIES WORKING GROUPS

Ozone and Odd Nitrogen Working Group

F. L. Fehsenfeld (chairman)

S. M. Anderson

A. C. Delany

O. T. Denmead

C. W. Fairall

G. K. Greenhut

G. L. Gregory

B. J. Huebert

S. L. Liu

J. A. Logan

R. Pearson, Jr.

M. J. Prather

B. A. Ridley

J. A. Ritter

M. O. Rodgers

D. H. Stedman

M. L. Wesely

Sulfur Working Group

C. E. Kolb (chairman)

M. O. Andreae

D. D. Baldocchi

P. D. Goldan

G. E. Taylor

R. G. Zika

Methane, NMHC, CO, and Tracers Working Group

L. P. Steele (chairman)

J. A. Businger

R. L. Desjardins

C. Farmer

D. R. Fitzjarrald

I. Fung

R. C. Harriss

C. S. Martens

G. W. Sachse

W. Shaw

A. M. Thompson

H. Westberg

S. C. Wofsy

FLUX TECHNIQUE WORKING GROUPS

Tower Micrometeorology Working Group

M. L. Wesely (chairman)
J. A. Businger
D. D. Baldocchi

A. C. Delany
D. R. Fitzjarrald
B. J. Huebert

Enclosure Working Group

O. T. Denmead (chairman)

P. D. Goldan
R. C. Harriss

Airplane Flux Measurements Working Group

C. W. Fairall (chairman)

R. L. Desjardins
G. K. Greenhut
J. A. Ritter
W. Shaw

Invited Presentations

M. O. Andreae — Sulfur species
O. T. Denmead — Enclosure techniques
D. R. Fitzjarrald and R. C. Harriss
— Results from ABLE-2B
D. H. Lenschow — Airplane techniques

S. C. Liu — Ozone
J. A. Logan — Nitrogen species
C. S. Martens — Hydrocarbons and tracers
M. L. Wesely — Tower techniques

EXECUTIVE SUMMARY

Great strides have been taken in recent years in developing technology for measuring concentrations of trace chemical species in the atmosphere, for investigating the role that various species play in the chemistry of the atmosphere, and for monitoring trends in atmospheric concentrations. Measurement of trends is well recognized to be important not only for understanding how the quality of our atmosphere is changing but also for predicting climate. We now have a broad general understanding of the links that many species have to other species within the separate families of chemical species: the nitrogen and ozone group, the sulfur group, and the carbon group. Yet, to be able to model and predict the chemical behavior of the atmosphere, we need to have a much better understanding of how and where the species are generated and lost and how they are transported and mixed. Indeed, the study of atmospheric chemistry is the study of sources, sinks, transformations, and transports of trace reactive chemical species in the atmosphere.

We cannot, therefore, escape the necessity of looking into the details of the processes involved in surface exchange of trace species and their subsequent transport and mixing throughout the troposphere. The flow patterns that are involved are complex and multiscale. In the boundary layer, which is the layer of the atmosphere that interacts with the surface on a time scale of a few hours or less, the motions are so chaotic that we call it turbulence and deal with its effects statistically. Adding chemical reactions to this already complex behavior means that many observational and modeling approaches are intractable. Fortunately, there are techniques for measuring these exchange and mixing processes that have proven useful, particularly near the earth's surface.

Studies that have been conducted so far have been able to address only a limited number of species in a limited set of circumstances. At present, most is known about exchange over land of those few trace species that can be measured with ease at trace levels (often in mixing ratio concentrations of less than 10^{-9}).

A specialists' workshop was conducted in New York City, in October 1987, to review air-surface exchange and flux measurement of trace species in light of what we know about their distributions and reaction rates, to develop plans for observational studies making use of recent technological advances in both chemistry

and micrometeorology, and to delineate areas of technological development that should be pursued.

The workshop brought together representatives from many different disciplines, from instrumentation specialists to numerical modelers, with interests ranging from the pristine atmosphere to regions affected by air pollution. The success of the workshop itself underlines the major conclusion that was drawn:

The problems confronting the prediction of changes in global air chemistry and related climate change are necessarily multidisciplinary and must be addressed by teams of researchers from many specialties.

Related to this is the need to consider the wide range of exchanges that occur, because of both differences in surfaces and differences in atmospheric structure. Therefore, workshop participants concluded that:

A continuing series of field experiments is needed, to span the spectrum of chemical exchanges and interactions that occur throughout the biosphere and which impact the troposphere.

Field studies cannot be conducted to address all surfaces and all exchange processes—only a subset of representative examples is possible. Accordingly, we concluded that:

Models are required to interpolate among existing results, to extrapolate to situations that have not yet been studied experimentally, and to incorporate the appropriate parameterizations. The models should then be verified with subsequent observational studies.

The most direct technique for measuring a vertical flux, which is the rate at which trace species are transported through a specified reference level per unit area, is by eddy correlation—computing the average of the instantaneous product of vertical velocity and fluctuations in concentration of a trace constituent. At this time, this is the only fundamentally direct technique for flux measurement that is in wide use and can measure changes of flux with height. The main disadvantage of eddy-correlation measurement is its difficulty, it requires fast-responding and sensitive detection of trace species, and concurrent measurements of vertical velocity. To date, it is

possible to measure eddy-correlation fluxes of only a few species e.g., O₃, NO, NO₂, CO, and CH₄. The results obtained from these measurements point to the desirability of developing this capability for more species. We therefore recommend the following:

1. *A major limitation to research on surface exchange and flux measurements is the lack of sensitive, reliable, and fast-response chemical species sensors that can be used for eddy-correlation flux measurement. Therefore, we recommend that continued effort and resources be expended in developing chemical species sensors with the responsiveness and sensitivity required for direct eddy-correlation flux measurements.*

Candidate species for continued effort include SO₂, H₂O₂, and nonmethane hydrocarbons. At the same time, all of the existing instruments for species flux measurement by eddy correlation are not without weaknesses; continued improvements in all the existing sensors, as well as existing water vapor sensors, would be valuable. In particular, sensors that measure mixing ratio with respect to dry air obviate the need for corrections to measured fluxes due to mass flux and, on aircraft, flow distortion.

Although eddy correlation is the most fundamental flux measuring technique, many times it is not feasible because of instrument limitations or lack of a proper experimental site, or because it is too expensive or sophisticated for particular applications. Therefore, other techniques also need to be developed and implemented. These include the gradient technique, which requires measurement of a concentration difference across a vertical displacement, and enclosure techniques, which require mean concentration measurements within an enclosure that acts as a reservoir for species emitted from or deposited to a surface covered by the enclosure. This means there is a requirement for accurate measurement of an absolute concentration or concentration difference that can be averaged over several minutes; fast response is not important. Therefore, we further recommend that:

2. *Continued development be pursued to obtain accurate mean concentration or concentration difference measurements, particularly for species for which no immediate possibility exists for eddy-correlation flux measurements.*

In contrast to enclosure methods, gradient and eddy-correlation methods do not interfere with the exchange at the surface; they measure the flux at some height above the surface, which may not, in some cases, be the same as the surface flux. Furthermore, flux measured above the surface may be affected by the characteristics of the surface, the mean wind, and the hydrodynamic stability. A major finding of the workshop was the importance of combining several

methods of flux measurement in intensive experimental programs; the variety of available methods is such that many different scientific questions can be addressed if an appropriate selection of methods is made from among the set of available techniques.

For some trace species, measurement techniques are already well advanced. Ozone is a notable example. Fast response sensors are already available to permit use of eddy-correlation methods (both on towers and aboard aircraft), and sensitivity is sufficient to resolve small vertical concentration differences, as is required for the application of tower gradient techniques. No other trace gas can yet be investigated with the confidence that is now attached to measurements of ozone and ozone fluxes; the existing set of ozone deposition data is large in comparison to that for all other trace reactive gases, yet even in this special case the available body of information consists largely of spot measurements of a few categories of surfaces, predominantly in the mid-latitudes. These include several agricultural surfaces, forests, rangeland, and ocean. The Atmospheric Boundary Layer Experiments (ABLE) have been successful in obtaining flux measurements of O₃, CH₄, CO, and NO₂ over the tropical rain forest and the Arctic tundra. These experiments have demonstrated the feasibility of carrying out intensive field investigations, utilizing several complementary measurement techniques for a suite of species, to obtain a more complete picture of the chemical behavior of particular biomes.

In recognition of the limited circumstances that have been investigated so far, we recommend that:

3. *Future experiments be planned for surfaces of importance to global budgets. These include tropical and boreal forests, tundra, taiga, agricultural croplands such as rice paddies that cover large areas, wintertime continental areas (snow covered), and especially the oceans. Experiments need to span both diurnal and seasonal cycles.*

Studies over the oceans should receive particular emphasis; even if average exchange rates are much lower than over land, the much greater surface area of the world's oceans raises them to prime importance. It is particularly important to obtain data from areas with differing biological productivity as a function of meteorological conditions and season. The primary platform for measurements over ocean is the aircraft. Existing aircraft measurements demonstrate that it is feasible to measure surface exchange by eddy correlation, but few data have thus far been obtained. Measurements over the tropical oceans and in high wind conditions are of particular importance.

It is clear that diurnal and seasonal changes are not sufficiently well understood even over more commonly studied surfaces. Carrying out studies to investigate these changes requires commitment to

development of facilities for surface flux measurements that can be deployed for extended periods. Moreover, comparisons between different sets of data are difficult, because of the common failure to report results in a manner that can be used in a surface-specific sense. We recommend, therefore, that:

4. *The results of surface exchange studies be reported, as much as possible, in ways that generalize the results for application to a wide range of meteorological conditions. For example, a useful way to specify deposition rates is by means of surface resistances. Furthermore, the state of surface vegetation should be reported whenever possible because of its strong effect on surface exchange.*

A critical step in the development of measurement capabilities, and in attaining confidence in the results, is to obtain agreement between concurrent measurements of a flux using independent techniques. This step not only provides assurance that different techniques provide valid results but also allows extension of flux measurements in time and space; for example, combining airplane and tower measurements permits vertical flux profiles from near the surface through the top of the boundary layer. The workshop gave a resounding endorsement of the continuing need for comparison studies and concluded that:

5. *Frequent comparison studies be carried out, especially in conjunction with field studies utilizing extensive micrometeorological capabilities.*

Although the workshop concluded that the highest short-term payoff in improved flux measuring capabilities lies in development of chemical sensors, participants also emphasized that there is need for further development of micrometeorological tools and techniques. Improved understanding of the physics of turbulent exchange is essential in the development and application of methods that might simplify flux measurement from moving platforms (e.g., ships and airplanes) and make flux measurements possible in situations that are currently not acceptable. Most field situations are far from perfect for flux measurement. Limiting flux measurement to "ideal" conditions is impractical and unnecessary. We need to measure over complex terrain and in situations of rapid time changes and large horizontal advective fluxes. Wavelengths of eddies responsible for vertical transport extend

over a broad range of scales. Further work on limitations in measurement accuracy and evaluations of measurement strategies is also needed when designing field programs and determining instrument specifications. Therefore we recommend that:

6. *Aerodynamic flux measuring methods must continue to be evaluated and extended to address situations of inhomogeneous land surfaces and routine measurement over the open ocean, provide guidance for instrument design and development, and determine limits of applicability for the different techniques. New flux measurement techniques need to be explored in light of new sensor technology and the requirements of the modeling community.*

The use of enclosures to investigate emissions from specific surfaces received intensive attention, with special scrutiny of the need for replication of measurements and for techniques that eliminate problems associated with imposed pressure differentials. We recommend that:

7. *Enclosure studies be conducted specifically to reveal details of the subsurface processes contributing to emissions.*

Finally, the ultimate goal of much of the effort in measuring surface exchange and vertical fluxes is to provide useful parameterizations for models of the atmosphere, from regional to global scales, and from several-hour forecasts to climate prediction. Therefore, we recommend that:

8. *Close interactions with the chemical, meteorological, and ecological modeling communities be included in all phases of field investigations, from the design of the experiment through the analysis of the data and presentation of the results. At the same time, modelers need to be aware of inherent limitations in spatial and temporal resolution of flux determinations in specifying their requirements for flux data.*

We hope that these conclusions and recommendations provide a framework to move forward in the development of new technologies for flux measurement, the design of field programs, the acquisition and use of flux data, and the application of field results to modeling studies.

INTRODUCTION

D. H. Lenschow and B. B. Hicks

The impact of man's activities on the global atmosphere is becoming increasingly evident. On local scales, the most noticeable changes are those associated with pollution released as a by-product of manufacturing, transportation, agriculture, residential heating, and other factors directly related to the modern way of life. Areas with high population density tend to be most affected by air pollution. But it is becoming increasingly evident that the health of the atmosphere is more than just a local problem; recent emphasis on the long-term consequences of continued emissions of chlorofluorocarbons and so-called greenhouse gases (including carbon dioxide) has awakened the public to the vulnerability of the climatic regimes that we know. On a global scale, many of the trace gases are likely to play an influential role in the climatic trends that are now being predicted.

The Global Tropospheric Chemistry Program (GTCP) grew out of these concerns. The program is in its infancy, but plans are already well advanced. The scope of GTCP is global, even though recent emphasis has been more on local and regional impacts of pollutants such as "acid rain." The initial report (from the National Research Council, 1984) on the need for a large-scale research effort on the chemistry of the troposphere was well received and spawned a second report on proposed plans for the U.S. research contribution (UCAR, 1986). Activities elsewhere have paralleled the U.S. efforts. In particular, both the European and U.S. plans call attention to the indisputable need for better understanding of chemical interactions in the atmosphere in order to identify causes of changes in the quality of the atmosphere that have now been detected and to predict future trends. We must identify and quantify the sources and sinks of important chemical species and determine how the related fluxes and concentration fields vary with time and height in the troposphere.

We are faced with the need to measure the chemical state of the troposphere and to extrapolate from available measurements in order to assess conditions at other locations and to predict changes that might occur. In general, measurements of air chemistry at remote locations call for high-quality instrumentation, often not yet adequately developed.

Extrapolation requires understanding the processes that determine the concentrations. The Global Tropospheric Chemistry Program emphasizes the need for better knowledge of exchange processes, especially in those biological and surface environments that constitute the sources and sinks of the chemical species of major interest. The relevant atmosphere-surface exchange environments vary from the tropical ocean (for chemical species such as dimethyl sulfide) to subarctic tundra (for many organic species such as methane). The range of environments is sufficient that considerable difficulties in measurement are imposed: dry and wet tropical land regions, agricultural regions, oceans, areas where vegetation is periodically burned, and subpolar land regions. Many chemical species must also be considered: CH_4 and other major hydrocarbons, CO and CO_2 , a variety of aldehydes and ketones, NO , NO_2 , and HNO_3 , organic nitrates, amines and acids, N_2O and NH_3 , dimethylsulfide and other sulfur species, (e.g., H_2S , SO_2 , OCS , and CS_2), O_3 , H_2O_2 , and a number of organoperoxy compounds and organohalogens.

Monitoring programs, whose main role is to keep track of changes as they happen, are already in place at a small number of carefully selected locations where high-quality data on key indicators of the state of the remote atmosphere are routinely measured. The data provided by these monitoring programs cannot be used to predict future situations with confidence; such unguided extrapolation of current trends is well known to be dangerous. Instead, an additional capability is required. We need to predict the concentrations of relevant chemical species in air, so that the consequences of uncontrolled chemical emissions and modifications of the biosphere, as well as the impacts of control strategies, can be assessed. These issues can be addressed with models that incorporate both meteorological and chemical processes. The need to develop and utilize these models underlies the need to improve our understanding of air-surface exchange of trace gases.

The atmosphere is normally near chemical steady-state, with input fluxes supplying trace chemicals at about the same rate as chemical reactions and surface sinks remove them. A change in any one of these

factors (reactions, input rates, and removal rates) will disrupt the existing balance. The trends that are now being observed correspond to such disruptions, caused largely by steadily changing emissions of the by-products of society into the atmosphere. Increased emissions will necessarily cause an increase in air concentrations, but estimation of the eventual steady-state level is far from simple. Any such computation must also take into account the appropriate rates of removal, due to chemical reactions in the air and the removal rates to the surface.

Most of what we know about atmosphere-surface interaction has resulted from studies involving conventional meteorological quantities—momentum, heat, and water vapor. Water vapor is of special interest as an analog for the exchange of other trace gases and because of its role (along with CO_2) in photosynthesis. The process known as transpiration involves biological tissue, stomatal openings, and turbulent exchange. Many trace gases exchange via the same pathways as CO_2 and water vapor, but others are surface-reactive and transfer efficiently to all available surfaces with which air comes in contact. Another set of trace gases is emitted from foliage as a by-product of evapotranspiration. Among such gases are reduced hydrocarbons (e.g., ethylene). Yet another set of trace gases derives from soils—nitrogen oxides, reduced sulfur species, etc. There is no general set of trace gases that is derived from all surfaces. Instead, different surfaces emit different sets of trace chemical species at different rates. These differences can sometimes be used as indicators of specific surface conditions; ethylene, for example, can be used as an indicator of plant water stress. Similarly, different surfaces have different deposition properties. A major question in global atmospheric chemistry concerns the quantification of the average fluxes of such trace species at the surface of the earth. It is clear that the exchange is highly variable both in space and in time. The answers that are needed relate to the total input to (and removal from) the global atmosphere. To obtain relevant data requires more than just a few experimental data points. In fact, a concerted and carefully orchestrated strategy is required.

The capability to measure atmosphere-surface exchange rates experimentally is limited. Chamber methods are useful to measure emission rates of some chemical species from soils and sometimes from vegetation. However, these methods are limited by their inability to measure deposition to the surface. The flux measured by chambers is thus the gross flux from the surface, not the net exchange between the surface and the air.

Micrometeorological methods (i.e., methods that measure flux in the air) measure the net exchange rather than the gross flux, as with chambers. Many different kinds of micrometeorological methods are available, ranging from methods requiring high reso-

lution in the measurement of species concentrations over half-hour averaging times to those with fractional-second response times and high signal-to-noise ratios. There is no single technique that can satisfy flux measurement needs for all trace gases in all situations, nor is there any flux-measuring capability yet in existence that will generate a long-term average for a large area. Furthermore, micrometeorological techniques have been developed for conserved variables; this is not the case for chemically reactive species.

Improved modeling capabilities need to be developed and tested on both regional and global scales for utilizing surface exchange measurements to predict species concentrations. This should be done in parallel with the development and deployment of improved flux-measurement techniques. Once proven acceptable, these models must then be used to assess the large-area, long-time averages of species concentrations that are required by global programs. The major goals of experimental programs must therefore be:

1. to identify those processes which must be included in the models,
2. to provide reference data sets to use in model development, and
3. to provide independent data sets for testing the models that are developed.

The overall strategy that results is to employ detailed experimental methods at carefully selected locations to develop models, which are then used to interpret information obtained using simpler methods at other locations and at other times. It is not the intent that complicated and expensive research methods be used directly to obtain the global averages that are sought, but instead that they provide a sound foundation for developing the tools by which the desired information can then be derived.

In general, there is more confidence in applying models to interpolate among existing data sets than in extrapolating beyond the bounds of existing understanding. Thus, the data sets generated to help develop process-related models of air-surface exchange should be obtained in a wide variety of conditions, spanning the range of situations that the models are required to address. Individual studies should be designed to demonstrate which processes are most important and then to yield formulations of those processes. Once developed, these detailed process models must be tested; independent sets of field observations obtained in new experimental situations must be used to quantify uncertainties and limitations in the general applicability of the tools that are developed. The models also play an important role in evaluating the sensitivity of concentrations to changes in the inputs and thus in determining the most relevant variables and sets of species to be studied.

In general, the process models that are developed are designed to derive flux information from relatively simple data obtained at places where direct flux measurements are not feasible. The driving information is usually concentration data, for the air and for the surface (or subsurface), together with sufficient additional information to quantify the rate of exchange between the surface and the atmosphere. At sea, for example, the "tool" that is needed is a flux relationship between the atmosphere and the surface in terms of concentrations in air, concentrations in water, and atmospheric and oceanic conditions that influence the diffusion in each medium and across the boundary between them. In the present context, the focus is on exchange through the atmosphere, with measurement techniques limited to those that are applied above the surface. Other measurement methods are feasible, in some circumstances, but are not addressed here. For the oceans, fluxes through the water below the surface may sometimes be measured more easily than through the air above it. Similar relations will then apply, using concepts that parallel the lines of this document. Relationships that involve both above-surface and below-surface concentrations necessarily involve the Henry's Law constant, applied to concentrations in the medium corresponding to the measurements or to the location of the controlling processes.

Workshop Details

The workshop summarized here focused on the need for detailed air-surface exchange information, as is required to develop and test exchange process models. The methods by which routine data can be used by those models to assess global averages of air-surface exchange were not discussed. This workshop focused on three sets of techniques: tower micrometeorological methods, aircraft techniques, and the use of chambers. Most attention was paid to the availability of trace chemical detection methods by which flux measurements could be made. No attention was given to several techniques that have been well surveyed elsewhere. In particular, the special case of dry deposition from polluted atmospheres has been addressed extensively in other recent workshops, of which proceedings summaries are now available. In consequence, the present document concentrates on surface fluxes at remote locations. More specifically, the workshop was designed to answer four questions:

1. How can we best address the goals specified in the Global Tropospheric Chemistry Program plans?
2. How should an optimal experimental program be structured?
3. What new experimental capabilities are now available for exploitation?

4. What especially promising techniques are best suited for exploratory investigation at this time?

The specific goals were to explore ways in which recent technological developments might be of assistance, to identify especially promising methods currently being developed or considered, and to suggest field programs optimally designed to capitalize upon these new developments. Experts from the atmospheric chemistry community (including those interested in both polluted and pristine atmospheres) joined with experts on relevant surface exchange and atmospheric transport mechanisms to categorize and clarify problems of flux measurement of trace chemical species. Discussion focused on those chemical species for which fluxes can be measured by available techniques and on those circumstances for which improvements could be anticipated in the near future. Discussion mainly concerned exchange between the atmosphere and the surface and flux divergence within the planetary boundary layer, although measurements at higher levels in the atmosphere were also discussed when techniques used for measurements in the boundary layer seemed suitable for this purpose.

The workshop took place from 19 to 23 October 1987 in New York, New York, on the campus of Columbia University. An appendix identifies the participants. Their membership on several working groups was arranged to concentrate attention on ozone and odd nitrogen species (F. C. Fehsenfeld, chairman); sulfur species (C. E. Kolb, chairman); and methane, nonmethane hydrocarbons, carbon monoxide, and tracer materials (P. Steele, chairman). Consideration of specific measurement methods was divided among enclosure techniques (O. T. Denmead, chairman); tower methods (M. L. Wesely, chairman); and aircraft methods (C. W. Fairall, chairman).

The following chapters of this document will present the results of the workshop deliberations.

1. Key Aspects of Species Related to Global Biogeochemical Cycles.

The concentrations and fluxes of chemical species important in the context of biogeochemical cycles: ozone and odd nitrogen, sulfur, methane, nonmethane hydrocarbons, and carbon monoxide.

2. Flux Measurement Techniques.

Advantages and shortcomings of enclosure techniques, towers, and aircraft.

3. Status of Chemical Sensors for Flux Measurement.

Sensors with long averaging times, as required for measurements involving enclosures and gradients, and sensors with rapid response as required for eddy correlation and variance methods.

4. Flux Measurement Program Plan.

Specific program plans designed to make optimal use of existing capabilities.

5. New Opportunities for Flux Measurement.

Key difficulties and challenges in the use of measurement techniques as well as needs and

opportunities related to the development of new sensors and new experimental approaches.

The success of the workshop and this report will depend on how correct we are in our assessments, how well we have foreseen the emerging needs in studying the chemical behavior of the atmosphere, and how fluently we have expressed our conclusions.

1 KEY ASPECTS OF SPECIES RELATED TO GLOBAL BIOGEOCHEMICAL CYCLES

M. Andreae, A. C. Delany, S. Liu, J. Logan, L. P. Steele, H. Westberg, and R. Zika

The important roles played by various trace species in global biogeochemical cycles have been discussed in *Global Tropospheric Chemistry: Plans for the U.S. Research Effort* (UCAR, 1986). In this chapter, we will limit discussion to the surface exchange and flux divergence of the key trace species, and related research needs. The species included are classified into three major groups—the oxidant and odd nitrogen group, the sulfur group, and the carbon group. Critical studies for each group will be identified and discussed. We note, however, that many of the studies are related to each other; therefore, carrying out concurrent studies addressing several species at the same time offers considerable attraction.

The surface exchange rate of a chemical species is usually a function of surface properties such as the kind and condition of vegetation, nutrient level, temperature, and moisture. Since measurements of surface exchange rates are limited in their temporal and spatial coverage, extrapolation to other locations and times is usually needed. Detailed understanding of how exchange rates depend on prevailing environmental conditions will greatly facilitate this extrapolation. The ultimate goal of studying surface exchange is to understand the basic biogeochemical mechanisms that control the exchange processes. A full discussion of these issues, however, is beyond the scope of this work. In the following discussions, the emphasis will be on the phenomenological aspects of surface exchange.

Discussion of the behavior of different chemical species in the troposphere necessarily involves consideration of both chemical and physical aspects of the air-surface system, and sometimes biological factors as well. The discussion will use commonly accepted descriptions of different parts of the atmosphere. The air in closest contact with the surface forms a constant flux layer, called the surface layer, some tens of meters thick, in which there is little flux divergence. This constant flux layer is the lowest part (less than about 10%) of the planetary boundary layer (PBL), which is typically 1 to 2 km deep in daytime, 100 to 500 m deep

at night over land, and 500 m to 1 km deep over the ocean. The PBL is that part of the lower troposphere that responds to changes at the earth's surface within a few hours and consequently over land exhibits a pronounced diurnal cycle of vertical mixing. During the daytime, convection causes strong mixing, and the PBL is often called the convective boundary layer (CBL). At night, vertical mixing is relatively weak, shallow, and intermittent, and the PBL is often called the nocturnal boundary layer (NBL). The structures of these various layers vary with terrain, latitude, seasons, etc., in ways that complicate the overall behavior of trace species and inject a strong meteorological component into any description of species concentrations, as well as of the change of species fluxes with height, called flux divergence.

Flux divergence plays a crucial role in studying the budgets and distribution of many trace chemical species. For example, flux divergences of species like NO_x and O_3 , whose concentrations can differ greatly between the boundary layer and the free troposphere, need to be estimated in order to evaluate their budgets. For the most part, however, flux divergence measurements will not be discussed in great detail since the techniques for measuring flux by eddy correlation apply equally well to multiple levels, as required for flux divergence estimates, and to a single level as required for measuring surface exchange. Other than eddy correlation, flux measuring techniques that can be used for estimating surface exchange are, in general, not applicable for measuring flux divergence.

Oxidant and Odd Nitrogen Group

The nonradical oxidants O_3 and H_2O_2 and the family of odd nitrogen compounds, including NO , NO_2 , NO_3 , N_2O_5 , HNO_3 , HNO_2 , PAN, and NH_3 , play a key and closely interconnected role in the oxidative state of the atmosphere. Because the chemistry of these species is so closely interrelated, it is convenient to consider them together as a family.

Table 1.1
Estimated Photochemical Lifetimes (in Summer)
of O₃, H₂O₂, NH₃, and NO_y

LIFETIME	REGION		
	(1) Tropical marine boundary layer	(2) Rural continental boundary layer	(3) Upper troposphere
Greater than 1 day	O ₃ , H ₂ O ₂ , HNO ₃ , NH ₃	Same as (1)	Same as (1) plus PAN, N ₂ O ₅ , other organic nitrates, NH ₃
1 hour to 1 day	NO _x , NO ₃ , some organic nitrates	Same as (1)	Same as (1) plus NO ₃ , N ₂ O ₅ , NO ₂
10 min. to to 1 hour	PAN, some organic nitrates, HNO ₂ *	Same as (1)	None
less than 10 min.	NO, NO ₂ *, and NO ₃ *	Same as (1)	Same as (1)

*During the daytime

Table 1.2
Estimated Lifetimes of O₃, H₂O₂, NH₃, and NO_y for Incorporation into
Cloud Water and/or Aerosols

LIFETIME	REGION		
	(1) Tropical marine boundary layer	(2) Rural continental boundary layer	(3) Upper troposphere
Greater than 1 day	PAN, NO _x , O ₃ , organic nitrates	Same as (1)	Same as (1) plus H ₂ O ₂ , HNO ₄ , N ₂ O ₅ , NO ₃ , HNO ₃ , and NH ₃
1 hour to 1 day	None	H ₂ O ₂ , N ₂ O ₅ , NO ₃ , HNO ₂ , HNO ₃ , NH ₃	None
10 min. to to 1 hour	H ₂ O ₂ , N ₂ O ₅ , NO ₃ , HNO ₂ , HNO ₃ , NH ₃	None	None
less than 10 min.	None	None	None

The major precursors of ozone can be divided into two groups: NO_x (i.e., $\text{NO} + \text{NO}_2$), and hydrocarbons and CO. Since CO and CH_4 are readily available in the troposphere, NO_x usually is the rate-limiting ozone precursor. The distribution of NO_x is very inhomogeneous (see Fehsenfeld et al., 1988), as expected from its short photochemical lifetime and highly localized sources. As a result, the ozone production rate should be a very strong function of location.

Table 1.1 gives a list of photochemical lifetimes of ozone, H_2O_2 , NO_y species, and NH_3 , while Table 1.2 gives the estimated lifetime for the loss of these compounds by incorporation into cloud water and aerosols. The lifetimes of these species range from less than ten minutes to more than a day. Therefore, their distributions and exchange fluxes depend on transport processes of various time scales.

We need to consider here not only surface exchanges but also exchanges between the boundary layer and the free atmosphere; except for a few highly reactive species that originate from surface emissions, boundary layer concentrations of trace chemical species are determined by both interaction with the surface and entrainment of air from the free atmosphere. This is particularly true in studying the global distributions and budgets of O_3 , H_2O_2 , NO_y species, and NH_3 .

Exchange of boundary layer air with the free atmosphere takes place through a variety of mechanisms. On a large (vertical) scale, convective clouds can transport boundary layer air up to near the top of the troposphere within a few minutes and can also bring air from the free atmosphere down to the surface in evaporation-driven downdrafts. On a small scale, both shear and convection can generate turbulence to overcome the static stability of the free atmosphere and cause entrainment of air into the boundary layer.

Since the chemical lifetimes of H_2O_2 , NO_x , and NH_3 are less than or comparable to the residence time of air in the boundary layer, the amount of these species exchanged between the boundary layer and the free troposphere may be considerably less than the amount introduced into the PBL. In addition, chemical processing in the PBL serves to convert NO_x to a variety of other NO_y species. Thus, both theoretical and experimental studies should be made to assess this exchange for O_3 , NO_y , and NH_3 .

A complication for measuring the emission or deposition flux for species such as NH_3 , NO_x , and amines (Farquhar et al., 1983), and perhaps also for other gases, is that a compensation point exists, a non-zero gas concentration in the leaf air spaces, which is in equilibrium with metabolites in plant cells. If the ambient concentration exceeds the compensation point, the gas is taken up by the plant from the atmosphere, but if the ambient concentration is less than the compensation point, the gas is emitted to the atmosphere. If enclosure techniques (see Chapter 2)

are used to estimate the flux of such chemical species, a correct estimate of the gas flux depends on maintaining gas concentrations in the air within the enclosure very close to ambient. "Closed" enclosure systems are thus unsuitable, and "open" systems will require large ventilation rates, so that leaf boundary layer resistances will be much smaller than stomatal resistances.

Emission rates of N_2O are relatively small compared to those of NH_3 and NO_x (Keller et al., 1986). Natural sources are likely to be the primary contributor, although there is probably some anthropogenic contribution. The only known N_2O sinks are in the stratosphere; surface deposition of N_2O is negligible.

Sources of NO_x , O_3 , and H_2O_2

Table 1.3 lists the important sources and sinks of NO_x . Most of the sources are on land and near the surface. Anthropogenic sources appear more important than natural sources, especially in winter, when there are fewer natural sources. Emissions of NO_x are primarily in the form of NO. Once emitted, NO is oxidized quickly to a mixture of NO and NO_2 in photochemical equilibrium, and then to other reactive nitrogen species, such as HNO_3 , PAN, NO_3 , and N_2O_5 . As pointed out by Lenschow and Delany (1987), the rapid photochemical reactions involving NO, NO_2 , and O_3 have a considerable impact on their flux and concentration profiles in the surface layer. Figure 1.1 shows a simplified reaction scheme of nitrogen species; a discussion of these reactions and time constants can be found in Logan (1983).

The emission rate of NO_x from soils has been measured primarily by the enclosure technique, as discussed by Galbally (1985) and as summarized in a recent report of the World Meteorological Organization (WMO, 1986; see Chapter 3). Results are summarized in Table 1.4, updated from the WMO report.

Recent comparisons of the enclosure technique and a local budget technique indicate that the methods give similar results (Parrish et al., 1987; Kaplan et al., 1988). The budget technique relies on the fact that at night the reaction of NO with O_3 is the dominant removal process for NO and that atmospheric reactions reforming NO from NO_2 are negligible. Hence, the net flux of NO from the soil must balance the total column loss of NO by reaction with O_3 , which may be calculated from vertical profiles of NO and O_3 at night. At least one study of soil emissions has employed the eddy-correlation technique (Delany et al., 1986).

The majority of NO flux measurements have been at mid-latitudes. As discussed in Chapter 3, emission rates measured with enclosures are highly variable, averaging about $1-2 \times 10^{-12} \text{ kg N m}^{-2}\text{s}^{-1}$ at mid-latitudes, while the few studies in the tropics give values of $8-11 \times 10^{-12} \text{ kg N m}^{-2}\text{s}^{-1}$, at least for dry soils.

Table 1.4
Measurements of NO Emissions from Soils

Surface Type	Flux $\text{kg N m}^{-2} \text{s}^{-1} \times 10^{12}$	References	Surface Type	Flux $\text{kg N m}^{-2} \text{s}^{-1} \times 10^{13}$	References
Ungrazed pasture (average)	1.6	Galbally and Roy, 1978	Terra firma forest, Brazil (mean: enclosure)	10.2	Kaplan et al., 1988
Grazed pasture (average)	3.5		(mean: vertical gradient)	12.6	
Grazed pasture (range)	-50	Galbally and Roy, 1981	(range)	9.2 to 16	
Fertilized grass (weighted annual average)	1.9	Johansson and Granat, 1984	Burned semiarid chaparral, California (mean) (range)	31 ^a 6 to 101 ^a	Anderson et al., 1988
Unfertilized barley (weighted annual average)	0.6	Johansson and Granat, 1984	Unburned semiarid chaparral, California (mean) (range)	13 ^a 0 to 35 ^a	Anderson et al., 1988
Cropland (range)	0.1 to 62		Fertilized corn, 5-30 day average ^b , Virginia (mean) (range)	25 6 to 67	Anderson and Levine, 1987
Unfertilized forest soil (median) (range)	0.3 0.1 to 0.8	Johansson, 1984	Soy, fertilized 3 months prior to study, summer average, Virginia (mean)	0.7 to 9.4	Anderson and Levine, 1987
Bare unfertilized soil, Finthen (average) (range)	2.2 -5.8 to 14.2	Slemr and Seiler, 1984	Unfertilized grass, Virginia (mean) (range)	3 (0.003 to 9.0)	Anderson and Levine, 1987
Bare unfertilized soil, Utrera (range)	-2.2 to 107	Slemr and Seiler, 1984	Wheat, dry season July, Colorado (mean) (range)	2 0.001 to 6.1	Anderson and Levine, 1987
Crested wheat grass (daily mean) (range)	7 -9.3 to 28	Delany et al., 1986	Wheat, dry season July, irrigated Colorado (mean)	10	Anderson and Levine, 1987
Ungrazed grassland (mean: Aug-Nov, 1985) (range)	3 0.028 to 65	Williams et al., 1987	Wheat, wet season May, Colorado (mean)	2.8	Anderson and Levine, 1987

^a Measurements of NO fluxes were made during July and December 1986 at times ranging from 1000 to 1700 LT, at both dry and irrigated sites.

^b Measurements were made starting 5 days after fertilization and continued for 25 days.

or nitrates in the tropical environment. Background concentrations of NO over the Amazon region increased by about 25% during the month-long expedition, as burning activity increased within and to the south of the study region (Torres and Buchan, 1988). Thus, while biomass burning was the dominant source of NO_x in the vicinity of fires and within plumes, it appeared that emissions from soils provided the major source in the mixed layer and in the convective cloud layer. Andreae et al. (1988b) used the ABLE-2A data to estimate that the global source of NO_x from biomass burning was 7.6 Tg N yr⁻¹, about 2/3 of the estimate given in Table 1.3. The latter figure was based on estimates of the nitrogen content of various biomass fuels, assessments of the extent of burning, and the assumption that 25% of fuel nitrogen is converted to NO.

Elevated concentrations of NO were observed in the vicinity of electrically active clouds over the Pacific Ocean during the first Chemistry Instrumentation Test Experiment (CITE-1) expedition (Davis et al., 1987; Ridley et al., 1987). Chameides et al. (1987) used these data in combination with estimates of the mass flux of air through convective clouds to estimate a global source for NO_x from lightning of 7 Tg N yr⁻¹. This estimate is very similar to that given in Table 1.3, which results from ground-based observations of NO₂ from lightning and satellite data for the total number of lightning flashes per year. The good agreement for the independent methods is remarkable, since both are based on very limited observations of NO_x production by electrical activity.

Table 1.5
Tropospheric NO_x Distributions in the Planetary
Boundary Layer (PBL) and Above*

Regions	NO _x (ppbv)
Industrialized PBL	0.5 - 10
Oceanic PBL (0 ~ 2 km)	0.001 - 0.01
Clean continental PBL	0.05 - 0.2
Biomass burning PBL	0.5 - 10
Free troposphere (2 ~ 12 km)	0.02 - 0.2

*Fehsenfeld et al., 1987

Table 1.5, adopted from Fehsenfeld et al. (1987), gives typical observed NO_x levels in five major regions of the troposphere and reflects our current knowledge of the distribution of NO_x sources. The inhomogeneity in NO_x distributions implies that some regions act as ozone sources while others act as ozone sinks (Liu, 1988). The net ozone production (or loss) rates for these regions are shown in Table 1.6. In steady-state conditions, the net ozone production (or loss) equals the flux divergence in a particular region, and the estimated flux divergences are comparable to the stratospheric flux divergences and the surface

deposition of ozone. This emphasizes the importance of measuring ozone flux divergence as well as surface deposition.

Table 1.6 shows that ozone production in the free troposphere also has a significant impact on the global ozone budget; yet the sources of free tropospheric NO_x, which plays an essential role in free tropospheric ozone production, are poorly understood. In addition to the contribution from industrial regions, the large biomass fires in the tropics also contribute to the production of ozone on a global scale (Delany et al., 1985). In order to evaluate the impact of anthropogenic activities on tropospheric ozone, the vertical flux divergences of NO_x, PAN, and other reactive nitrogen species emanating from the boundary layer in industrialized regions must be measured.

The ozone budget in the winter half of the year and the seasonal variation of ozone are not understood. This may have important implications for assessing the role of anthropogenic emissions on ozone concentration fields and for estimating possible adverse effects on ecosystems by exposure to high ozone concentrations. Measurements of surface exchange rates and flux divergences of ozone and its precursors in the winter season will resolve some of the key questions involved.

H₂O₂ is produced in both gas-phase and aqueous-phase chemical reactions that involve odd hydrogen species. Like ozone, H₂O₂ formation depends strongly on the distributions of NO_x and hydrocarbons. The photochemical lifetime of H₂O₂ is relatively short—about two days in summer at mid-latitudes. As a result, we expect considerable spatial and temporal variation in the distribution of H₂O₂. Therefore, as in the case of ozone, flux divergence plays a major role in the budget and distribution of H₂O₂.

Deposition of NO_x, O₃, and H₂O₂

Wet and dry deposition are the major sinks for reactive nitrogen species. Soluble species such as HNO₃, NO₃, and N₂O₅ are readily scavenged by precipitation. Ehhalt and Drummond (1982) and Logan (1983) estimate that more than half of the total loss of reactive nitrogen species occurs through wet deposition. Huebert and Robért (1985) have found virtually no surface resistance to HNO₃ exchange from the atmosphere to grass; under these conditions, its deposition is determined by aerodynamic resistance. In some circumstances, HNO₃ deposition may be controlled by phase equilibria (Brost et al., 1988; Huebert et al., 1988). The same can be expected for N₂O₅, which is readily converted to HNO₃ in the presence of surface moisture.

Deposition velocities (v_d —the ratios of surface fluxes to air concentrations at some reference level, typically 2 m height) for NO₂ in the range of 0.3–0.8 cm s⁻¹ have been inferred for cement, soil, grass, and agricultural crops from field and laboratory studies,

Table 1.6.
Net Ozone Production or Loss in Summer from Various Regions Averaged
over Each Hemisphere and Compared with Stratosphere O₃ Flux

Net Production or Loss				
	NH		SH	
	(kg m ⁻² s ⁻¹) × 10 ⁺¹²	(cm ⁻² s ⁻¹) × 10 ⁻¹⁰	(kg m ⁻² s ⁻¹) × 10 ⁺¹²	(cm ⁻² s ⁻¹) × 10 ⁻¹⁰
Free troposphere ≥ 2 km	40	5	20	2.5
Industrial areas	8-24	1-3	4-12	0.5-1.5
Oceanic boundary layer	-36	-4.5	-36	-4.5
Clean continental boundary layer	-44	-5.5	-8	-1
Biomass burning areas	1.6	0.2	1.6	0.2
Stratospheric flux	56	7	32	4

while values for NO are considerably lower, < 0.1 – 0.2 cm s⁻¹ (Judcikas and Wren, 1978; Bottger et al., 1978; Galbally and Roy, 1981; Varhelyi, 1980). Wesely et al. (1982b) investigated loss of NO_x over a soybean field, using an eddy-correlation technique. They reported a maximum deposition velocity for NO₂ of 0.6 cm s⁻¹ during the day, with a minimum value of 0.05 cm s⁻¹ at night during windy conditions. These, however, are uncertain due to the nonspecific nature of their NO₂ measurements. Garland and Penkett (1976) reported deposition velocities for PAN of 0.25 cm s⁻¹ over grass and soil.

The deposition of NO and NO₂ on water surfaces should be negligible because of the low solubility of these chemical species (Lee and Schwartz, 1981). There is no published measurement of the deposition velocities for NO, NO₂, or PAN under winter conditions. Since the photochemical lifetimes of NO_x and PAN become longer in winter, dry deposition may play an important role in their budgets, and measurement of the deposition of NO_x and PAN for winter conditions should be a high priority.

Dry deposition of particulate NO₃⁻ depends very much on the size distribution of the particles involved, or, in some cases, on particle-gas interconversion (Brost et al., 1988; Huebert et al., 1988). (In both the continental and marine boundary layers, there may

be situations in which aerosol nitrate evaporates and deposits as HNO₃ vapor.) Coarser particles tend to have larger gravitational settling velocities, while fine particles are transported much like gases. There are serious shortcomings in our understanding of the dry deposition of particles. This problem will be discussed in Chapter 4.

Considerable work has been done on measurements of deposition of ozone over various surfaces for summer daytime conditions (e.g., Aldaz, 1969; Galbally and Roy, 1980; Lenschow et al., 1981, 1982; Wesely et al., 1981; Wesely, 1983; Greenhut, 1983; Cobeck and Harrison, 1985; and Kawa, 1988). Over land, daytime deposition velocities range from 0.2 to 2 cm s⁻¹ during the summer. Photosynthetically active vegetation has a relatively small surface resistance to ozone. Measurements over oceans and fresh water (Galbally and Roy, 1980; Wesely et al., 1981; Lenschow et al., 1982; Kawa, 1988), although limited, are sufficient to demonstrate that surface resistances are large and result in deposition velocities in the range of 0.02 to 0.1 cm s⁻¹. Measurements under nighttime conditions are relatively few. However, this may not be a serious problem for evaluating the ozone budget, because deposition at night is limited by transport processes. As a measurement strategy for ozone deposition, the highest priority probably should be given to measurements under winter conditions.

Both wet and dry deposition are significant sinks for H_2O_2 . There have been few measurements of either, because reliable instruments for measuring H_2O_2 have been available only recently (Heikes et al., 1986).

Ammonia

Ammonia, the main nitrogen-containing compound in primordial earth's atmosphere, is now present only in trace amounts. It is unique among atmospheric trace species as the only basic gaseous species present in significant concentrations (typically 0.1 to 19 ppbv [7.7×10^{-11} to 1.5×10^{-8} kg m^{-3} STP]) near ground level. For this reason, its accession to the atmosphere, the dispersion and transformations it undergoes there, and its subsequent deposition are of great interest in many earth sciences, including meteorology, atmospheric chemistry, soil science, agronomy, and ecology.

Concentrations in "clean" air over land are typically in the range of 1.3 to 13 ppbv (10^{-9} to 10^{-8} kg m^{-3} STP) (Ayers and Gras, 1980), although concentrations in rural areas with much livestock production may be very much higher, up to 330 ppbv (2.5×10^{-7} kg m^{-3} STP) as a daily average (Vermetten et al., 1985). Concentrations in clean air over the oceans are quite low, < 0.13 ppbv (10^{-10} kg m^{-3} STP) (Ayers and Gras, 1980).

A precursor of the chemical subunits of early life, ammonia is now formed in nature from the biological degradation of proteins in soil organic matter, plant residues, and animal wastes. Smaller amounts are also emitted from fertilizer breakdown and from industrial and combustion processes.

There is considerable guesswork in published estimates of NH_3 emissions. Galbally (1985) discusses some of the problems. Among more recent estimates are those made by Crutzen (1983) in an up-date of an earlier ammonia budget of Söderlund and Svensson (1976). Crutzen's estimates of annual global emissions are:

Biomass burning	< 60 Tg N/year
Emissions from natural fields	< 30 Tg N/year
Excreta from domestic animals	10 to 20 Tg N/year
Coal burning	4 to 12 Tg N/year
Excreta from wild animals	2 to 6 Tg N/year
Emissions from fertilized fields	< 3 Tg N/year

The biggest source, biomass burning, is probably the most uncertain, so it is important that its magnitude be verified. Vines et al. (1971) were unable to detect NH_3 in the smoke of bushfires, small fires in the laboratory, or large forest fires. They suggest that NH_3 that formed during the pyrolysis of nitrogen compounds would probably be oxidized to water and molecular nitrogen at the flame temperatures prevailing in bushfires. Crutzen, on the other hand,

attributes to Söderlund and Svensson (1976) the statement that NH_3 is a surprisingly stable compound in combustion systems, and Galbally (1985) expresses the view that a significant fraction of the nitrogen must be volatilized as NH_3 during the heating and burning of plant material. Recent measurements of NH_3 emissions from laboratory-scale biomass fires yield an estimate of 3.2 Tg N (NH_3) yr^{-1} for the global annual emission (Andicac, personal communication, 1989; data from W. M. Hao, Max Planck Institute for Chemistry, Mainz, FRG).

The next largest NH_3 source suggested by Crutzen is release from natural (unfertilized) fields, up to 30 Tg N yr^{-1} . As discussed by Crutzen and by Galbally (1985), this is difficult to estimate because soils and plants can be either sources or sinks. Crutzen's estimate is based on a model of NH_3 production and transport in soils developed by Dawson (1977). The model predicts that the concentration of NH_3 contained in air within the soil is always very much larger than in the free atmosphere (by a factor of between 70 and 300), so that the soil is always a source of atmospheric NH_3 .

Malo and Purvis (1964) and Hannawalt (1969), however, concluded from laboratory and field experiments that soils could be substantial sinks for atmospheric NH_3 . Although the atmospheric concentrations they employed in the laboratory and measured in the field (39 to 78 ppbv [3 to 6×10^{-8} kg m^{-3} STP]) were rather larger than normal ambient values, they were, nevertheless, still much smaller than the values Dawson predicts for soil.

Dawson's model also neglects the possible absorption of NH_3 from air as it diffuses through the canopy space. Hutchinson et al. (1972) have shown that plants can absorb NH_3 gas by diffusion through stomata, and Denmead et al. (1976) found strong evidence for the existence of a closed NH_3 cycle in plant canopies, whereby NH_3 released from the decomposition of litter at the soil surface is reabsorbed by the foliage above. In other work, Denmead et al. (1978) found that at normal concentrations (up to 13 ppbv [10^{-8} kg m^{-3} STP]), atmospheric ammonia was taken up by a corn crop (plant plus soil) when the soil surface was dry, but sustained NH_3 losses from the crop occurred when the surface was moist. They suggest that the net exchange is a balance between absorption by the plants and emission from the soil. The latter is strongest when water is being evaporated. Crutzen (1985) suggests that a significant release of NH_3 to the atmosphere could occur in early spring, when the soil is moist, fresh vegetation is not well developed, but dead material on the ground is abundant and the soil is being heated strongly.

Whether plants themselves lose or gain ammonia appears to be controlled by the NH_3 compensation point. Farquhar et al. (1980) have found that fo. the

plant species they examined, the compensation point is close to normal clean-air concentrations, although it increases with increasing temperature, partly because of the effects of temperature on the equilibrium vapor pressure of NH_3 solutions and increases also during senescence, presumably because of changes in plant metabolism (Farquhar et al., 1979). The temperature dependence has been suggested as a reason for the apparently higher atmospheric concentrations of NH_3 in tropical regions.

The fact that compensation points are normally close to ambient concentrations makes considerable sense. Plants with higher compensation points would be at an ecological disadvantage. Given all this, it seems that in normal clean air, atmospheric exchange of NH_3 will be of small consequence to the nitrogen budget of many agricultural crops, except during periods of elevated temperature or in senescence, but atmospheric exchange may be more important in natural communities with smaller nitrogen turnovers.

Excreta from domestic animals is the next largest source on Crutzen's list and the one that many believe may be the largest. Crutzen's estimate is based on average rates of urea excretion in urine and feces by livestock, and an assumption that 30% of the nitrogen in the urea would be volatilized as NH_3 . Estimates of the latter range from 10 to 45% (Lenhard and Gravenhorst, 1980).

From aircraft measurements of the concentration of NH_3 and NH_4^+ in the air at 100 m and 700 m above a rural area in western Germany, Lenhard and Gravenhorst (1980) estimated upward fluxes of NH_3 and NH_4^+ and concluded that these could be maintained entirely by NH_3 volatilization from domestic animal excreta, again assuming that 30% of the excreted urea nitrogen is volatilized as NH_3 . Galbally et al. (1980) also estimated that the major emissions of NH_3 to the atmosphere in Australia were from this source, some 70%. The most detailed estimates currently available are those of Buijsman et al. (1987), who calculated that 81% of the total anthropogenic NH_3 emissions in Europe were from livestock wastes. They also estimated that natural emissions of NH_3 in Europe (from uncultivated land areas) contribute only 0.6 Tg N yr^{-1} , compared with livestock emissions of 4.3 Tg N yr^{-1} and total anthropogenic emissions of 5.3 Tg N yr^{-1} .

Other minor sources include coal burning, excreta from wild animals, emissions from fertilized fields, and industrial emissions (< 1 Tg N yr^{-1}). Apart from excreta from wild animals, these are the best-documented sources, but, even so, there are still some unknowns. In calculating emissions from fertilized fields, for instance, Crutzen takes the NH_3 contribution as about 5% of the annual fertilizer use of almost 60 Tg N, but published estimates of NH_3 loss from fertilizer application range from 0 to 50%, depending

on fertilizer type, soil, weather conditions, and methods of application.

Two trends in modern agricultural practice are worth noting here. One is the increasing use of urea as a fertilizer. Buijsman et al. (1987) suggest an emission factor of 10% for urea, which is twice Crutzen's figure. The second is a shift to minimum cultivation practices, which means that more fertilizer is spread on the soil surface, where its gaseous decomposition products can be easily lost to the atmosphere, instead of being incorporated within the soil, where released NH_3 can be quickly fixed by the soil exchange complex. Additionally, the use of more nitrogen fertilizers in developing countries, where agricultural practices are often inefficient, will probably lead to higher NH_3 emissions.

Ammonia is returned to the earth's surface as NH_3 and NH_4^+ very efficiently by both wet and dry deposition, so that the majority of emitted NH_3 is probably deposited in the vicinity of its sources. While the flux densities of nitrogen from these sources (typically, 1 to 2 $\times 10^{-3}$ kg N m^{-2} yr^{-1} [3.2 to 6.4×10^{-11} kg N m^{-2} s^{-1}]) compared with fertilizer applications of $\sim 10^{-2}$ kg N m^{-2} yr^{-1} (3.2×10^{-10} kg N m^{-2} s^{-1}) are relatively small in comparison with inputs of nitrogen to fertilized fields, they are certainly of consequence in the nitrogen balance of natural ecosystems.

A new environmental effect of atmospheric NH_3 is now emerging, particularly in regions of high NH_3 turnover, as in Europe (Buijsman et al., 1987). Serious soil-acidifying effects have been observed, which could be attributed to wet deposition of NH_4^+ and dry deposition of NH_3 and ammonium aerosols.

The role of the oceans is largely unknown. Some measurements of NH_3 in marine air by Ayers and Gras (1980) suggest that the atmospheric concentration is close to the equilibrium gas concentration to be expected for seawater, which suggests that the oceans are unlikely to be net sources or sinks. At present, there are likely too few measurements of NH_3 in surface air over the oceans or in ocean surface waters to decide this question (Galbally, 1985).

Sulfur Group

Both natural and anthropogenic sources contribute to the global sulfur budget. Anthropogenic sulfur emissions are dominated by the release of SO_2 from fossil-fuel burning. Several authors have recently reviewed these emissions and presented detailed source allocations (e.g., Möller, 1984; and Cullis and Hirschler, 1980); the estimates fall into a relatively narrow range of about 70 to 100 Tg S yr^{-1} .

Various attempts to derive a global atmospheric budget for sulfur have suggested that natural emissions of a magnitude comparable to man-made emissions

are necessary to balance this budget (for a review, see Freney et al., 1983). However, since the calculations of natural emissions from the difference between anthropogenic emissions and total deposition fluxes involve very large uncertainties, they cannot be expected to provide a meaningful estimate.

This section is an overview of the processes that result in the natural emissions of sulfur species and provides, where possible, estimates of these fluxes. Only fluxes of natural gaseous sulfur species are given extensive coverage here. For detailed discussions of other emissions, such as sea salt sulfate and volcanic emissions, the reader is referred to the reviews by Andreae (1985, 1986).

Production of Volatile Biogenic Sulfur Compounds

Sulfur is an essential element to biological organisms. Two biological pathways lead from sulfate (the major sulfur source for almost all organisms) to reduced sulfur compounds: assimilatory and dissimilatory sulfate reduction. Volatile organosulfur compounds are produced from nonvolatile sulfur

metabolites in biota either through the formation and release of volatile sulfur metabolites in healthy living cells or as a consequence of decomposition. The most important product released from live cells, especially by plants, is dimethylsulfide (DMS), which is discussed later in some detail. The major pathway to the formation of H₂S, however, is through dissimilatory sulfate reduction. Under favorable conditions, the rate of sulfate reduction to H₂S can be quite high, on the order of several tens of $\mu\text{g m}^{-2} \text{s}^{-1}$. However, this process occurs only when a mixing barrier prevents oxygen from entering the system. (The escape of H₂S from the system is, of course, limited by the same barrier.) Furthermore, in the presence of oxygen, H₂S can be consumed by bacteria in a layer only a fraction of a millimeter thick. Consequently, the large amounts of H₂S that are produced in the coastal and marine environment are not usually transferred to the atmosphere (Andreae, 1984). Only a small fraction of the H₂S produced can escape under exceptional conditions in shallow water. H₂S emissions from the marine environment are, therefore, limited to such near-shore environments as estuaries and salt marshes.

Table 1.7
Summary of Biogenic Sulfur Emission Measurements*

Source	Location (State)	Month (1985)	Number of Samples	Geo. Mean Emission	Mean Sample Temperature (°C)
<i>Soils</i>				$\text{kg S m}^{-2} \text{s}^{-1} \times 10^{14}$	
Inceptisol	ID	3, 4, 9, 10, 11	17	4.5	10.9
Entisol	ID	3, 4, 5, 10	11	16.9	11.9
Alfisol	ID	5, 6, 10	15	26.6	
Mollisol	IA	7	15	18.4	38.4
Histisol, bare	OH	7	18	341.0	32.9
Tidal shore	NC	8	8	374.0	36.3
Saline marsh (with grass)	NC	8	25	580.0	32.7
Salt water	NC	8	5	51.6	31.4
Fresh water	NC	8	4	264.0	29.6
<i>Crops</i>					
Oats (with soil)	IA	7	11	1.6	35.4
Misc. vegetables (with soil)	OH	7	6	123.7	29.3
				$\text{kg S kg}^{-1} \text{s}^{-1} \times 10^{14}$	
Corn	IA, OH	7	36	103.0	28.9
Soybeans	IA	7	16	210.6	32.8
Alfalfa	WA	9	6	179.0	22.4
<i>Trees</i>					
Deciduous	IA, OH, NC	7, 8	55	47.1	29.5
Coniferous	NC	8	13	31.1	29.2

*Lamb et al., 1987

Sulfur Emissions from Continental Ecosystems

Due to the lack of representative data, estimates of the flux of biogenic sulfur gases from terrestrial soils and plants have been highly uncertain, ranging from 3 to 110 Tg S yr⁻¹ (Andreae, 1986). Here, we will focus on the results of recent measurements of emissions from freshwater wetlands, inland soils, and terrestrial plants.

The concentrations of dissolved volatile sulfur compounds in freshwater bodies tend to be much lower than those in the surface layer of the oceans (Adams et al., 1981; Froelich et al., 1985; Iverson et al., 1989). However, based on measurements of DMS concentrations in water from freshwater wetlands in Ontario, Nriagu et al. (1987) recently proposed a DMS emission rate of 2.5×10^{-12} kg S m⁻² s⁻¹ for such ecosystems and suggested that H₂S emissions of a similar magnitude may be occurring. These fluxes may, however, be overestimated, since the exchange coefficient appropriate for the hydrodynamic regime of the bog is not known and a rather high value was assumed. It is also likely that very high sulfate loading from anthropogenic pollution may have enhanced sulfur flux from these wetlands. Recent studies in Alaska suggest extremely low emissions of volatile sulfur from bog and tundra ecosystems (Martens, personal communication, 1988).

Adams et al. (1981) determined the flux of sulfur gases from soils in the eastern and southeastern United States. Their flux data showed several orders of magnitude variability between sites and between sampling periods at the same site; for nonsaline soils, they ranged from 6.6×10^{-14} to 1.1×10^{-11} kg S m⁻² s⁻¹. Most of the flux from inland soils was in the form of H₂S (66%); the rest was COS (13%), CS₂ (13%), DMS (7%), and a trace of DMDS (2%). Delmas et al. (1980) measured an average H₂S flux of 2.2×10^{-12} kg S m⁻² s⁻¹ from oxic lawn soils in France. Jaeschke et al. (1980) found fluxes of H₂S between 3.3×10^{-14} and 3.3×10^{-11} kg S m⁻² s⁻¹ from marshland soils in the Ems River region of northern Germany. Much higher fluxes were estimated from tropical soils in the Ivory Coast by Delmas et al. (1980): 9.7×10^{-12} to 2.8×10^{-11} kg S m⁻² s⁻¹.

Most recent studies have found much lower flux estimates from soils. In a large study of soil emissions conducted partly at the same sites as those used by Adams and coworkers, values about ten times lower than those reported previously were obtained by Goldan et al. (1987) and Lamb et al. (1987b) (Table 1.7). The differences between these values and those reported previously are believed to be due largely to experimental problems in the older studies. Preliminary results from measurements of soil emissions in wet tropical forests in Brazil during the dry season as follows: $(2.2 \pm 0.2) \times 10^{-13}$ kg S(DMS)

m⁻² s⁻¹, $(2.2 \pm 0.5) \times 10^{-14}$ kg S(CH₃SH) m⁻² s⁻¹ and $(3.7 \pm 1.7) \times 10^{-14}$ kg S(H₂S) m⁻² s⁻¹. These values give a total flux of short-lived sulfur species of $(2.7 \pm 0.43) \times 10^{-13}$ kg S m⁻² s⁻¹ (Andreae and Andreae, 1988). During the wet seasons, even lower values were observed. However, due to the small number of measurements and sites involved, our ability to extrapolate from these data is very limited.

The emission of sulfur gases from vegetation, including trees, is well established. The emission of H₂S from leaves is light-dependent; it increases strongly with the intensity of light and drops to very low values in the absence of light (Wilson et al., 1978; Filner et al., 1984). Emission of H₂S also increases as a result of root injury, high levels of atmospheric SO₂, and increased levels of soil water sulfate or bisulfite. Based on studies with various crop plants, Filner et al. (1984) estimated a worldwide emission of volatile sulfur from plants on the order of 7.4 Tg yr⁻¹, whereas Winner et al. (1981) estimate ~50 Tg yr⁻¹. Adjusting these values to the leaf areas and biomass values characteristic of tropical forests, fluxes of about 2.7×10^{-12} to 27×10^{-12} kg S m⁻² s⁻¹ can be predicted. Filner et al. (1984) also report the emission of CH₃SH by plants under some conditions. The emission of DMS from trees was observed by Lovelock et al. (1972); a flux of 5×10^{-13} to 10^{-11} kg S m⁻² s⁻¹ is estimated from their data for a forest with a leaf mass of ~2 kg (dry weight) m⁻². In a recent study on sulfur gas emissions from plants and soils, Lamb et al. (1987b) found emission fluxes in the range of 10^{-13} to 10^{-12} kg S m⁻² s⁻¹ from various crops and trees. The mean sulfur flux from deciduous trees was 5×10^{-13} kg S m⁻² s⁻¹ during summer conditions (mean sample temperature: 29.5°C). Emissions from soybeans and corn were dominated by DMS, while deciduous trees emitted similar amounts of H₂S and DMS. These fluxes are comparable to or greater than the sulfur gas emission fluxes that have been reported from vegetated inland soils.

Comparison of the emissions of COS from bare and vegetated soils showed that the vegetation canopy was a sink for this gas, reducing the flux of COS from soils to the atmosphere (Goldan et al., 1987; Fall et al., 1988). The uptake of COS by vegetation has been proposed as the major global sink for this compound (Brown and Bell, 1986).

The fluxes of DMS, H₂S, and CH₃SH from the soil/plant system of the Amazon forest were determined during the 1985 dry season by a gradient/flux technique (Andreae and Andreae, 1988). The mean fluxes were 4.2×10^{-13} and 2.2×10^{-13} kg S m⁻² s⁻¹ for DMS and CH₃SH respectively (Andreae et al., 1989a). Since these fluxes are much larger than the observed soil fluxes, most of the sulfur emissions must come from the plant canopy. In the case of DMS,

the vertical profiles through the forest canopy suggested that emission takes place only during the daytime and that the forest canopy is a sink for this species during the night.

If these observations are representative for remote continents worldwide, an assumption which is supported by the existing data for sulfate deposition (Galloway, 1985; Andreae et al., 1989b, and references therein), the biogenic sulfur emission from continents must be near the lower end of the range given in Table 1.10, and emissions from land biota must play a subordinate role in the continental sulfur cycle over the continents worldwide, being overshadowed by marine and anthropogenic sources essentially everywhere.

Emissions from Coastal Wetlands

Emissions of sulfur gases from saline marshes and intertidal areas vary widely between sites, between seasons, and even between days (Ancja et al., 1982; Hansen et al. 1978; Adams et al., 1981; Jaeschke et al., 1980; Steudler and Peterson, 1984; Ingvorsen and Joergensen, 1982; Cooper et al., 1987; DeMello et al., 1987). The results from flux-chamber measurements range from undetectable to nearly 6.3×10^{-8} kg S $m^{-2} s^{-1}$ during peak periods. Typical emission rates for various sulfur species are presented in Table 1.8.

Many of the reported differences are caused by diurnal and seasonal variations. The production of oxygen by photosynthesis leads to rapid oxidation of H_2S in surface layers of intertidal sediments and marshes, thereby preventing most of the H_2S produced in the anoxic zone from escaping into the atmosphere. At night, the anoxic zone moves to the sediment surface, and the emission of H_2S increases by several orders of magnitude (Hansen et al., 1978; Revsbech

et al., 1983). COS is produced from organosulfur compounds by photochemical reactions (Ferek and Andreae, 1984). The strong diurnal variability in COS emissions from salt marshes reported by Carroll et al. (1986) may be related partly to the photochemical dependence of the production rate and partly to soil-temperature and tidal cycles.

It is difficult to assign an average value to the flux of volatile sulfur compounds from coastal wetlands. However, even if we were to use a relatively high estimate of 10^{-2} kg S $m^{-2} yr^{-1}$ for the average annual flux and combine it with the total global coastal wetland area of 380,000 km^2 , we would obtain a global flux of ~ 4 Tg S yr^{-1} , which is only a small percentage of the total biogenic emissions.

Emissions from Biomass Burning

The composition of sulfur species emitted from fires is still quite uncertain. It had been assumed that SO_2 was the major product, but H_2S , COS, and sulfate aerosol have also been observed and may be important. The global emission rate for COS from biomass burning has been estimated to be 0.11 Tg S yr^{-1} . Although this is only a minor fraction of the sulfur flux from fires, it is a significant component in the atmospheric cycle of COS (Crutzen et al., 1979).

Sulfur species recently measured in aerosols generated by biomass burning in Brazil suggest that global sulfur biomass emissions may be on the order of 2.6 Tg S yr^{-1} (Andreae et al., 1988b). The differences between the results of these direct measurements and the estimates given above may be due to lower sulfur content of the biomass or to a lower volatilization efficiency.

Table 1.8
Emissions of Volatile Sulfur Compounds from Coastal Wetlands*
In Units of (kg S $m^{-2} s^{-1}$) $\times 10^{11}$

Compounds	Various		
	Saline Wetlands	Salt Marshes	Salt Marshes
H_2S	1.9	1.7	7.6
COS	0.29	—	1.1
MeSH	0.29	≤ 6.0	—
DMS	0.70	2.1	4.8
CS_2	0.38	≤ 0.6	0.6
DMDS	0.03	≤ 2.6	1.1
Total S	3.49	< 35.0	15.0

*Andreae, 1986 (The two columns at right are from different studies.)

Emissions of Volatile Sulfur Species from the Oceans

Bingemer (1984) has made the only measurements of sulfur gas flux from seawater in a chamber system at zero wind speed using the DMS naturally present in seawater. For DMS concentrations of 4×10^{-8} to 9×10^{-7} kg S(DMS) m^{-3} , he found fluxes that compare reasonably well with the predictions from theory. For other gases, however, we have to rely entirely on extrapolations based on relatively poorly developed theories. The uncertainties involved in estimating transfer fluxes with this approach introduce a potential error of as high as a factor of two into the estimates of oceanic sources of most species.

Alternative methods to measure the flux (e.g., eddy correlation or gradient techniques) are difficult. No fast-response sulfur gas sensors suitable for eddy-correlation measurements are yet available for any sulfur gas in the remote atmosphere. Nguyen et al. (1984) have used the gradient method onboard ship by taking samples at different levels above the waterline. Although the results are comparable to the predictions from gas-transfer calculations, they may contain substantial errors because of the influence of the ship on airflow characteristics. Since a realistic wave climate is difficult to simulate inside an enclosure, sulfur-gas fluxes across the air/sea interface have not been measured by this technique. Therefore, in the following discussion of the fluxes of individual sulfur species, predictions are made using the transfer model, which uses gas concentrations measured in seawater and boundary-layer air.

In open ocean waters, DMS is the predominant volatile sulfur compound (Barnard et al., 1982; Andreae et al., 1983; Andreae and Barnard, 1984; Nguyen et al., 1984; Cline and Bates, 1983; Bingemer, 1984). Although other compounds, especially CS_2 and CH_3SH , may also be present in coastal waters (Turner and Liss, 1985), their limited distribution and relatively low concentrations allow for only minor contributions to the global atmospheric sulfur budget. DMS is produced near the ocean surface by phytoplankton from an intracellular biochemical precursor, dimethylsulfonium propionate.

The analysis of large data sets and of the vertical distribution of DMS in the marine water column clearly show that the DMS concentration in seawater is related to the abundance of phytoplankton. Nevertheless, a direct correlation between total plankton abundance and DMS concentration within a given region has not yet been established because of the substantial differences in the DMS output rate of different plankton species (Andreae et al., 1983; Barnard et al., 1982). As Table 1.9 shows, when emissions of DMS from different marine biogeographic regions are compared, emissions from large oceanic regions of relatively low productivity appear to be as important

to the global flux as those from localized "hot spots" of high productivity, e.g., upwelling areas.

Based on a large data set from a wide variety of oceanic biogeographical zones, Andreae and Racmndonck (1983) have calculated an average DMS concentration for each zone and a global sea-to-air flux of ~ 40 Tg S yr^{-1} . This estimate is subject to an uncertainty of about ± 20 Tg, most of which derives from the uncertainties involved in using the "stagnant film" model to estimate air-sea transfer. Other researchers have recently published comparable flux estimates based on geographically limited concentration data sets (Nguyen et al., 1984; Bingemer, 1984; Cline and Bates, 1983).

To verify these estimates, it is important to find independent checks on the flux of DMS from the oceans. DMS concentrations of 100 to 300 pptv (2.8×10^{-10} to 8.4×10^{-10} kg DMS m^{-3} STP) are consistently found from a number of measurements in remote marine atmospheres (Andreae and Racmndonck, 1983; Andreae et al., 1985). These concentrations are consistent with the measured reaction rate of DMS with OH and a sea-to-air flux of the same magnitude as estimated above (Graedel, 1979; Chatfield and Crutzen, 1984).

Concentrations of one to a few $\times 10^{-9}$ kg S(COS) m^{-3} of COS are found in surface seawater (Rasmussen et al., 1982; Ferek and Andreae, 1984; Turner and Liss, 1985). Since observed concentrations are almost always higher than the equilibrium concentration relative to the overlying atmosphere, a net sea-to-air flux exists essentially across the entire ocean surface. Using samples collected without considering the diurnal cycle and only separated into coastal and open-ocean values, Rasmussen et al. (1982) estimate a global COS flux from the oceans of 0.3 Tg S yr^{-1} . Based largely on coastal data and interpolation from an observed relationship of DMS and COS, Ferek and Andreae (1984) estimate a global flux of 0.5 Tg S yr^{-1} .

Carbon disulfide in seawater was first found by Lovelock (1974), who measured an average concentration of 4.4×10^{-10} kg S(CS_2) m^{-3} in 35 samples taken from the open Atlantic. Inshore values were about an order of magnitude higher. Recent measurements by Kim and Andreae (1987) have been used to estimate an oceanic CS_2 flux of 0.2 Tg S yr^{-1} , which is small relative to the oceanic DMS flux.

Although H_2S , CH_3SH , and DMDS have occasionally been reported, their concentrations appear to be insignificant relative to other oceanic sulfur emissions. A recent report of sulfur-containing amino acids in the marine boundary layer (Mopper and Zika, 1987) indicates that they and their atmospheric oxidation products could be another significant source of sulfur over the oceans.

Table 1.9
DMS Concentrations and Fluxes for the World Oceans

Biogeographic Region	Area (10 ⁶ km ²)	Mean Conc. (kg DMS m ⁻³) × 10 ⁸	Total Flux (Tg S yr ⁻¹)
Oligotrophic (tropical/low productivity)	148	15	6-19
Temperate	83	13	3-10
Upwelling (coastal and equatorial)	86	30	6-22
Coastal/shelf	49	17	3-6
		Mean: 19	Total: 19-54

Summary of Natural Sulfur Emissions

The fluxes of the sulfur compounds SO₂, H₂S, COS, DMS, CS₂, and sulfate are summarized in Table 1.10. Large uncertainties obviously exist in both the chemical speciation and the magnitude of these fluxes. Although the estimated sea salt aerosol flux introduces a very large uncertainty into the total estimate, even after removing this component the range of estimates for the gaseous flux is still 38 to 89 Tg S yr⁻¹.

Clearly, better estimates of sulfur fluxes are needed to reduce this uncertainty. The flux estimates are most sensitive to inaccuracies in the major constituents. Therefore, SO₂, SO₄²⁻ particulates and aerosols, DMS, and H₂S are given the highest priority as species for which precise and accurate flux measurements are needed. Table 1.10 also indicates the most critical study regions for flux measurements.

Deposition of Sulfur Species

Reduced sulfur species are oxidized in the atmosphere to SO₂ and particulate SO₄²⁻. The atmospheric sulfur cycle is completed by the wet and dry removal of SO₂ and SO₄²⁻. On continental scales, the ratio of dry to wet deposition of sulfur appears to

be of the order of unity (Shannon, 1981; Galloway et al., 1984).

Dry deposition of SO₂ and particulate SO₄²⁻ has been studied extensively in the industrialized countries because of concern over acid deposition (e.g., Hicks et al., 1987). The deposition of SO₂ on various surfaces has been observed to be moderately rapid, with deposition velocities of 0.3 to 0.6 cm s⁻¹ in summer. In winter, the deposition velocity is significantly smaller. The deposition of particles larger than about 2 μm is controlled by gravitational settling. These particles tend to be deposited locally, while smaller particles can be transported over long distances. The average deposition velocity for SO₄²⁻ particles is about 0.1 to 0.5 cm s⁻¹ in summer and about half that in winter.

Uptake of COS by various plant species has been observed by Taylor et al. (1983), Kluczewski et al. (1983, 1985), and Goldan et al. (1988). They show that the surface resistance of COS is similar to that of CO₂ under various conditions of controlled illumination, temperature, and CO₂ concentration. This similarity provides a means for estimating global COS uptake by plants. The annual uptake is estimated to be from 0.1 to 0.3 Tg S yr⁻¹. This appears to be the largest global sink for COS (Goldan et al., 1988).

Table 1.10
Estimates of Natural Sulfur Emissions (in Tg S yr⁻¹)

	SO ₂	H ₂ S	COS	DMS	CS ₂	Sulfate	Other	Total
Sea spray						38.00-320		38.0-320
Dust						3.00-32		3.0-32
Total Particulates						1.42-352		42.0-352
Volcanoes	7.4-9.3	1.0	0.010	—	0.010	< 3	?	10.0-13
Soils and plants	—	3.0-10	0.2-0.6	0.2-4	0.6-0.8	—	1.0	5.0-13
Coastal wetlands	—	1.0	0.1	0.6	0.06	—	0.1	1.9
Biomass burning	2.6	?	0.1	—	?	?	?	≥ 2.6
Oceans (gases)	—	1.6-6.4	0.4	19.0-51	0.3	—	?	35.0-58
Total Gases	10.0-13	6.0-19	1.0-1.3	19.0-54	1.0-1.3	≤ 3	1.0	38.0-89

Carbon Group

The global atmospheric carbon budget is dominated by CO₂, and this aspect of the carbon cycle has been studied intensively for many years (Bolin et al., 1979; Bolin, 1981; Trabalka and Reichle, 1986). Nevertheless, it is sobering to realize that even after considerable effort it is still not possible to adequately reconcile the measured distribution of CO₂ in the atmosphere with the surface exchange that constitutes the major sources and sinks of this gas (see Tans et al., 1989). Nor is it possible to account satisfactorily for the strong, asymmetric meridional gradient of ¹⁸O in atmospheric CO₂ (Franczy and Tans, 1987). While CO₂ may dominate the carbon budget, it is clear that fluxes of other, much less abundant carbon species play key roles both in the carbon cycle itself and in the broad chemistry of the troposphere. For example, carbon monoxide (CO) is present in the troposphere at an average concentration of about 0.03% of that of CO₂, but the quantity of CO₂ formed each year by the oxidation of CO by OH is significant when compared to the quantity of CO₂ released directly into the atmosphere by the burning of fossil fuels. Naturally occurring nonmethane hydrocarbons (NMHC) are present at concentrations almost two orders of magnitude lower than those commonly observed for CO, but they significantly affect the formation of tropospheric ozone in both rural (Trainer et al., 1987) and urban locations (Chameides et al., 1988). During the atmospheric oxidation of methane (CH₄) and NMHC to CO and CO₂, much of the carbon flux passes through the

species formaldehyde, but its concentration in the troposphere is typically less than one part per billion by volume (Dawson and Farmer, 1988). Another organic species that influences the formation of oxidants in the atmosphere is acetone, since it acts as a precursor of peroxyacetyl nitrate (PAN), which may then act as a source of reactive nitrogen in the remote troposphere (Arnold et al., 1986).

The following sections, together with Table 1.11, provide a summary of what is currently known about the surface exchange of the key carbon species.

Carbon Dioxide

Carbon dioxide does not play a direct role in the chemistry of the troposphere. Nevertheless, the warming of the earth's surface and troposphere, as well as the cooling of the stratosphere above 20 km, that are likely to result from continuing increases in global CO₂ concentration will have consequences for the abundances of many chemically active trace gases in the atmosphere. Over the oceans and vegetated land surfaces, there can be significant fluxes of CO₂ both to and from the atmosphere. The flux of CO₂ from a variety of crops and forested regions has been measured for many years, using a variety of techniques. Some of these techniques, such as the dynamic or static chamber techniques, have been shown to have deficiencies (e.g., Baldocchi et al., 1986). Over agricultural surfaces, CO₂ flux has been measured by using a stability-corrected aerodynamic formulation (Verma and Rosenberg, 1976 and 1981). The eddy-correlation technique has been used to measure both

Table 1.11
Carbon Species Concentrations and Global Release Rates

Highest Priority Species ¹	Critical Study Regions	Mixing Ratio Ranges in Each Region	Annual Release Rate	Comments
CH ₄ ¹	Natural wetlands	1.7-4 ppmv	100-200 Tg CH ₄ yr ⁻¹	
	Rice paddies	1.7-8 ppmv	60-170 Tg CH ₄ yr ⁻¹	
	Enteric fermentation (animals)		65-100 Tg CH ₄ yr ⁻¹	
	Biomass burning		50-100 Tg CH ₄ yr ⁻¹	
	Termites		10-100 Tg CH ₄ yr ⁻¹	
	Landfills		30-70 Tg CH ₄ yr ⁻¹	
	Oceans	1.7 ppmv	5-20 Tg CH ₄ yr ⁻¹	
	Freshwaters		1-25 Tg CH ₄ yr ⁻¹	
	Methane hydrate destabilization		0-100 (future) Tg CH ₄ yr ⁻¹	
	Coal mining		25-45 Tg CH ₄ yr ⁻¹	
CO	Gas drilling, venting, transmission		25-50 Tg CH ₄ yr ⁻¹	
	Biomass burning	Up to 1 ppmv	400-1600 Tg CO yr ⁻¹	High concentrations in haze layers over Amazonia
C ₃ H ₈ (isoprene) ²	Continents	70 to 150 ppbv		
	Oceans	50 to 100 ppbv		
C ₁₀ H ₁₆ (terpenes) ²	Hardwood and tropical forests	1-50 ppbv C	350 Tg C yr ⁻¹	Released daytime only; temperature dependent
	Coniferous forest	0.2-2 ppbv C		Temperature dependent
C ₃ H ₆ (propene)	Rural continental	0.1-0.5 ppbv C	480 Tg C yr ⁻¹	Ocean source very patchy. Concentrations up to a few ppb over ocean source regions
	Remote continental	a few ppbv		
C ₂ H ₄ (ethene)	Oceanic	0.1 ppbv C		Ocean source very patchy. Concentrations up to a few ppb over ocean source regions
	Rural continental	a few ppbv		
<i>Other Key Species:</i> CH ₂ O CH ₃ CHO (CH ₃) ₂ CO HCOOH CH ₃ COOH CH ₃ Cl	Remote continental			
	Oceanic			

¹ Annual release rates from Cicerone and Oremland, 1988.

² Annual release rates from Zimmerman et al., 1978

the CO₂ emission from the floor of a deciduous forest (Baldocchi et al., 1986), and the CO₂ flux above the forest canopy (Verma et al., 1986). Eddy-correlation measurements of CO₂ flux from an aircraft have been reported by Desjardins et al. (1982 and 1989). Micrometeorological techniques have also been used to measure CO₂ flux over coastal ocean sites (Smith and Jones, 1985; Wesely et al., 1982a), but the values were significantly larger than those found by isotopic techniques (Broecker et al., 1986). The discrepancy has been discussed by Wesely (1986) and Smith and Jones (1986). Measurements of CO₂ concentrations in conjunction with other trace gases has sometimes been the basis for making estimates of the fluxes of these trace gases, as in the case of biomass burning (Crutzen et al., 1979; Seiler and Crutzen, 1980; Crutzen et al., 1985).

Methane

Fluxes of methane to the atmosphere have been measured or estimated from many known source types: wetlands (Svensson and Rosswall, 1984; Harriss and Sebacher, 1981; Sebacher et al., 1986), rice paddies (Cicerone and Shetter, 1981; Cicerone et al., 1983; Holzapfel-Pschorn and Seiler, 1986), animals (Crutzen et al., 1986), municipal solid waste (Bingemer and Crutzen, 1987), termites (Zimmerman et al., 1982; Seiler et al., 1984; Fraser et al., 1986b), biomass burning (Greenberg et al., 1984; Crutzen et al., 1985), and fossil fuel utilization (Ehhalt and Schmidt, 1978; Crutzen, 1987). Virtually all of the direct flux measurements have relied upon some variation of the enclosure technique. A notable feature of the results for wetland environments is the large range (approximately two orders of magnitude) of measured fluxes. For a variety of wetland sites in Alaska, Sebacher et al. (1986) found that the methane fluxes were significantly related to the water depth at each site. Large variations in methane fluxes have also been observed for termites, where the flux is strongly dependent upon the species of termite (e.g., Fraser et al., 1986b). In some cases fluxes of methane from the atmosphere into the soil have been measured (Keller et al., 1983; Seiler et al., 1984). More recently, fluxes of methane were measured with eddy-correlation techniques during the ABLE-3A experiment held in the Alaskan Arctic during July-August 1988. A fast-response methane sensor based upon the use of a helium-neon gas laser (Kolb et al., 1986) was used for flux measurements from an instrumented tower, while another fast-response sensor using a tunable diode laser (Sachse et al., 1987a,b) was used on board the NASA Electra to measure fluxes over large expanses of tundra.

In many cases the methane fluxes have an intrinsic interest, but usually the fluxes are extrapolated to the regional or global scale for the purpose of

compiling global inventories of the sources and sinks of atmospheric methane. Over the past decade there have been several attempts to understand the global budget of methane in this way (Ehhalt and Schmidt, 1978; Sheppard et al., 1982; Khalil and Rasmussen, 1983; Seiler, 1984; Blake, 1984; Crutzen, 1987; Bingemer and Crutzen, 1987; Cicerone and Oremland, 1988). Given the very large uncertainties involved in extrapolating to the global scale from fluxes measured over areas of perhaps a few square meters, it is not surprising that there remain significant disagreements over the relative importance of various global sources of methane.

Carbon Monoxide

The global atmospheric budget of carbon monoxide, and its associated uncertainties, have been thoroughly discussed (Logan et al., 1981; WMO, 1986; Seiler and Conrad, 1987; Warneck, 1988). As much as 40% of the global source is attributed to anthropogenic activities, such as the burning of fossil fuels, agricultural burning, and the clearing of forests. One important feature of the CO budget is that at least 50% of the sources do not involve surface exchange of CO itself. Rather, the CO is produced in the atmosphere by oxidation of both biogenic and anthropogenic hydrocarbons. In addition, perhaps 40% of the global CO production occurs in tropical regions (Sachse et al., 1988; Andreae et al., 1988b).

Many of the terms in the global CO budget are not based upon direct measurement of CO fluxes. In fact, much of the information we have about the CO budget has been inferred from considerations of gas-phase chemistry (Logan et al., 1981), the measurement of CO emission factors from various types of combustion (Logan et al., 1981; Crutzen et al., 1985b; Greenberg et al., 1984; Andreae et al., 1988b), and estimates of the production and release of nonmethane hydrocarbons (Zimmerman et al., 1988). Since the tropics are thought to be such an important region for CO production, direct measurement of CO fluxes over large areas of the tropics would be very desirable. The first set of such measurements was made during the ABLE-2B flights over the Amazon Basin during the wet season (April-May) of 1987 using airborne eddy-correlation techniques.

The dominant sink mechanism for CO is oxidation to CO₂ by the hydroxyl radical, accounting for about 90% of the total. The remainder is thought to be lost by uptake in soils.

Nonmethane Hydrocarbons

It is now clear that the global flux of carbon into the atmosphere as nonmethane hydrocarbons (NMHCs) greatly exceeds the flux of carbon as CH₄. This flux is dominated by the release of biogenic NMHCs from vegetation, principally trees. The most important of these biogenic NMHCs are isoprene

(C_5H_8) and the monoterpenes ($C_{10}H_{16}$) such as α -pinene. In some tree species, such as pines and firs, the primary NMHCs emitted are the monoterpenes, while in other species (e.g., oaks and aspens) the primary NMHC product is isoprene. Some species, such as spruce and eucalyptus, produce both isoprene and monoterpenes (Rasmussen, 1981). Zimmerman et al. (1988) estimated that in the Amazon forest, isoprene accounted for approximately 20% of the gas-phase carbon of the NMHCs and that isoprene emissions were equivalent to approximately 2% of the net primary productivity of the forest (the net amount of carbon fixed during photosynthesis). The global annual release of isoprene from vegetation has been estimated as 450 Tg, with almost half of this total coming from tropical forests (Rasmussen and Khalil, 1988).

There have been relatively few attempts to measure fluxes of NMHCs into the atmosphere from the world's oceans. The available measurements indicate that the fluxes are small relative to those seen from land vegetation. Bonsang et al. (1988) have estimated an annual global release from the oceans to the atmosphere of 5.2 Tg (as carbon) of the C_2 to C_6 alkanes and alkenes.

The total annual emission into the atmosphere of biogenic NMHCs from the contiguous United States has been estimated as 31 Tg, with an uncertainty of a factor of three (Lamb et al., 1987a). By contrast, these authors estimate the anthropogenic NMHCs released from the U.S. in 1983 as 18 Tg. There is a strong seasonal and regional dependence of the biogenic emissions, with over half of the U.S. total occurring in the three summer months and approximately half the U.S. total coming from the southeastern and southwestern regions of the country (Lamb et al., 1987a). The total anthropogenic NMHC emissions in the U.S. are lower than the biogenic emissions; the anthropogenic releases occur principally from urban and industrial locations, which account for about 3% of the total land area, corresponding to areal fluxes about 20 times larger than those for biogenic source regions (Lamb et al., 1987a).

A variety of methods has been used to measure directly the fluxes of biogenic NMHCs. Some data are from measurements on live plants in a laboratory environment (Tingey, 1981), but most reported fluxes are from measurements made in the field. The laboratory measurements showed that higher temperatures increase the release of both isoprene and monoterpenes. Isoprene emissions occur only during daylight, with an increasing emission rate as the light intensity is increased. Monoterpene emissions do not vary with light intensity (Tingey, 1981). Field methods which have been used are an enclosure technique (Zimmerman, 1979a and b), a micrometeorological approach (Knoerr and Mowry, 1981; Lamb et al., 1985), and an atmospheric tracer technique (Lamb et

al., 1986). The three methods give good agreement in measuring isoprene emission rates (Lamb et al., 1986).

The principal sink for atmospheric NMHCs is oxidation by the hydroxyl radical. Oxidation by species such as ozone and by the gaseous nitrate radical (NO_3) during the night does occur but constitutes a smaller sink (Winer et al., 1984). The reaction between isoprene and the hydroxyl radical is so rapid that during the daytime in the mixed layer over a tropical forest, isoprene controls the concentration of hydroxyl radicals (Jacob and Wofsy, 1988). Such oxidation of NMHCs leads to the formation of a variety of oxygenated substances such as aldehydes, organic acids, ketones, and organic nitrates (Lloyd et al., 1983; Kamens et al., 1982), which may undergo further rapid reactions to eventually produce carbon monoxide. Such oxidation of isoprene and other NMHCs over tropical forests has been observed to cause significant increases in the CO levels in the boundary layer (Gregory et al., 1986; Zimmerman et al., 1988). Oxidation of NMHCs can also lead to the formation of particulate matter.

Direct deposition of NMHCs to the surface may also occur, but it probably provides a relatively small sink compared to oxidation. The effectiveness of wet deposition for any particular species would depend upon its solubility in water as well as the pH of the precipitation droplets.

Organics

The species included in this category are those carbon-containing compounds (both vapor phase and particulate) other than CH_4 , CO, the NMHCs, and the entirely man-made chlorofluorocarbons. Relatively little is known about this class of compounds in the atmosphere. For an extensive survey of the literature on the subject, the reader is referred to Duce et al. (1983). In this section we will concentrate on those areas where there have been recent advances in our understanding.

Formic acid and acetic acid are known to contribute to the acidity of precipitation, particularly in areas remote from significant anthropogenic influences (Keene and Galloway, 1988). Recent measurements by several investigators have greatly improved our understanding of the sources of these acids. Vapor phase concentrations of these acids typically range from less than 1 ppb to a few ppb (Dawson et al., 1980; Talbot et al., 1988; Andreae et al., 1988a). It is known that both acids are emitted from burning biomass and from motor vehicle exhausts (Talbot et al., 1988). Formic acid is produced by the oxidation of isoprene, while acetic acid is not (Jacob and Wofsy, 1988). It is likely that both acids are also emitted directly from vegetation (Graedel et al., 1986). Over the Amazon Basin, Andreae et al. (1988a) showed that over 98% of the total formic acid and over 99% of the total acetic acid are present in the gas phase, with

very small amounts present as aerosol. They found the highest concentrations of aerosol formate and acetate in haze layers associated with biomass burning. At a site in eastern Virginia, Talbot et al. (1988) also found both organic acids almost completely ($\geq 98\%$) in the gas phase, and that there were significant seasonal variations in the acid concentrations. The current knowledge of formic and acetic acids in the troposphere has recently been reviewed by Keene and Galloway (1988).

Research Needs

Based on the above discussion, we list in Tables 1.11, 1.12, and 1.13 the important nitrogen and ozone,

sulfur, and hydrocarbon group species for which surface exchange needs to be studied. For each of the three groups the species are ranked into two priorities—highest priority species and other key species. The critical regions for study are listed for each species. Although not specified, it is obvious that measurements of temporal variations of the fluxes are essential, especially when surface exchange is related to biogenic processes.

Typical mixing ratio ranges in each region are listed as a guide for the required instrumental sensitivity and dynamic ranges. Also included are the expected ranges of surface flux or surface deposition velocity. In certain cases, surface resistance instead of deposition velocity is listed.

Table 1.12
Oxidant and Odd Nitrogen Species Concentrations and Surface Fluxes

Highest Priority Species	Critical Study Regions	Mixing Ratio Ranges in Each Region ppbv	Surface Flux Ranges ($\text{kg m}^{-2} \text{s}^{-1}$) $\times 10^{12}$ or Deposition Velocity v_d (cm s^{-1})	Comments on Fluxes
O ₃	Continents oceans	1 to 200 1 to 100	$v_d = 0.01$ to 1.5 $v_d = 0.01$ to 0.1	Seasonal variation is strong Small but important
	Tropics, agricultural regions	0.001 to 10	0.1 to 100	
NO	Tropics agricultural and industrial oceans	0.01 to 10 0.01 to 100	$v_d = 0.1$ to 1.0 $v_d = 0.01$ to 0.5	v_d based on O ₃ values v_d over oceans has never been measured
	Tropics agricultural and industrial oceans	0.01 to 10	$v_d = 0.2$ to 2.0	Currently unknown; will probably be hard to measure
PAN	Tropics agricultural and industrial oceans	0.01 to 100 0.01 to 0.01	$v_d = 0.02$ to 1.0 $v_d = 0.01$ to 1.0	Surface resistance is very small
HNO ₃	Tropics agricultural and industrial oceans	0.01 to 1	$v_d = 0.5$ to 3 $v_d = 0.3$ to 0.7	
	Tropics agricultural and industrial oceans	0.01 to 20	$v_d = 0.1$ to 3	Ocean values depend on surface conditions
H ₂ O ₂	Tropics agricultural and industrial oceans	0.01 to 10 0.01 to 5	$v_d = 0.1$ to 3 $v_d = 0.1$ to 3	
	Tropics agricultural and industrial oceans	0.1 to 50	$\pm (0.1$ to 1.0)	Downward fluxes are closer to the lower end of the range
NH ₃	Tropics agricultural and industrial oceans	0.1 to 50 0.001 to 1.0	0.1 to 10	Destroyed in the stratosphere
	Tropics	280 to 320		
N ₂ O	Tropics	?	?	Concentrations are ill-defined, and there is considerable uncertainty about surface deposition rates. Therefore, their fluxes may be important. Development of diagnostics would be useful. None presently exist.

Other Key Species

- NO₃
- N₂O₅
- HONO
- HO₂NO₂
- NH₄⁺

Table 1.13
Sulfur Species Concentrations and Surface Fluxes

Highest Priority Species	Critical Study Regions	Mixing Ratio Ranges	Surface Flux Ranges $\text{kg m}^{-1} \text{s}^{-1} \times 10^{12}$ (-) = sink, (+) = source	Comments
SO_2	Industrial regions (sources) temperate biomes, tundra, boreal forests, oceans (sinks)	1 to 100 ppbv (regionally polluted)	(-) 50 to 500 (regionally polluted)	Large anthropogenic sources need deposition studies to characterize deposition concentration and geographic extent
SO_4^- particulates and aerosols		5 to 200 pptv (clean)	(-) 10^{-2} to 10 (clean)	
Dimethylsulfide H_2S		1 to 500 pptv 1 to 500 pptv	(-) 5 to 50 (regionally polluted) (-) 10^{-2} to 10 (clean) (+) 2×10^{-3} to 5 (+) 2×10^{-3} to 5	
<i>Other Key Species</i>				
OCS	Dry tropics wet tropics oceans temperate biomes Arctic tundra	400 to 600 pptv	(±) 2×10^{-3} to 5 (+) 2×10^{-3} to 10^{-1}	
CS_2		≤ 50 pptv	(-) ?	
Dimethylsulfoxide		≤ 50 pptv	(-) ?	
Methane sulfonic acid		≤ 50 pptv	(-) 1×10^{-3} to 2	
Methane Sulfonate CH_3SH		≤ 50 pptv < 50 pptv	(-) ? (+) 2×10^{-3} to 0.2	
Sulfur containing amino acids and their oxidation products		< 50 pptv	(±)	

2 FLUX MEASUREMENT TECHNIQUES

M. L. Wesely, D. H. Lenschow, and O. T. Denmead

Several techniques have been developed to measure the rates of exchange of chemical species between the atmosphere and the surface. Principal among these are the aerodynamic methods, which quantify fluxes in air from tower and aircraft platforms, and nonaerodynamic methods, which usually involve a mass balance at or very near the surface. Each method has its advantages and disadvantages, as will be evident in the discussions that follow. None of the approaches is new; many represent extensions, modifications, or improvements of methods initially developed for estimating the fluxes of heat, momentum, and moisture important in meteorology and agriculture. To set the background for the detailed examination of modern applications of these methods to the surface exchange of chemical species, a brief historical review is appropriate.

Direct measurements of surface fluxes were apparently first attempted in order to estimate evaporation rates by using buckets and pans containing carefully monitored amounts of water exposed to ambient conditions near the surface. To this day, evaporation pans are standard in many meteorological observation systems. It is recognized, however, that these devices rarely, if ever, measure the evaporation rate characteristic of the surface in the vicinity of the pan and certainly do not measure characteristic evaporation when the surrounding surface is not wet. The term "potential evaporation" is used to describe the results obtained from a pan or from a thoroughly wetted surface. An important step toward measuring actual evaporation was taken with the development of the weighing lysimeter, which measures the rate of water loss from an isolated surface sample containing both soils and vegetation that are representative of the surrounding surface. Initial development took place in the 1930s (Hatfield, 1988). Weighing lysimeters now provide a standard of evaporation measurement in the agricultural scientific community.

Pans and lysimeters used for studies of the surface exchange of water have obvious counterparts in studies of trace gas and particle exchange: static and flow-through chambers used for measuring trace gas exhalation and surrogate surfaces used to investigate particle deposition. Despite the long history of development, it is clear that no technique that

interferes with the processes that influence surface exchange can yield accurate measurements of the exchange from similar surfaces that are unaffected. For example, surrogate-surface measurements of deposition cannot easily be extended to nearby natural surfaces. Likewise, chamber techniques can distort the effects of atmospheric turbulence on exchange and the environmental conditions important in biological processes that affect exchange.

Aerodynamic methods for measuring exchange rates of trace chemical species are also founded on a long history of meteorological research. In general, modern methods rely on the measurement of either vertical gradients of time-averaged concentrations or on turbulent fluctuations of concentration. Gradient methods began with studies of wind near the surface and date back more than 70 years; Hellman (1915) and Johnson (1929) provide some early examples. Studies of near-surface atmospheric profiles were soon extended to temperature (e.g., Best, 1935). Eddy correlation, which involves sensing of turbulent fluctuations, was explored in the same period by workers such as Scrase (1930) but did not come to the forefront until electronic data-processing techniques became readily available in the 1960s.

The first eddy-correlation flux measurements from aircraft seem to be those reported by Bunker (1955). He estimated vertical air velocity by measuring vertical aircraft acceleration and horizontal airspeed fluctuations in conjunction with the aerodynamic characteristics of the airplane. Vertical velocity and airspeed fluctuations were used to compute an estimate of momentum flux, and sensible heat flux was measured by combining the output of a fine wire thermometer with the vertical velocity fluctuations. These early measurements, although somewhat crude by today's standards, established the usefulness of aircraft as platforms for turbulent flux measurements.

For the aerodynamic methods, it is not always clear that the flux measured in the air is the same as that at the surface. Rapid temporal changes in concentrations, large spatial inhomogeneities, fast chemical reactions, and a shallow boundary layer relative to the measurement height can all cause significant flux changes with height (i.e., flux divergence or convergence). As a result, it is usually necessary to

estimate or measure the spatial and temporal trends in local concentrations and wind field, the characteristic times of chemical reactions relative to vertical turbulent mixing, and the temporal and spatial variability of boundary-layer height.

It is often best to use more than one method to measure fluxes, to provide independent evaluations and to assess errors caused by some of the problems mentioned above. The following three sections discuss some of the more promising methods now available, using towers, airplanes, and enclosures. Tower and aircraft techniques are discussed separately, because they tend to provide complementary spatial and temporal coverage and their technological requirements are somewhat different.

Tower-Based Flux Measurement Systems

Tower-based instrumentation systems for measuring air-surface exchange are well proven, convenient, and economical. Measurements at several meters above the surface can be used to quantify the average vertical exchange over several hundred square meters, along a path extending several hundred meters upwind and with a cross-wind breadth that increases with distance from the sampling tower. This "footprint" is not defined precisely, causing some difficulty when attempting to evaluate the air-surface exchange above a particular type of surface that borders other types nearby. The measured exchange rate incorporates fluxes to and from individual plants, surfaces beneath plant canopies, and individual portions of the surface such as leaves in a canopy. In summary, the sampling performed by tower-based flux measuring systems is representative of bulk surface properties over an area that depends on the height of the measurements.

Many tower-based methods of measuring the air-surface exchange of trace substances have been reviewed in recent publications concerned with dry deposition and surface energy balance (Kanemasu et al., 1979; Businger, 1986; Hicks, 1986; Hicks et al., 1986b). Much of the discussion here is based on the more detailed descriptions available in these publications and the references cited in them.

Traditional micrometeorological approaches are frequently used to measure air-surface exchange of trace chemicals. The methods addressed here fall most clearly into the category of micrometeorological techniques: eddy correlation, use of vertical gradients or profiles, and calculations of fluxes from variances of turbulent fluctuations. In some specific situations, however, alternatives may be required. Small-scale mass balances may be computed by integration of vertical profiles in horizontally homogeneous conditions, when vertical mixing is weak and the height of the upper boundary of the mechanically mixed layer in contact with the surface (the "lid" on vertical

mixing) can be accurately estimated. Extremely stable atmospheric conditions or dense vegetative canopies can provide the opportunity for such mass balance studies. Carefully designed dual tracer methods provide another alternative. The sampling strategies must be precisely tailored to the physical conditions of the experiment. Similarly, special tracers can be employed. For example, ^{222}Rn or ^{220}Rn can, in special circumstances, provide information on exchange coefficients for nonreactive gases. Finally, numerical diffusion models can be used to obtain estimates of air-surface exchange with rather simple sampling strategies, if a small, isolated area of uniform emissions or uptake is well defined.

Inferential methods of surface exchange are designed to obtain operational estimates of dry deposition for which standard micrometeorological methods may be too difficult or too expensive to apply routinely. Inferential approaches are not considered here because they are not sufficiently direct; they are, in fact, based on parameterization experiments that employ more direct approaches. Surrogate surfaces may sometimes be appropriate for routine measurement of dry deposition but are not considered here because they do not measure fluxes that are directed upward.

Several requirements for micrometeorological measurements of vertical fluxes should be kept in mind. Substantial atmospheric nonstationary or horizontal advection should be avoided, or the effects should be taken into account by appropriate measurements and calculations. Flux divergences resulting from changes in the mean concentrations, entrainment through the top of the PBL, or mesoscale divergence may have to be evaluated, or at least detected, so that errors in micrometeorological flux estimates can be identified. For substances that undergo very rapid chemical reactions in air, measurements must be taken sufficiently close to the surface that the resulting changes of flux with height are small, if the intent is to evaluate exchange rates at the surface. This problem has arisen for measurement of fluxes of O_3 , NO , and NO_2 and may be most easily addressed by use of both flux and profile measurements combined with modeling of chemical reactions. For many purposes, the complications of the chemistry can be avoided by measuring NO_x , which is a conserved parameter with respect to ozone oxidation and fast photochemistry.

Measurement of fluxes over nonuniform terrain requires especially careful analysis. In eddy correlation over sloping terrain, the proper distinction must be made between cross-streamline turbulent flux and mean transport. Established flux-gradient relationships may not be valid over nonuniform surfaces or complex topography. Likewise, the relationships between turbulent fluctuations and fluxes above nonuniform surfaces may be different from those over uniform surfaces.

In all cases, it is essential that sensors not respond significantly to chemical species other than those intended. However, even if concentrations are perfectly measured, traditional micrometeorological techniques will probably not yield useful estimates of vertical fluxes if the ratio of flux to mean concentration F_e/C has a magnitude less than about 0.01 cm s^{-1} .

Fluxes of chemical species at the surface should be measured concurrently with fluxes of momentum, and sensible and latent heat, in order to evaluate gas-phase physical resistances to vertical transport and thus to allow computation of surface resistances or conductances. Knowledge of sensible and latent heat fluxes also permits computation of the corrections necessary to measure concentration in air in other than mixing-ratio units (see Webb et al., 1980). These corrections arise because temperature and humidity fluctuations associated with sensible and latent heat fluxes influence the volumetric concentrations of all trace species in the air and hence cause the appearance of an exchange that is not associated with chemical exchange at the surface itself. This induced flux can contribute significantly to the species fluxes in a CBL if (1) concentration is measured in units other than mixing ratio with respect to dry air, (2) $|F_e|/C < 1.0 \text{ cm s}^{-1}$, and (3) the latent and sensible heat fluxes are typical of a daytime continental boundary layer.

For interpretation of surface resistances to be useful in developing parameterizations for use in models, the surface should be fully documented. For example, it may be necessary to identify soil type, to measure soil moisture, to identify plant species in surface vegetation, and to determine biophysical parameters such as leaf area index--preferably as a function of height.

Eddy Correlation

Eddy correlation is a well-established technique that has the primary advantage of measuring turbulent diffusive fluxes directly across a near-horizontal plane above the surface. It requires a rigid platform unencumbered by significant aerodynamic obstacles. The fluxes are computed as covariances of the fluctuations of vertical wind velocity with fluctuations of concentration or mixing ratio at the same point and time (e.g., Brutsaert, 1982).

Perhaps the most difficult requirement in using eddy-correlation methods to measure fluxes of trace substances is the need for fast-response sensors. For example, suitable sensors have yet to be fully developed for nonmethane hydrocarbons, organic sulfur compounds, N_2O , NH_3 , and many other species. Substances for which fast-response sensors are currently available include O_3 , CO , SO_2 , CH_4 , sulfate particles, NO , NO_2 , and CO_2 , in addition to wind components, temperature, and water vapor. Some recent technological advancements that offer promise

for other species are discussed in Chapter 3. Figures 2.1 and 2.2 show examples of recent results for fluxes of momentum, heat, water vapor, O_3 , and SO_2 . As is often the case, these fluxes were measured at heights of 5 to 15 m and over time intervals of 30 minutes. We see that there is a typical variability of 10% to 20% in flux estimates from half-hour to half-hour for sensors not significantly affected by noise. (The SO_2 sensor used for the fluxes in Figure 2.2 is noisy.)

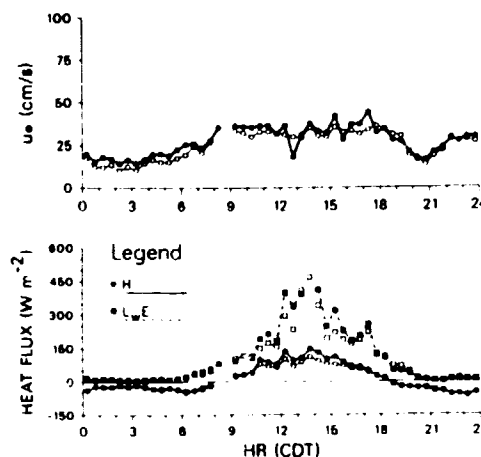


Figure 2.1. Friction velocities u_* and heat fluxes measured by eddy correlation (solid symbols) and by the normalized standard deviation method (open symbols) 12 m above a tall grass prairie in Kansas during June 1987.

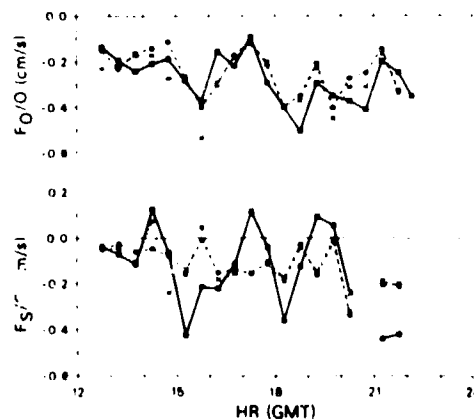


Figure 2.2. Ozone and sulfur dioxide fluxes normalized by mean concentrations above short grass, based on tower measurements made in the Federal Republic of Germany during late winter. The solid lines represent eddy correlation, and the other lines are applications of the normalized standard deviation technique, in which the standard deviations of the concentration fluctuations are extracted from noisy signals via calculations involving covariances with humidity and temperature fluctuations.

Table 2.1 summarizes some of the sensor characteristics needed for various levels of accuracy in flux estimates. Often the most demanding requirement is for fast response. Figure 2.3 shows the effects of a time constant (based here on a critically damped, first-order response) on the accuracy of eddy flux estimates, in a manner similar to that used nearly 30 years ago by Priestley (1959). The curves are calculated using the procedures described by Wesely (1983); we assume a perfectly responding vertical wind sensor colocated with a chemical sensor. If, as a rough approximation, we assume that the ratio of horizontal wind speed U to height z is 1 m s^{-1} per meter, then the time constant t_c should be $< 0.15 \text{ s}$ in order to ensure an accuracy of 10% or better. (A sensor with $t_c = 0.1 \text{ s}$ will measure 72% of the variance of the input signal, and its phase will be shifted by 32° at 1 Hz.) Alternatively, the calculation used to generate the curves in Figure 2.3 can be used to correct the measured flux due to the sensor time constant. This procedure becomes increasingly unreliable, however, when attenuation becomes more than about 30%.

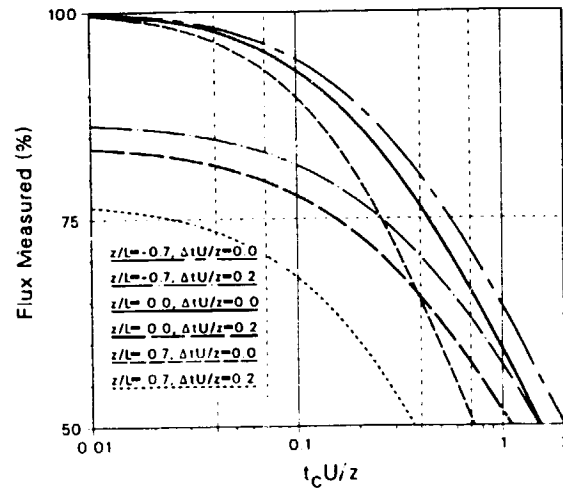


Figure 2.3. The calculated amount of chemical flux found by eddy correlation, in which the chemical sensor has a first-order response time constant of t_c and delay time of Δt , and otherwise ideal characteristics.

Table 2.1

Estimates of Some Sensor Requirements to Achieve Specified Levels Of Accuracy in Eddy-Correlation Flux Estimates from Towers*

	Frequency Response :		Delay Time Δt (s)	Separation Distance d
	Maximum t_c (s)	Minimum f (3dB) (Hz)		
10% accuracy	$0.15z/U$	$1.1U/z$	$0.1z/U$	$0.2z$
30% accuracy	$0.6z/U$	$0.3U/z$	$0.4z/U$	$0.5z$

*Neutral atmospheric stability is assumed and height z is between 1 and 50 meters.

A delay time Δt , such as might be associated with ducting the air sample from an intake to a sensing chamber, and a separation d between the species sensor and the vertical velocity sensor can cause significant flux underestimates. The effects of a delay time can be counteracted by shifting one time series with respect to the other in the analysis procedures. The effects of sensor separation can be minimized by mounting sensors as closely as possible, but this requires that the sensors be small; otherwise aerodynamic flow distortion can result. Small, aerodynamically streamlined sensors also have the advantage of reducing the effects of flow distortion on the measured flux (Wyngaard and Zhang, 1985; Wyngaard, 1988b). To a first approximation, calculations indicate that the flux attenuation for

certain values of $\Delta t U/z$ are equivalent to that obtained for the same values of $t_c U/z$. This near equivalence of delay times to time constants can be discerned from the curves shown in Figure 2.3. Field tests and calculations indicate that the attenuation associated with values of d/z multiplied by numerical coefficients ranging from 0.5 to 1.0 is about the same as corresponding values of $t_c U/z$, when the wind direction is perpendicular to a line connecting the vertical wind and chemical sensors.

Table 2.2 gives examples of the effects of poor sensor signal-to-noise ratios on half-hour eddy-correlation estimates of vertical flux. The noise is assumed to be nonatmospheric and not correlated with fluctuations of vertical wind velocity. Lenschow and Kristensen (1985), and Wesely and Hart (1985) have studied the effects of uncorrelated noise on covariance

estimates. The estimates of added run-to-run variability in Table 2.2 are based on the equations of Wesely and Hart (1985), in which the value of the numerical coefficient $f^* = 2.0$ is assumed for sensors contaminated with band-limited white noise and $f^* = 0.2$ for noise entering the signals at lower frequencies; the computed normalized standard deviations shown in Table 2.2 are proportional to $f^{*-1/2}$. These evaluations of precision are conservative, because the assumed values of f^* are smaller than those often obtained

in field experiments. Field experience has shown that standard deviations representing the run-to-run variability of eddy fluxes measured from towers with low-noise sensors over periods of 30 minutes typically correspond to about 15% of F_e/C . Hence, to calculate overall precision of measured actual eddy fluxes, the estimates shown in Table 2.2 should be vector summed with about $0.15F_e/C$. Such measures of variability are inversely proportional to the square root of the total length of sampling time.

Table 2.2
Estimates of Increased Variability of 30-Minute Averages
Of Eddy Fluxes from a Noisy Chemical Sensor*

Type of Noise	Mean Signal-to-Noise Ratio					
	300	100	30	10	3	1
Band-limited white noise	<0.01	0.01	0.02	0.08	0.25	0.82
Peaked near frequencies of flux-carrying eddies	0.01	0.03	0.08	0.25	0.75	2.6

*The estimates are expressed as the standard deviation of vertical flux divided by mean concentration at a height near 5 m, in units of cm s^{-1} . This assumes a moderate wind speed ($U \approx 3.5 \text{ m s}^{-1}$) with neutral atmospheric stability over a moderately rough surface, 40 cm s^{-1} for the standard deviation of vertical wind fluctuations (σ_w).

Eddy Accumulation

Eddy accumulation is a variant of eddy correlation that does not require fast-response chemical sensors (Desjardins, 1972; Speer et al., 1985). Instead, air is pumped into either of two traps for accumulating mass (or volume), depending on whether the local vertical wind velocity is positive or negative, at a rate proportional to its magnitude. Then the flux can be computed as the difference in mass, numerically weighted by the factor relating vertical wind speed to pumping rate. Also, it is usually necessary to determine any residual mean vertical velocity that is produced by the wind sensor, even after appropriate high-pass filtering of its signal, and to add its product with mean concentration to the computed eddy flux in order to obtain the best estimate of vertical flux. A fast-response wind sensor is needed, just as in conventional eddy correlation. Measurement periods can be fairly short, say 30 minutes, as in other micrometeorological techniques, but eddy accumulation can also be applied continuously over much longer time periods in order to accumulate amounts sufficiently large for precise chemical analysis (provided that such extended sampling is not prohibited by considerations of stationarity, as discussed above). A variation of

eddy accumulation that uses electronic memory bins rather than volume or mass accumulation is described by Desjardins (1977) and Desjardins et al. (1984).

Hicks and McMillen (1984) review many of the requirements for eddy accumulation, including that for extremely precise control over the pumping of sample air through the two collection systems. They find that the amounts of the collected chemical substances of interest should be measured with a relative accuracy of $\pm 0.4\%$ in order to achieve an accuracy in F_e/C of $\pm 0.1 \text{ cm s}^{-1}$. Although systems currently under development have shown marked improvement, further technological refinement is necessary in order to achieve accuracies comparable to those obtained with more conventional micrometeorological techniques. Despite difficulties, the ability to apply eddy accumulation to measuring the vertical flux of many trace substances remains very attractive because it requires relatively standard chemical analysis rather than the complicated fast-response methods used in normal eddy correlation. In addition, we should not rule out the possibility that innovations might reduce the stringent technical requirements for pumping and valve control (Reid et al., 1984; Buckley et al., 1988).

Vertical Gradients or Profiles

Gradient and profile techniques have been used extensively to estimate vertical fluxes of trace substances (e.g., Brutsaert, 1982) and have been used successfully to evaluate ammonia exchange, nitric acid vapor deposition, and biogenic hydrocarbon emissions from various surfaces (Dabney and Bouldin, 1985; Huebert and Rob rt, 1985; Lamb et al., 1985). These experiments are noteworthy because some other approaches have been significantly less productive; fast-response sensors for eddy-correlation and variance methods to measure such fluxes are not always available, and tracers or small-scale mass balance approaches usually require much more effort to achieve comparable accuracy. Gradient and profile techniques require measuring concentrations with a high degree of relative accuracy. Even when this is accomplished, one should expect half-hour estimates of F_e/C to have a minimum run-to-run variability corresponding to a precision (standard deviation) of about 15%.

In conventional profile techniques, concentrations of the substance of interest are measured at several levels on a tower, and profile is analyzed using flux-gradient relationships available in the scientific literature. Steady-state atmospheric conditions and a flat, uniform surface are required. Because of these stringent requirements, it is usually easier and more reliable to use a form of Bowen ratio similarity, in which the transfer velocities for trace substances are assumed to be the same across the same height interval at a given location. Although it is probably not always valid over nonuniform or densely vegetated surfaces, this approach has met with considerable success, most notably in the well-known Bowen ratio energy-balance technique for evaluating sensible and latent heat flux. For trace substances, a modified Bowen ratio is used, in which the concentration difference between the two levels of the trace substance of interest, ΔC , is measured with a high degree of relative accuracy, along with some reference quantity whose flux and difference can be measured fairly easily, e.g., temperature or water vapor.

A central assumption in the modified Bowen ratio approach is that the transfer velocity F_e/C is the same for the species of interest and the reference quantity. Experiments have shown that this is often a poor assumption over deep vegetative canopies, because the sources and sinks for different materials in the canopy tend to be dissimilar, even for heat and water vapor. Inside canopies, the lack of knowledge about the distributions of sources and sinks can effectively

prohibit use of profile and gradient methods as a primary means to infer vertical fluxes (Denmead and Bradley, 1987).

It is fairly standard practice in using conventional Bowen ratio methods to interchange the sampling positions of the two pairs of sensors approximately every 15 minutes. In this way, the question of accuracy of the absolute measurements of temperature or mass concentration is largely obviated. It is then the required relative accuracy, or combined precision of two measurements of concentration, that we must keep in mind. To this end, the magnitudes of the concentration differences divided by the mean concentration can be shown to be

$$\Delta C/C = -F_e(Ck u_*)^{-1} [\ln(z_2/z_1) + \psi_1 - \psi_2], \quad (2.1)$$

where u_* is the friction velocity, k is the von K rm n constant, and the ψ s are adjustments for atmospheric stability at the upper measurement height z_2 and the lower height z_1 . Values of u_* range from 10 cm s⁻¹ for light winds to 100 cm s⁻¹ for strong winds over deep vegetative canopies. Table 2.3 shows some results of the above equation for a twofold change in height, a range of values of normalized fluxes, and various atmospheric stability conditions. For example, for neutral atmospheric stability and moderate wind speeds over low vegetation, the concentration difference across a twofold change in height would be approximately 5% of the magnitude of the normalized mean concentration $|\Delta C/C|$ for $|F_e/C| \approx 1.0$ cm s⁻¹. Thus, to achieve a precision of 10% in the flux estimate, the concentrations would have to be measured with a combined precision of 0.5%. This required precision value would be proportional to the normalized flux and, for neutral stability, would double for each additional factor of two between the heights of measurement.

Variance Techniques

Variance techniques provide indirect estimates of vertical fluxes but require fast-response instruments of the type used in eddy correlation. The computations tend to be simpler than in the case of eddy correlation, since a measurement of vertical wind speed is sometimes not needed and the requirement for fast response can be slightly reduced in some cases. Variance techniques require additional information to obtain the sign of the flux. The comments to follow are largely based on some recent work by Wesely (1988).

Table 2.3

Value of Normalized Difference in Concentration ($\Delta C/C$), Expressed in Percent, Calculated for a Two-Fold Change in Height (z_2 is the Upper Level) for Various Atmospheric Stability Conditions, Emission (or Deposition) Velocities (F_e/C), and Friction Velocities (u_*)

u_*	Moderately Unstable $z_2/L = -0.7$			Neutral $z_2/L = 0.0$			Moderately Stable $z_2/L = 0.7$		
	F_e/C : 0.1	0.5	1.0	0.1	0.5	1.0	0.1	0.5	1.0 cm s ⁻¹
Light winds									
10 cm s ⁻¹	0.6%	2.8%	5.6%	1.7%	8.7%	17.3%	6.1%	30.5%	61.1%
20	0.3	1.4	2.8	0.9	4.3	8.7	3.1	15.3	30.5
Moderate winds									
30	0.2	0.9	1.9	0.6	2.9	5.8	2.0	10.2	20.4
60	0.1	0.5	0.9	0.3	1.4	2.9	1.0	5.1	10.2
Strong winds, deep vegetation									
100	*	*	*	0.2	0.9	1.7	*	*	*
Formulation includes u_*	56 $F_e/(Cu_*)$			173 $F_e/(Cu_*)$			611 $F_e/(Cu_*)$		

*Represents unrealistic atmospheric conditions.

In an approach similar to the modified Bowen ratio technique discussed above, the ratios of the standard deviations of two scalar quantities can be used to estimate the flux of one if the flux of the other is measured, without knowledge of atmospheric stability. With variance techniques, the main constraint on accuracy is much different than with mean gradient measurement, in that errors depend directly on sensor noise that is unrelated to atmospheric fluctuations. Related variance methods include normalized standard deviation and the correlation coefficient technique, which can be successful if atmospheric stability is evaluated and certain semi-empirical functions are known. Iterative calculations involving measured variances of fluctuations of temperature and vertical wind speed can be used in place of direct flux measurements, in order to determine atmospheric stability.

Examples of the results of this approach are shown in Figures 2.1 and 2.2. These results demonstrate that variance techniques provide a means of checking results from eddy correlation and seem to provide estimates of fluxes with less run-to-run variability. Further, recent work has shown that the atmospheric signal of concentration fluctuations can be extracted from a

noisy signal if the standard deviation is estimated as the ratio of a covariance with another scalar quantity to the standard deviation of that "reference" scalar; the reference scalar must be measured with a very large fluctuation signal-to-noise ratio. Alternatively, three covariances utilizing two reference scalars can be employed successfully. This assumes that the correlation coefficient between any two of the scalar quantities is unity, which appears to have been the case for the successful measurements illustrated in Figure 2.2, where humidity and temperature were used as reference scalars.

Aircraft-Based Flux Measurement Systems

The primary advantage of aircraft for measuring fluxes lies in their mobility. An aircraft can probe the entire depth of the PBL (with the exception of the first few meters) and can obtain statistically significant measurements about an order of magnitude faster than is possible with tower measurements. Furthermore, an aircraft can be used for either vertical profiling, horizontal legs, or some combination of the two. Compared to fixed-point measurements, which are limited to sampling air advected by the wind, aircraft

can measure along a path at any arbitrary angle with respect to the wind and can measure in a frame of reference that moves with the wind. This makes it possible to use aircraft in budget studies: evaluating the transport and time rates of change of a particular species and thereby obtaining as a residual the rate of production or loss by chemical reactions. For the most part, towers are not very suitable for obtaining flux measurements over inhomogeneous terrain and are difficult to use in remote land areas (e.g., forests, swamps, and tundra) and over the ocean. By contrast, these situations present no particular problems for aircraft; indeed, low-level measurements are generally easier to carry out over sparsely populated regions and the ocean than over populated regions.

Unfortunately, the aircraft's mobility also has its disadvantages. Aircraft motion needs to be accurately measured and corrections applied to the data. Since aircraft need to fly relatively fast compared to the mean wind speed in order to stay airborne, faster instrument response is required than for fixed-point measurements. Furthermore, corrections may have to be made for compressibility, adiabatic and frictional heating, and flow distortion induced by the aircraft. Long uninterrupted time series and changing or modifying instruments in flight are also not possible. Generally, instrument packaging requirements are also more stringent on an aircraft than at fixed-point sites, for example, constraints on size, weight, power consumption, and operation in a vibrating and turbulent environment.

It is clear that fixed-point and aircraft measurements are complementary—the disadvantages of one are compensated for by the advantages of the other. The effective design of field programs will, therefore, often include both techniques. There are numerous examples of coordinated experiments that have included both aircraft and fixed-point flux measuring systems. Recent cases are the Amazon Boundary Layer Experiment (ABLE-2B) and the First ISLSCP (International Satellite Land-Surface Climatology Project) Field Experiment (FIFE).

Eddy Correlation

Flux measurement from aircraft entails observations of both the air velocity and the quantity whose flux is being measured. Because the aircraft is a moving platform, air velocity is not a straightforward measurement (Lenschow, 1986). An aircraft has complete three-dimensional freedom to move, depending on control surface and power settings and on velocity and density fluctuations of the air. Therefore, the velocity and angular orientation of the aircraft relative to the earth as well as the velocity of the air relative to the aircraft must be measured. Since the aircraft typically flies an order of magnitude faster than the wind, measuring the air velocity involves calculating

a small difference between two large numbers.

The airplane velocity can be obtained from integrated accelerometer outputs on an inertial navigation system (INS), from radiation transmitting and receiving devices such as Doppler radars or radar altimeters, or by radio navigation techniques. For turbulence measurements, the components of airplane velocity can be measured with sufficient resolution and response time with the available INS. Furthermore, the INS can also provide the fast-response, high-resolution attitude angles that are required to transform air velocity measurements into an earth-based frame of reference.

The longitudinal component of air velocity (true airspeed) is usually obtained from the pressure difference between the dynamic pressure port of a Pitot tube and the static pressure from either the Pitot tube or a static port on the aircraft fuselage. The pressure difference must be corrected for air density, which is calculated from static pressure and air temperature, before computing the true airspeed. The transverse (lateral and vertical) air velocity components are usually measured either by means of vanes or from pressure differences between ports separated by 60° to 90° on a hemispherical probe or on the nose of the aircraft itself. If vanes or a hemispherical probe are used, the sensors are usually mounted on a boom forward of the aircraft to reduce as much as possible the airflow distortion induced by the aircraft. This is a convenient location as well for other sensors, such as thermometers or hygrometers, whose outputs may be affected by flow distortion.

Instead of trying to minimize the flow distortion effects of the fuselage, it is possible to make use of measurements of pressure perturbations on the nose of the aircraft that are caused by the fuselage. Since these pressure perturbations are approximately linearly related to the flow angles, they can be used to measure the flow angles. As pointed out by Wyngaard (1988b), flow distortion can seriously contaminate flux measurements from aircraft if species densities are measured in regions of strong flow distortion, such as near the fuselage. Thus, measuring the transverse velocity by means of ports on the aircraft nose, without using a nose boom, may not obviate the need for some kind of structure that would allow the measurement of species density fluxes in a region not strongly affected by flow distortion. Flow distortion effects do not impact fluxes if mixing ratio is measured instead of partial density.

Another way to obtain airspeed and flow angles is by measuring the Doppler shift of reflected laser beam transmissions in front of the aircraft (Keeler et al., 1986). This offers the possibility of an absolute velocity measurement in all weather conditions, including flights in clouds and precipitation.

Because of the relatively high speed of aircraft relative to the wind, the requirement for accuracy of

air flow and attitude angles is stringent. A reasonable figure for short-term velocity accuracy necessary to measure turbulence fluctuations is 0.1 m s^{-1} . This corresponds to an angular accuracy of 0.001 rad or 0.06° . Attitude angles are difficult to measure this accurately except with an INS.

The vertical turbulence flux of a species with instantaneous concentration $C(t)$ is given by \overline{wC} , where $C = \overline{C} + c$, \overline{C} is the mean of C , c is a departure from the mean, w is the vertical air velocity, and the overbar denotes an average over a length (or time) long enough to give a statistically reliable result. The mean vertical velocity near the earth's surface is usually assumed to be zero, but, as pointed out earlier, it is necessary to correct for effects caused by heat and water vapor fluxes if concentration is measured in units other than mixing ratio with respect to dry air (Webb et al., 1980). Earlier, we also pointed out that measuring species density instead of mixing ratio can result in significant errors in flux measurement due to flow distortion (Wyngaard, 1988b); these are important reasons to strive for instruments that can measure mixing ratio.

Since the flux is computed from concentration (preferably mixing ratio) fluctuations, an accurate mean value of the species concentration is not necessary; only the fluctuations need to be resolved. Throughout most of the mixed layer, we find that the normalized standard deviation of species concentration σ_c/\overline{C} , must be > 2 , where $\overline{C} = (\overline{wC})_0/w_*$, w_* is the convective velocity (typically of the order of 1 m s^{-1}), and $(\overline{wC})_0$ is the surface flux of C . As a practical rule, we would like to resolve at least 10% of the standard deviation, so that we would like to have a minimum resolution $e' \sim 0.2(\overline{wC})_0/w_*$, in order to be able to measure flux of C throughout most of the mixed layer. As pointed out earlier, it is also possible to use noisy species sensors if the noise is not correlated with the vertical velocity.

Another important question in measuring turbulence fluxes is the averaging length L_{wc} (or time, in the case of fixed-point measurements) needed to obtain a satisfactory measurement of \overline{wC} in a horizontally homogeneous stationary field of turbulence. As discussed by Lenschow and Stankov (1986), the relative error in a flux measurement over a distance L_{wc} is

$$\epsilon_{wc} \approx \left[\frac{2(r_{wc}^{-2} + 1)\lambda_{wc}}{L_{wc}} \right]^{1/2}, \quad (2.2)$$

where λ_{wc} is the integral scale of \overline{wC} and r_{wc} is the correlation coefficient between w and c . Lenschow and Stankov (1986) have used observations to estimate L_{wc} for 10% accuracy (i.e., $\epsilon_{wc} = 0.1$) as $L_{wc}/z_i \approx 430(z/z_i)^{2/3}$, where z_i is the PBL height. This means that a flight leg of about 200 km is needed for 10% precision of flux measurement in the CBL above the

surface layer. (This convective layer is often referred to as the mixed layer.)

In a similar way, averaging length or time can be estimated in the surface layer (where the turbulent eddies scale with height above the surface) for both tower and aircraft flux measurements. Figure 2.4 presents a normalized cospectrum of vertical velocity and a scalar variable (e.g., species concentration) in the surface layer of a neutral or convective boundary layer. (The cospectrum can be considered a decomposition of the flux as a function of frequency.) The data for this curve were obtained from Schmitt et al. (1979), who plotted cospectra of both water vapor and temperature versus vertical velocity computed from tower measurements. The curve is normalized so that the area under the curve gives unity scalar flux, i. e.,

$$\int_0^\infty [nC_{wc}(n)]d \ln n = 1, \quad (2.3)$$

where C_{wc} is the cospectrum and $n \equiv fz/U = z/\lambda$ is the normalized frequency. This can be used to provide a rule of thumb for the minimum averaging time T required to obtain an accurate flux estimate, and the maximum allowable sampling interval Δt required to resolve species fluxes as a function of wind speed and height for tower measurements, and airspeed and height for airplane measurements in the surface layer.

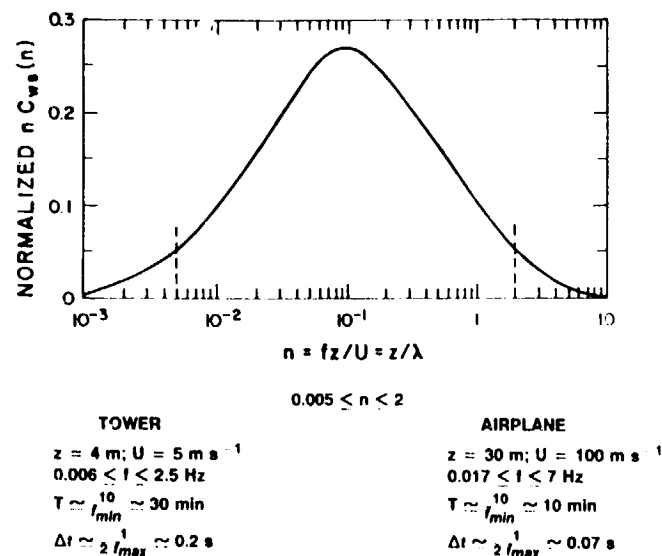


Figure 2.4. A schematic diagram of a typical cospectrum of vertical velocity and a scalar variable in a convective surface layer. The examples show typical averaging times T and sampling intervals Δt for flux measurements from both towers and aircraft.

The two dashed vertical lines at $n = 0.005$ and $n = 2$ are the frequencies at which the curve of frequency times the cospectrum is $\sim 20\%$ of its

maximum; the maximum is at $n \approx 0.1$. The flux contained within these two limits is $\sim 93\%$ of the total flux. The value of T is estimated over a period that includes at least ten samples of the lowest frequency f_{min} that contributes significantly to the flux, while Δt is estimated as the reciprocal of twice the highest frequency resolved in the cospectrum f_{max} (also known as the Nyquist frequency) that contributes significantly to the flux.

Chemical species sensors must either be placed near the air flow sensors, or the longitudinal spatial separation must be taken into account by shifting the time base of the recorded signals so that the signals are aligned in time. An additional delay may result from ducting air from outside through a sensor located inside the aircraft. If the species sensors are displaced transversely from the air flow sensors, the cospectrum of the the velocity component and species concentration is reduced by an amount that can be computed by the formulation derived by Kristensen and Jensen (1979).

Several efforts have been made in the last decade to assess the accuracy with which aircraft sense the dynamic and thermodynamic fluctuations of the atmosphere. This can be done in several ways, but one of the most useful involves intercomparison of measurements from two aircraft flying in wingtip-to-wingtip formation (LeMone and Pennell, 1980; Nicholls et al., 1983). Lenschow and Kristensen (1988) developed an expression for the error variance of a variable measured on each aircraft as a function of averaging time and separation. They show that for averaging times of more than a few minutes, the error variance contributed by the spatial variability of the turbulence in the CBL is small enough that wingtip-to-wingtip intercomparisons can be useful for intercalibration of aircraft systems. Such intercomparisons should be a part of any measurement program involving multiple aircraft. Because of the complexity of aircraft technology, calibration drifts and other errors are always a possibility and may not be obvious from a routine inspection of data.

Figure 2.5 shows an example of airplane flux measurements over two different types of surfaces, demonstrating how horizontal variability in temperature, humidity, and ozone fluxes can be resolved with aircraft measurements. The value of aircraft is maximized when their measurements are combined with those from towers or other platforms to obtain concurrent long-term flux measurements from particular locations. Comparisons between surface platforms and low-flying aircraft (Nicholls and Readings, 1979; Davidson et al., 1988) indicate that

there is agreement between platforms that is within the statistical uncertainty discussed above.

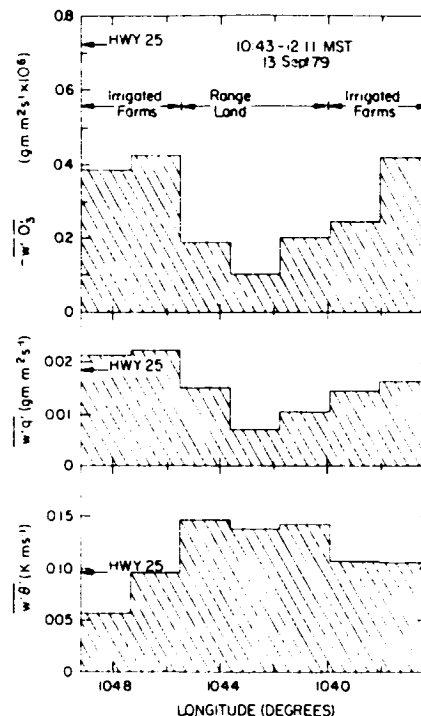


Figure 2.5. Results of aircraft eddy-correlation flux measurements of ozone, water vapor, and temperature on an east-west flight track at about 200 m above ground over eastern Colorado. Each estimate is an average of an eastward and a westward flight leg. The flux estimate labeled 'HWY 25' was obtained from north and south flight legs very nearly over Interstate Highway 25 directly north of Denver (from Lenschow et al., 1981).

Budget Studies

The budget for the mean concentration of a species C is given by

$$\frac{dC}{dt} = \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = -\frac{\partial \overline{w\bar{c}}}{\partial z} + Q_c, \quad (2.4)$$

where U is the mean wind speed oriented along the x axis and Q_c is the sum of the sources and sinks of C due to chemical reactions. With an aircraft, we can measure either (1) with respect to the local flow, and estimate only the time rate of change of mean species concentration (the expression to the left of the equal sign), or (2) with respect to a fixed geographic location, and estimate both the time rate of change and the horizontal advection of the mean concentration (the middle expression).

Integrating (2.4) vertically through the depth of the CBL for case (2), and using the relation for the flux at the top of the boundary layer (Lilly, 1968) $(\overline{w\bar{c}})_{z_t} = -w_* \Delta C$, where ΔC is the change in C across the top

of the PBL and w_e is the entrainment velocity through the top of the PBL, we have

$$z_i \frac{\delta \langle C \rangle}{\delta t} \approx (\overline{w\bar{c}})_0 + w_e \Delta C - \langle U \rangle z_i \frac{\partial \langle C \rangle}{\partial x} + \langle U \rangle \Delta C \frac{\partial z_i}{\partial x} + \langle Q_c \rangle z_i, \quad (2.5)$$

where δC is the change in C over a time interval δt , and $\langle \rangle$ denotes an average through the depth of the boundary layer.

All the terms in (2.5), except the last, can be measured in a well-designed experiment by using aircraft over a horizontally homogeneous surface in a CBL with a well-defined top. The aircraft must be equipped to measure both the mean and turbulent fluctuations of C , as well as turbulent fluctuations of w . Once w_e has been determined from measurements of the quantities in the relation $w_e = -(\overline{w\bar{c}})_z / \Delta C$ by use of a particular scalar variable (e.g., temperature, humidity, or ozone), it can then be used in evaluating the budgets of other scalars for which turbulent fluctuations may not be measured, provided the mean concentration of the scalars both within and across the top of the PBL are measured. In that case, if there are no significant chemical sources or sinks, the surface fluxes of other scalars may be estimated; or, alternatively, if surface flux of a trace species can be estimated from, for example, a deposition velocity, an emission rate, or surface-based flux measurements, it may be possible to estimate the chemical reaction rate of that species. Tracer species, such as radioactive isotopes or chemical species not found naturally in the environment, can also be useful as surrogates in carrying out budget studies over particular biomes. Further details of measurement requirements for budget studies are given by Lenschow (1984). Williams (1982) discusses the accuracy required for obtaining deposition velocity from measurements of the mean horizontal advection into and out of a reference "box."

Enclosure-Based Flux Measurement Systems

While methods that do not disturb the sample area will always be preferred for measuring trace gas fluxes, there are circumstances in which they are not feasible or desirable, and enclosures are the only practicable technique. Such circumstances might arise because (1) available sensors have limited sensitivities or response times, (2) the large uniform areas required in conventional micrometeorological approaches are not available, or (3) the corrections for density effects associated with the simultaneous transfers of sensible heat and water vapor, as discussed earlier, make micrometeorological approaches difficult if not impractical. A number of the trace gas fluxes of interest here fall into the last category.

As Table 2.4 shows, for some gases with large emission rates and small backgrounds (e.g., NH_3), the Webb (Webb et al., 1980) corrections are negligible, but for others (such as CO_2 and N_2O), they can be as large as or larger than the true flux (e.g., Figure 2.6). In this situation, the corrected flux becomes questionable. Furthermore, there are many situations (such as within plant canopies) where conventional micrometeorological approaches cannot be used (Denmead and Bradley, 1987). For these cases, enclosure techniques may be the only feasible alternative.

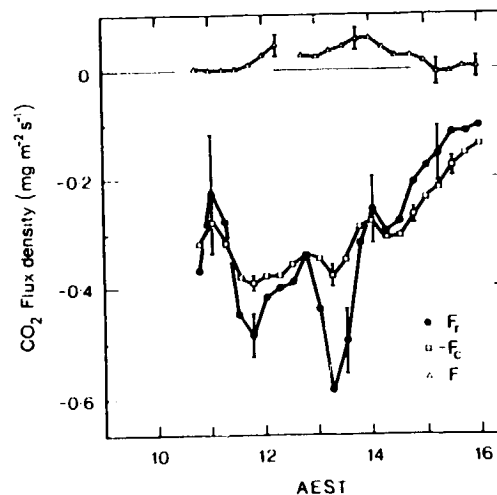


Figure 2.6. Fluxes of CO_2 versus time over a bare field and corrections for density effects associated with simultaneous transfer of heat and water vapor (from Leuning et al., 1982). The flux F is true CO_2 flux measured by an appropriate gradient method. The flux F_e is the correction (calculated following Webb et al., 1980), which should be added to the measured flux F_r to obtain the true flux. The measured eddy flux of CO_2 over the bare field was about 50% of what might be expected over a healthy wheat crop.

The disadvantages of enclosures are: (1) they interfere with the transfer processes that normally operate in the natural environment, (2) they create artificial microclimates, and (3) they sample only a very small area of the surface.

Gas Exchange at the Soil Surface

Enclosures work by restricting the volume of air with which gas exchange occurs, thereby magnifying changes in gas concentration. Two basic systems are employed: closed systems, in which no replacement of air in the chamber head-space occurs and the composition changes continuously, and open systems, where air flows through the enclosure at a controlled rate and the composition approaches steady state (different from ambient).

In the first case, the surface flux density is calculated from the rate of change of species

Table 2.4
 Corrections for Density Effects Due to Heat and Water Vapor Transfer for Some Trace Gas Fluxes

Gas	References	Surface	Typical Gas Density $\text{kg m}^{-3} \times 10^9 \text{ STP}$	Typical (corrected) Flux $\text{kg m}^{-2} \text{s}^{-1} \times 10^9$	Ratio Corrections/Flux
CH ₄	Bartlett et al., 1985	Salt marsh	1000	0.25	0.56
CH ₄	Seiler et al., 1984	Rice paddy	1000	4	0.04
CO ₂	Denmead, Bradley & Ohtaki (unpublished)	Pine forest (winter)	600×10^3	-380	0.76
NH ₃	Denmead et al., 1974	Grazed pasture	10	0.5	0.02
NH ₃	Harper et al., 1983	Fertilized pasture	600	10	0.06
NH ₃	Hutchinson et al., 1982	Cattle feedlot	1200	103	0.01
N ₂ O	Denmead et al., 1979	Grassland	670	0.06	10.50
N ₂ O	Mosier & Hutchinson, 1985	Cornfield	670	0.75	0.84
N ₂ O	Lemon, 1978	Muck soil	680	-2.5	0.25
NO	Galbally & Roy, 1978	Pastures, soils	4	0.007	0.53
NO ₂	Wesely et al., 1982b	Soybeans	15	-0.076	0.18
O ₃	Wesely et al., 1982b	Soybeans	75	-0.72	0.05
SO ₂	Galbally et al., 1979	Pine forest	24	-0.04	0.31
SO ₂	Galbally et al., 1979	Rye grass	33	-0.19	0.07

concentration; in the second, from the difference in the concentration of species entering and leaving the enclosure (Denmead, 1979). Both systems have problems: closed systems, through the build-up in gas concentration in the enclosure air and its effects on soil emission rate; open systems, because of the slow approach to equilibrium and the possible effects of air flow on pressure inside the enclosure.

For convenience in discussion, we consider gas emissions, i.e. situations in which gas is produced in the soil and emitted to the atmosphere; the same considerations apply to gas uptake.

The obvious disadvantage of closed systems is that concentrations of gas in the enclosed atmosphere can build up to levels where they inhibit the normal emission rate (or, where uptake is occurring, concentrations can be depleted enough to reduce gas exchange significantly). Denmead (1979) gives some examples from studies of the emission of N_2O in closed systems (Figure 2.7). Most investigators limit enclosure times to periods in which the gas concentration changes linearly with time, indicating a steady uninhibited flux rate. Others (Mosier and Hutcheon, 1985; Galbally et al., 1985) employ formulae that allow for the effects of the increased concentration on the emission rate,

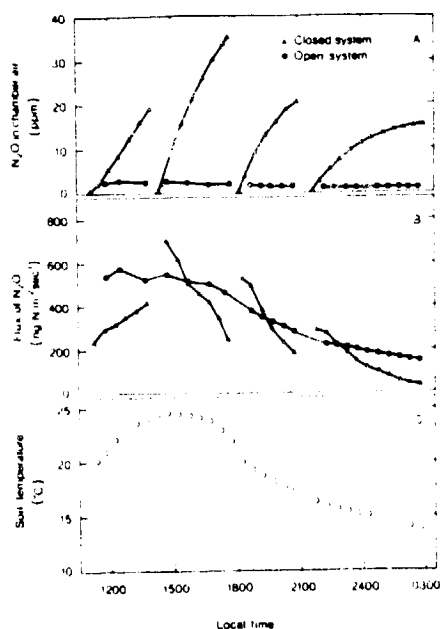


Figure 2.7. Concentrations and fluxes of N_2O and soil temperatures in closed and open enclosure systems operated side by side (from Denmead, 1979). Breaks in the records are where lids were removed from enclosures and then replaced. Flux of N_2O in the open system followed variation in temperature of the top 0.03 m of soil. Removal and replacement of the lid had no apparent effect. The flux of N_2O in the closed system was high immediately after lid replacement, when N_2O concentration in soil air was much higher than in the enclosure air, then declined as N_2O in the enclosure built up.

but this procedure assumes that the concentration of gas in the soil air is unaffected by changes in concentration in the atmosphere above. In fact, changes in the enclosure gas concentration generate changes in soil gas concentration, which can have profound influences on the rates of gas emission at the soil surface. Denmead (1979) details such effects experimentally (Figure 2.7), and Jury et al. (1982) have considered the problem from a theoretical standpoint.

Most operators of closed systems seeking "continuous" measurements try to restrict enclosure periods to quite short times, typically 15 to 20 minutes, and allow some hours for the soil gas profile to re-establish itself before measuring again at the same site (e.g., Blackmer et al., 1982). Open systems are, of course, more suited to continuous measurement.

For some gases, such as NO , the apparent exhalation rate results from a quite complicated balance between the actual emission rate, chemical transformations in the enclosure atmosphere, and equilibria between the emitted gas and the soil and/or vegetation in the enclosure. Galbally et al. (1985) describe a method for estimating the true emission of NO from the apparent rate that involves the estimation of as many as three coefficients.

Absorption of emitted species, such as NH_3 and sulfur gases, on walls and tubing is often a serious problem and should always be investigated before enclosures are employed. Even in flushed systems, corrections may be needed when the source strength is changing on time scales that are short in comparison with the flush-gas residence time or the sample acquisition time (Goldan et al., 1987).

Gas produced in the soil diffuses along a concentration gradient to the soil surface, where it is dispersed into the air above. The transfer process at the soil-air interface can be described in terms of a surface-to-air transfer coefficient k defined by

$$F_c = k(\rho_{co} - \rho_{ca}), \quad (2.6)$$

where ρ_{co} and ρ_{ca} are species densities at the soil surface and in the air above. If k in the enclosure is different from that in the field, the soil and ambient gas concentrations at equilibrium (when the surface flux balances the rate of production) will also be different. Thus, when the enclosure is first operated, there will be a period in which gas concentrations in soil and air adjust to new equilibrium values. Estimates of the equilibrium flux during this time will be erroneous.

Denmead (1979) gives an approximate solution for the time for equilibration following a step change in k . In the enclosure systems he describes, k was about 1/10 that in the open, and equilibration required from 15 to 90 minutes, depending on flow rate.

While exact knowledge of k is not usually necessary provided sufficient time is allowed for equilibration, there are some situations involving post-emission gas reactions in the enclosure, such as those

described for NO , where the value of k is required in calculating the surface exchange rate (Galbally et al., 1985). A similar situation probably exists for NH_3 when vegetation is present in the enclosure. Denmead et al. (1976) found a closed cycle in plant canopies, in which NH_3 released at the soil surface was absorbed by the foliage above (Figure 2.8).

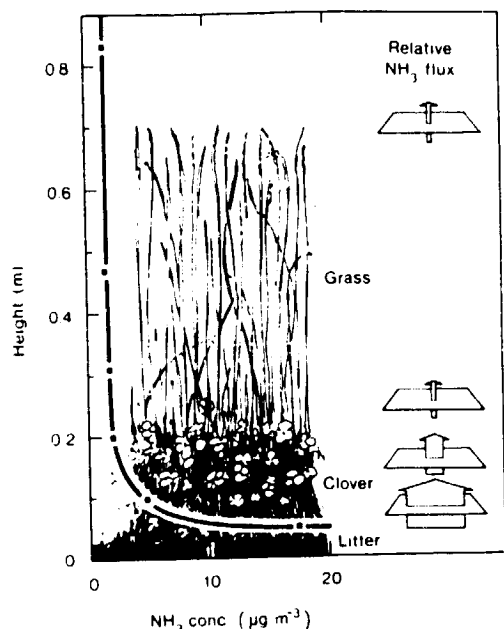


Figure 2.8. A schematic depiction of a closed ammonia cycle in a pasture canopy (after Denmead et al., 1976). Ammonia released from decomposition of litter at the ground is subsequently reabsorbed by foliage above.

Finally, we note that whereas k does not usually influence the production rates of gases in soils, it may have a strong influence on gas transfer between the air and plants, and the air and water. This is discussed in later sections.

The question of whether atmospheric pressure fluctuations might enhance the diffusion of gases across the soil surface has been debated for a long time (Fukuda, 1955; Farrell et al., 1966; Kimball and Lemon, 1971; Delwiche et al., 1978). The topic has been examined in the context of enclosure systems by Kimball (1978) and Lemon (1978) among others, but there does not yet seem to be a clear consensus on its importance. It is generally recommended that the enclosed atmosphere should be connected with the outside atmosphere so that pressure fluctuations can propagate into the enclosure head-space, although the amount of filtering of the pressure fluctuations that occurs in the connecting apertures is usually not known.

Perhaps of as much importance is the question of the best aerodynamic design for enclosures. It seems possible that the bluff-body effects of many enclosures on the pressure field could induce viscous flows of air through the soil into the enclosure head-

space, with important consequences for the apparent emission rate. Again, there does not seem to be any recent research on this topic, but it would seem to lend itself nicely to experimental investigation.

A related question is the effect of gusts in sweeping out the contents of open enclosures. Denmead (1979) recommends the use of interior baffles to overcome the problem, but, again, proper aerodynamic design seems to be required.

Probably more important than all of these is the problem created by pressure deficits or excesses in the head-space, which leads to flows of air from or to the underlying soil. Small pressure changes are easily induced in the head-space through withdrawing air from it or pumping air into it, and they can have spectacular effects. Denmead (1979), for instance, found that a pressure deficit of only 100 Pa in the enclosure was sufficient to induce a tenfold increase in N_2O emission (Figure 2.9).

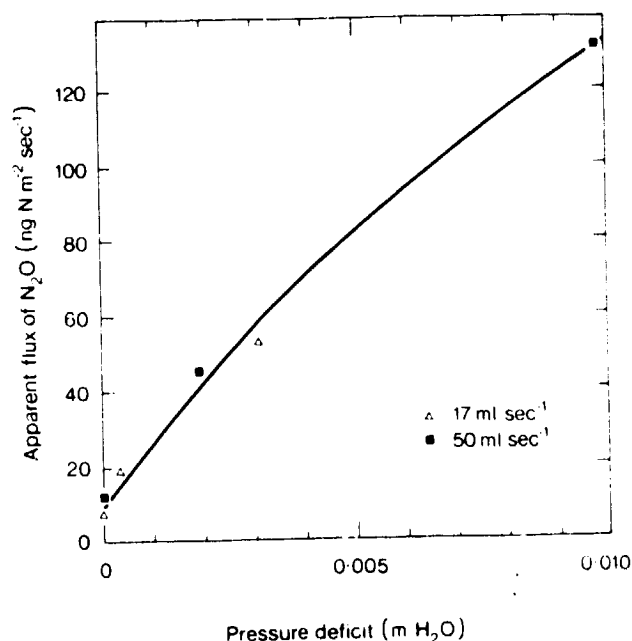


Figure 2.9. Effect of pressure deficit in an open enclosure system on flux of N_2O from soil (Denmead, 1979).

Many of the trace species of interest result from biological activity: e.g., CO_2 , CH_4 , NH_3 , N_2O , and NO . Most biological processes are temperature dependent, with a Q_{10} (change of activity for a 10°C change in temperature) of 2 to 3, and undergo large diurnal changes (e.g., Denmead et al., 1979; Figure 2.7). Therefore, maintaining a soil temperature inside the enclosure that is close to that outside is important. However, soil temperature results from energy partitioning at the soil surface; maintaining the natural energy balance of the outdoors is a virtual

impossibility in enclosures. If gas flux measurements are to extend over several days, it may be wiser to use several short enclosure periods than to measure continuously at the same site.

Given the temperature dependence of many trace gas emissions, and uncertain phase relationships resulting from differing production zones and differing diffusion properties in the soil profile (Blackmer et al., 1982; Jury et al., 1982), the minimum period for flux measurement would seem to be 24 hours. Spot measurements, although often published, are usually quite misleading; the practice of reporting spot measurements in "annual" units like "kg ha⁻¹ year⁻¹" can only be deplored. Furthermore, some species, such as N₂O, emit episodically, depending on rainfall and soil water supply. The minimum measuring period might then be an entire drying cycle.

Jury et al. (1982) raise questions with more general implications. These center around the sites of gas production in soils and the slowness of gas transfer by molecular diffusion in the soil air. When production occurs deep within the soil, the appropriate sampling period for a production event may be many days. (Today's N₂O emissions, for instance, may be last week's denitrification.) If continuous sampling over several days is required, then open systems, which have minimal effects on soil concentration profiles, seem to be the only useful option.

Fluxes from soils are distinguished by their extreme point-to-point variability. Variations in soil emission rates of a factor of two within distances of a few meters are commonplace, and ten-to-one variations occur quite frequently (e.g., Matthias et al., 1980; Galbally et al., 1985). Therefore, enclosure measurements tend to be highly variable. By contrast, tower measurements typically integrate fluxes over hundreds of square meters upwind of the site. Consequently, although enclosures can detect minute fluxes of trace species, the measurements must be replicated extensively (probably more than is usually practiced). The fast-developing field of geostatistics may offer means for choosing the minimum number of replicates, and for statistically sound interpolation and extrapolation procedures.

Gas Exchange between Plants and the Air

Many of the considerations applying to gas exchange at the soil surface apply here as well, but gas exchange between plants and the air is generally a more complicated process. For one thing, there are many exchange surfaces: the soil surface and all the leaves in the plant canopy. Furthermore, gas exchange to and from leaves usually involves two stages: transport in the air across the often-turbulent leaf boundary layer, and diffusion through stomata, small pores in the leaf connecting its internal air space with the outside. The stomatal opening is affected by many

environmental factors, including humidity, water stress, light, and CO₂ concentration. Thus there is a pressing need to keep the enclosure microclimate close to that outside, so that the plant physiology and gas exchange are near normal. Providing sufficient ventilation to keep CO₂ concentrations close to ambient is one such requirement that is often neglected.

A further complication for many species is the existence of a compensation point, i.e., a non-zero gas concentration in the leaf air spaces that is in equilibrium with metabolites in plant cells. If the ambient concentration exceeds the compensation point, the gas is taken up by the plant from the atmosphere, but if the ambient concentration is less than the compensation point, the gas is emitted to the atmosphere. Ammonia is one such example, and it seems probable that compensation points exist for other nitrogen compounds, like NO_x and amines (Farquhar et al., 1983), and perhaps for some sulfur-containing gases as well.

For such chemical species, a correct estimate of the gas flux depends on maintaining gas concentrations in the air within the enclosure very close to ambient. Closed enclosure systems will thus be unsuitable, and open systems will require large ventilation rates so that leaf boundary-layer resistances are much smaller than stomatal resistances.

The studies of Ashenden and Mansfield (1977) on SO₂ damage to plants are noteworthy here. Much of the early work with SO₂ was done in chambers with low rates of air movement, in which relatively high concentrations of SO₂ were reported to be harmless to plants. However, through wind-tunnel experiments, Ashenden and Mansfield showed that the lack of effect at low wind speeds was due to the relatively high boundary-layer resistance, which was almost twice the leaf diffusive resistance. At higher wind speeds, the boundary-layer resistance was only 20% of the diffusive resistance, and much more SO₂ was taken up by the plants. Ashenden and Mansfield went on to suggest that the sensitivity of a plant to a particular pollutant should not be measured in terms of only the concentration and length of exposure.

Gas Exchange at a Water Surface

There are two obvious problems involving gas exchange at a water surface. One is the very strong dependence of gas exchange on wind speed. Rates of gas transfer from the bulk of the water to the water surface and from the surface to the atmosphere are strong functions of wind speed, or friction velocity (Broecker and Peng, 1974; Deacon, 1977; Wesely et al., 1982a; Liss, 1983). Hence, flux rates in enclosures, with preset ventilation rates, will usually not be representative of fluxes from undisturbed water bodies. The best use of enclosures would seem to be to establish the wind-speed dependence of the

relevant transfer coefficients for application to "real-world" situations, as Sebach et al. (1983) have done for methane emission. However, as these authors point out, a limitation in this procedure is that it is usually not possible to reproduce in enclosures the wind-wave interactions and bubble escapes of larger water bodies, both of which are believed to enhance gaseous emissions in high winds (e.g., Wesely et al., 1982a).

A second problem in the use of enclosures, particularly over shallow bodies of water, is possible changes in the energy balance: changes in the receipt and loss of radiant energy because of the enclosure walls, changes in energy partitioning because of the different net radiation and different wind speeds, and changes in the resulting surface temperature. In turn, these can be expected to influence thermal stratification and convection patterns in the water

as well as surface gas concentrations. The great importance of all these factors to gas transfer between the bulk of the water and the surface in shallow bodies of water has been demonstrated by Leuning et al. (1984) and Trevitt et al. (1988).

Conclusions

The discussion here points out that there is no single system or technique for flux measurement that is universal. Rather, a combination of techniques must be used, depending on the environmental conditions and the technology of species measurement. There are also situations where flux measurements may not be feasible by any means known at present, for example, in cases of extreme horizontal inhomogeneity or of species with extremely short lifetimes or small fluxes.

3 STATUS OF CHEMICAL SENSORS FOR FLUX MEASUREMENTS

S. M. Anderson, A. C. Delany, F. C. Fehsenfeld, P. D. Goldan, C. E. Kolb, B. A. Ridley, and L. P. Steele

Typical mixing ratios for the priority atmospheric trace species discussed in Chapter 1 range from the parts per million to the parts per trillion level. Accurate measurement of such small chemical concentrations under field conditions, particularly of reactive species such as NH_3 , NO_2 , SO_2 , H_2O_2 , CH_2O , and O_3 is a major continuing challenge for atmospheric scientists.

The stringent requirements for chemical sensors utilized in the micrometeorological flux measurement techniques presented in Chapter 2 pose an even tougher challenge. The fast-response sensors (1 to 10 Hz) needed for tower- or aircraft-based eddy-correlation measurements or the high-precision concentration measurements needed for gradient profile studies (standard deviations of less than 1%) require sensitivity and/or accuracy that is, in general, beyond the current state of the art for measurements of most trace species concentrations. Although we do not explicitly discuss errors in flux measurement induced by nonlinear sensor response, they can also be significant in measuring means and fluctuations of trace species. Kristensen and Lenschow (1988) have examined the effects of nonlinear dynamic sensor response on measured means in a turbulent environment, but it appears that no one has considered its effects on flux measurements.

This chapter is a review of available chemical field measurement techniques for the trace species currently recognized as important in the evolving global atmosphere. This review also includes discussion of capabilities now undergoing development and testing that could be available for field work in the next year. Particular emphasis is placed on those technologies that seem most likely (either now or with further development) to satisfy the requirements of micrometeorological flux measurement procedures.

The following sections review contemporary techniques for trace species measurement. The first section summarizes methods for the oxidants, ozone and hydrogen peroxide, and members of the odd nitrogen family. The following section discusses measurement

techniques for carbon monoxide, methane, and nonmethane hydrocarbons. The third section presents a summary of methods for detection of sulfur species, while the final section discusses particulate and aerosol detection.

Chemical Sensors for Oxidant and Odd Nitrogen

Because of the close links between the chemistry of the nonradical oxidants O_3 and H_2O_2 , and odd nitrogen compounds, including NO , NO_2 , NO_3 , N_2O_5 , HNO_3 , HNO_2 , PAN, and NH_3 , it is frequently necessary to measure concentrations and/or fluxes of many species simultaneously in order to acquire sufficient insight into atmospheric processes. This section will review the status of detection technologies for these species and identify those species that can adequately resolve high-frequency fluctuations as required by the eddy-correlation flux measurement technique.

Ozone Detectors and Flux Divergence Measurements

In situ analyzers for ozone have been developed to the point where major field measurement programs are feasible without new technology. Two kinds of detecting mechanisms are widely used: chemiluminescence and ultraviolet photometry. Chemiluminescence, using nitric oxide as a reagent, has been used to make instruments with very fast response (bandwidths greater than 20 Hz), high sensitivity (below 0.1 ppbv), high specificity, and very low drift during operation. This method is preferred for many eddy-correlation measurements from both aircraft and towers.

It is of particular importance that the complete mechanism of nitric oxide-ozone chemiluminescence is well known, including all important kinetic rate constants. Thus, it is possible, in principle, to establish a calibration and measured operating parameters from these data. However, for practical reasons, chemiluminescence instruments are normally

calibrated against a photometric analyzer, which is an absolute standard.

Nitric oxide-ozone chemiluminescence has three limitations that, fortunately, do not significantly reduce its applicability. The first is a slight interference from water vapor, which is easily removed from eddy-flux measurements of ozone if simultaneous fast-response humidity measurements are made (Lenschow et al., 1981). The second limitation is the shot noise arising from discrete photons detected by the instrument. Since this noise is uncorrelated with measurements of vertical velocity, it does not bias estimates of the vertical flux by eddy correlation. Moreover, the current generation of instruments has sufficiently high sensitivity that shot noise does not contribute significantly to flux uncertainty. Shot noise does, however, contribute to both the power spectrum and variance of the ozone signal. Since at high frequency (in the inertial subrange region of atmospheric turbulence) the ozone spectrum is proportional to the $-5/3$ power of frequency, shot noise, which is white, tends to obscure the power spectrum for many typical atmospheric conditions. This limits the use of dissipation techniques for estimating ozone flux. Currently available sensitivities are probably adequate for using dissipation techniques within a few meters of the surface over land but are likely to be inadequate for measurements over water. If there is a strong need to employ dissipation techniques, the sensitivity of the nitric oxide-ozone analyzers can probably be increased to the point where power spectra over land could be measured to frequencies as high as 10 Hz. The third limitation is that the reagent nitric oxide is both toxic and difficult to remove from the vacuum pump exhaust. Thus, there is a potential for contaminating NO_y measurements in collocated surface experiments.

Chemiluminescence with ethylene or other olefins, such as cis-2-butene, is also used to measure ozone. This technique has the following disadvantages: (1) the reaction is slower and less sensitive than nitric oxide chemiluminescence, (2) the mechanism of light production is much slower, and (3) the temperature dependence of light emission is much greater. Suitably designed units can have a bandwidth as large as 1 Hz, making them suitable for tower-based eddy correlation at sampling heights of >5 m. An advantage is that the reagent olefin does not interfere with NO_y detection; however, it may be a factor if hydrocarbon measurements are collocated with the ozone sensor.

Ultraviolet photometry is the basis of practical, absolute ozone measurements generally made at the mercury 253.7 nm line. Commercial units have bandwidths of 0.03-0.05 Hz, while state-of-the-art research instruments have 1 Hz sampling (Profitt and McLaughlin, 1983; Profitt, 1985). Any of these devices can be used for gradient measurements, although the former typically have such a low precision (a

few ppbv) that gradient applications are precluded in many common meteorological situations. The faster-correlation measurements. It should be noted that practical UV photometry is intrinsically a differential measurement. This property can and ought to be applied to gradient measurements. The major interference of this category of instrument is light scattering from ambient aerosols. While filters are employed by some investigators to remove particles, they can introduce additional uncertainties into the measurements.

In addition, tunable diode laser (TDL) IR absorption spectrometers and luminol chemiluminescence detectors are under development for in situ measurements. The availability of satisfactory techniques for in situ measurement lessens the requirement for development of TDL and luminol techniques for fast-response ozone measurements. Furthermore, TDL ozone instruments resemble those discussed for other species in later subsections. Therefore, they will not be discussed further here.

Remote sensors for tropospheric ozone concentration profiles are largely limited to IR and UV differential absorption lidar (DIAL) systems. Both types of systems have undergone extensive development in recent years, with the IR sensors offering somewhat greater spatial resolution at the expense of greatly reduced range. UV DIAL systems have been used to obtain ozone profile measurements at high resolution (50 m) through the entire troposphere. The exact performance of an ozone DIAL system is, however, more dependent on atmospheric conditions than are lidar wind profilers. Ozone concentration, temperature, aerosol distributions, and the spatial and temporal resolution requirements all affect the operational parameters selected for a particular measurement. This diversity of operational parameters, although providing an important means for optimizing the performance of the instrument for a particular measurement, nevertheless makes evaluating "typical" performance characteristics difficult.

Hydrogen Peroxide Detectors

A number of techniques are emerging to measure H_2O_2 . However, these techniques do not yet have the sensitivity and/or response times needed to measure H_2O_2 flux by eddy-correlation techniques. Thus, experimental flux measurements are currently restricted to gradient and enclosure studies. Instrument comparisons have been carried out using many of the currently available detection methods, but the results from these studies are not yet available. The newly emerging techniques include: (1) the enzyme catalyzed dimerization of p-hydroxyphenyl acetic acid with continuous flow concurrent extraction (Lazrus et

al., 1986), (2) the same enzyme analytical technique with diffusion collection of the H_2O_2 (Hwang and Dasgupta, 1986; Dasgupta and Hwang, 1985; Dasgupta et al., 1986), (3) the enzyme analytical technique with nitric oxide pretitration of the ozone and subsequent collection of the H_2O_2 in an isopinger (Tanner et al., 1986), (4) tunable diode laser absorption spectroscopy (Slemr et al., 1986) and (5) cryogenic trapping with peroxyate chemiluminescence detection (Jacob et al., 1986). Hartkamp and Backhausen (1987) review and evaluate several techniques for measurement of H_2O_2 .

A highly selective, general-purpose detection method for many compounds is infrared TDL absorption spectrometry. A lead salt diode laser produces tunable radiation having a linewidth that is narrow compared to the Doppler-broadened vibrational-rotational lines for H_2O_2 and thus permits high selectivity. The laser repeatedly scans a single vibrational-rotational line: this serves to cancel background noise and allows measurements of absorbances lower than 10^{-5} . Absorption by H_2O_2 takes place within a White cell having a base path of 1.5 m and is operated at a pressure of 25 torr to minimize pressure broadening of individual lines. Present instrument configurations permit response times of 0.6 min. with detection limits of approximately 0.3 ppbv H_2O_2 with extended (>5 min.) signal averaging (c.f., Slemr et al., 1986).

The enzyme-supported detection of H_2O_2 is an innovative approach to detection of trace species in the atmosphere. Lazrus et al. (1986) report the detection of H_2O_2 and organic peroxides (ROOH) by first scrubbing them from the air into an aqueous solution using a continuous flow concurrent extraction. Next, 0.4 ml m^{-1} of scrubbing solution is drawn with the air sample into a glass coil; the velocity of the air spins the scrubbing solution to the walls, and the peroxides are dissolved into solution. The collection efficiency for H_2O_2 is estimated to be 100%; for methyl hydroperoxide and peroxyacetic acid, it is about 60%. The collection efficiency is lower for the organic hydroperoxides with higher molecular weights. The analytical chemistry for H_2O_2 is based on the reaction of peroxides with *p*-hydroxyphenylacetic acid (POPHA) in the presence of the enzyme peroxidase. This reaction forms the dimer of POPHA, which fluoresces with an emission wavelength of 420 nm when excited at 326 nm. Both H_2O_2 and short-chain organic hydroperoxides drive the analytical reaction.

Current instruments have detection limits of approximately 0.15 ppbv. The principal artifact identified is O_3 , which may form some H_2O_2 in the solutions used in these instruments (≥ 0.1 ppbv H_2O_2 equivalents). At present, the response time (10% to 90% for square wave analyte injection) is approximately 100 s.

Detectors for Odd Nitrogen Species

Whereas specific fast-response instruments have been developed and applied to micrometeorological flux determinations of O_3 (Pearson and Stedman, 1980; Lenschow et al., 1981; Gregory, 1987), instrument development for odd nitrogen has been directed towards maximizing sensitivity and specificity for ambient concentrations. With a few exceptions (Delany et al., 1986; Stedman, personal communication), little attention has been given to the provision of fast response for eddy-correlation applications. Consequently, most measurements of the surface exchange of odd nitrogen constituents have used enclosure, gradient, or budget techniques (Galbally and Roy, 1978; Johansson, 1984; Williams et al., 1987; Huebert and Robert, 1985). The species listed in Table 3.1 can be divided into three categories. The first includes those that hold promise for near-future eddy-correlation measurements using either towers or aircraft. The second includes those species for which monitoring techniques currently remain restricted to slower sampling methods. The third includes those species for which reliable techniques for even low sampling rates are not yet available, where details remain to be resolved before application to flux measurements, or where further instrument tests are needed.

The first category includes the TDL, LIF, and chemiluminescence instruments designed to measure NO. Many of these detectors have undergone measurement comparison tests successfully and have impressive sensitivities at low frequency (<1 Hz). Consequently, for locations where the mean NO concentrations are near or in excess of 0.1 ppbv, these instruments may be adequate for moderately fast-response (≤ 5 Hz) flux measurement approaches. For example, the fast-response O_3 instrument of Pearson and Stedman (1980) utilizes the NO/ O_3 chemiluminescence technique with NO as the reactant. Although it is much easier to generate high-reactant concentrations of NO than the reverse, where O_3 is used as the reactant, it should be possible to extend the frequency response of the chemiluminescence technique to 5–10 Hz. However, it must be emphasized that all but one of the NO or NO_2 instruments require an inlet system for aircraft or tower applications. The exception is the open cell, ambient pressure infrared diode laser technique, which is currently under development (Kolb et al., 1986; Anderson and Zahniser, 1988). Most of these instruments are large and are not "turn-key" operable. Clearly, adequate investigation (on-site and laboratory) of inlet lag times, surface effects, and true frequency response are necessary. Such tests would also be required for the direct NO_2 measurement instruments of Table 3.1 (i.e., TDL, luminol, and laser-induced fluorescence).

Table 3.1 Current Species Measurement Technologies — Oxidants and Odd Nitrogen Species

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
O ₃	Open path TDLAS ¹	Direct, no sampling	0.1 s	0.1 ppbv	To be evaluated	Under development	Kolb et al., 1986; Anderson and Zahniser, 1988
	Gas/liquid chemiluminescence (Eosin and relatives) ²	Batch	0.1 s	0.3 ppbv	0.2 ppb if thermally controlled	Still under development, U. of Denver. A "conventional" luminol detector with a different reagent solution insensitive to NO ₂ but sensitive to ozone. Lightweight, low power. No known interferences — also may be under development at Scintrex	Ray et al., 1986
	UV absorption	Continuous or batch	1-10 s	1-3 ppbv	1-3 ppb		Commercial versions available
	NO chemiluminescence ³	Continuous	0.05 s	0.5 ppbv	> 0.5% at levels of 5 ppbv or higher	Slight interference from H ₂ O vapor, correctable from simultaneous measurements of moisture time series	Pearson and Stedman, 1980; Lenschow et al., 1981
	Ethylene chemiluminescence	Continuous	0.5 s	0.5 ppbv	1.3 ppb		Commercial version available
H ₂ O ₂	Closed path TDLAS	Continuous	1 s - several minutes	~ 10 ppbv	To be supplied	Under development, no interferences, detection limits of ~ 1 ppb for 1 minute measurement times	Slemr et al., 1986

continued

Table 3.1 (Page 2)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
NO	Dual enzyme fluorimeter ⁴	Batch	60 s	0.1 ppbv	0-1 ppb	Slow response — spaghetti machine	Lazrus et al., 1986
	Open path TDLAS ⁵	Direct, no sampling	0.1 s	0.1 ppbv	To be verified	Under development	Ko et al., 1986; Anderson and Zahniser, 1988
	NO/O ₃ chemiluminescence	Continuous	1 s	10 pptv	1%	At 5 Hz, 50 pptv — sensitivity projected	Carroll et al., 1985; Drummond et al., 1983
	Two-photon laser/induced fluorescence ⁶	Continuous	0.1-2000 s	150 pptv/1 s 5 pptv/30 s	± 2%	Improved sensitivity may be possible	Bradshaw et al., 1985, 1989
NO ₂	Closed path TDLAS	Continuous	0.3 s — several minutes	0.3 ppbv	To be verified	Under development, no interferences	Schiff et al., 1983; Edwards and Ogram, 1986
	NO/O ₃ chemiluminescence and photolysis ⁵	Continuous	1 s	15-20 pptv	1%	Lag times or phase shift require measurement for higher-frequency operation	Kley and McFarland, 1980
	Photofragmentation/two-photon laser-induced fluorescence ⁷	Continuous	5-2000 s	250-pptv/1 s	± 2%	Requires subtraction of ambient NO mixing ratio; large sensitivity improvements may be possible	Bradshaw et al., 1988
	Luminol	Continuous	0.3 s	1 pptv	± 2%	PAN and O ₃ interferences are possible; commercial version available from Scintrex-Unisearch	Wendel et al., 1983

continued

Table 3.1 (Page 3)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
	Long path absorption	Direct, no sampling	1 s- 1 hour	Untested	Variable	Sensitivity and stability dependent on atmospheric conditions. Detection limit of 0.08 ppbv for measurement time of ~ 20 min.	Platt and Perner, 1980
PAN	Air carrier gas, GC with luminol detection	Continuous or batch	1 sample/ 30 s is as fast as has been demonstrated	10 pptv	Not applicable to GC	No known interferences in GC method. No compressed gases required. Nonlinear calibration necessary at low end. Low power and weight requirements. Still under development, U. of Denver/Scintrex	Burkhardt et al., 1988
	Electron capture gas chromatography ⁸	Continuous or batch	.02 Hz	40 pptv	4% (precision)		Penkett and Brice, 1986
HNO ₃	Closed path TDLAS	Continuous	1 s to several minutes	To be verified	To be verified	Under development, no interferences	Schiff et al., 1983
	Tungstic acid	Continuous	15 min.	0.1 ppbv	10%	Potential interference from organic nitrates	Braman et al., 1982
	HNO ₃ by nylon or impregnated filter ⁹	Batch	30 min. (direct trade between speed and sensitivity)	0.1 ppbv	No drift but filter zero is a problem	Ion chromatographic analysis, very slow; only possible for gradients. Problem with nylon formulations changing so the NO ₂ interferes	Huebert and Lazrus, 1980

continued

Table 3.1 (Page 4)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comment	References
NO ₃	Long path absorption	Direct, no sampling	1 s	Untested	Variable	Sensitivity and stability dependent on atmospheric conditions. Detection limit of ~ 1 pptv for times of ~ 20 min.	Platt et al., 1984
	Photofragmentation two-photon laser-induced fluorescence ¹⁰	Continuous	60-2000 s	80 pptv/60 s	± 15%		Rodgers and Davis, 1988
NO _y	Long path absorption	Direct, no sampling	1 s - 1 hour	Untested	Variable	Sensitivity and stability dependent on atmospheric conditions. Detection limit of 0.02 ppbv for measurement times of ~ 20 min.	Platt and Perner, 1980
	Hot molybdenum ¹¹	Continuous	0.01-1 s	(0.01 ppbv for 1 s sample)	10%	See Fehsenfeld et al., 1987. NO _y technique inter-comparisons.	Dickerson et al., 1984
	Master blaster + luminol ¹²	Continuous	10 s	50 pptv	< 25 ppt	Compared against master blaster + (NO + O ₃) chemiluminescence.	Bakwin et al., 1988
	Master blaster + converter Au/CO ¹³	Continuous	1 s	10 pptv	1%	Lag times or phase shift require measurement for higher frequency operation.	Fahey et al., 1985
	Chemical conversion/two-photon laser-induced fluorescence ⁸	Continuous	5-2000 s 5 pptv	150 pptv/1 s 5 pptv/30 s	± 2%		Bradshaw et al., 1985, 1988

continued

Table 3.1 (Page 5)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
NH ₃	Open path TDLAS	Direct, no sampling	0.1 s	To be evaluated	To be evaluated	Under development	Kolb et al., 1986; Anderson and Zahniser, 1988
	Closed path TDLAS	Continuous	1 s - several minutes	To be evaluated	To be evaluated	Under development	MacKay and Schiff, 1984
	Tungstic acid denuder ¹⁴	Continuous	15 min.	0.1 ppbv	10%		Braman et al., 1982
	MO ₃ denuder ¹⁵	Continuous	15 min.	0.1 ppbv	10%		Langford et al., 1988
	Wet trapping ¹⁶	Batch	1-2 hours	0.5 ppbv	n/a		Denmead et al., 1976; Denmead et al., 1977
	Dry trapping ¹⁷	Batch	1-2 hours	0.5 ppbv	n/a		Ferm, 1979
	VUV-photo-fragmentation/laser-induced fluorescence ¹⁸	Continuous	60-2000 s	15 pptv/60 s	± 10%		Stickel et al., 1988
	Condensation	Batch	10-15 min.	50 pptv		Sampling time dependent on ambient water vapor	Dawson and Farmer, 1984

END NOTES — Table 3.1

1. *Tunable Diode Laser Description:* The attractiveness of tunable diode laser absorption spectroscopy (TDLAS) for atmospheric trace gas sensing stems from the broad wavelength coverage available (3–30 μm for sub-77K lasers), enabling virtually any IR-active species to be detected. Both types of instruments listed in Table 3.1 couple TDL light sources with a multipass absorption cell. In the closed path version, ambient air is drawn through a sampling system into a reduced pressure absorption cell to exploit the Doppler-limited spectral resolution afforded by the inherently narrow laser line widths. In the open path system, the multipass mirror set is positioned in the free air to maximize frequency response and sample integrity and relies on the rapid tunability of TDLs to relieve spectral congestion. The fundamental limits set by the minimum detectable fractional absorption ($\sim 10^{-5}$), molecular IR line strengths, and useful absorption path lengths ($\sim 100\text{ m}$) can provide detection limits in the sub-ppbv range.

From a practical viewpoint, the relative complexity of the optical train required for laser mode separation and the need to operate these lasers below 77K has reduced the utility of TDL systems in fixed environments. Extension of recent developments in higher temperature, single mode lasers to a broader wavelength range is improving this situation considerably. Coupled with further improvements in detectable fractional absorption demonstrated using RF modulation ($10^{-6} - 10^{-7}$), in path lengths using new types of multipass cells ($\sim 1\text{ km}$), and the capability for simultaneous multilaser/multispecies instruments, TDL systems will probably become powerful tools for atmospheric trace gas measurement.

2. A system in which an air compressor provides both carrier gas (through an FeSO_4 trap) and sample (when the scrubber is bypassed) to a short column terminating in a standard luminol detector. Sensitivity and nonlinearity are a function of additives to the luminol solution and will remain the subject of discussions among users.

3. Ambient air is mixed with 5% to 10% nitric oxide (99% cp grade) and the resulting chemiluminescence is measured with a cooled, red-sensitive photomultiplier. The method is sensitive, fast, and quite specific. The only known interference is a slight quenching from water vapor, which is readily corrected if moisture is measured simultaneously. If O_3 flux is to be measured, the preferred correction is with the moisture flux.

4. Gas phase H_2O_2 is absorbed in water and determined by derivitivation/fluorimetry. Enzymatic reactions are used to distinguish H_2O_2 from organic peroxides.

5. Instruments all use well-known chemiluminescent reaction between NO and O_3 . Specifications given for research versions where care taken for flow, temperature, humidity, and ozone stabilization. NO_2 is detected as NO by ultraviolet photolysis ($\lambda > 320\text{ nm}$) of NO_2 (efficiency $\sim 50\%$).

6. *Laser-Induced Fluorescence Techniques:* Laser-induced fluorescence provides a highly sensitive and spectroscopically selective method for measurement of a number of species of atmospheric interest. Early instruments exploiting this technique employed single photon and were therefore limited to the detection of strongly fluorescent molecules such as NO, SO_2 , or OH or to detection of weakly fluorescent molecules at high concentration, such as NO_2 . Recent efforts have extended the applicability of the technique through the use of laser photofragmentation and two-photon, background-free, fluorescence excitation schemes.

Although detectable by single-photon excitation, current NO laser-induced fluorescence sensors employ a two-photon excitation approach. In this method, NO molecules are first excited into their lowest-lying electronically excited state by absorption of 226 nm laser photon. Subsequently a fraction of these excited NO molecules absorb a second laser photon at $\sim 1080\text{ nm}$ and are excited into a higher electronically excited state by absorption of a second laser photon at $\sim 1080\text{ nm}$. The resulting fluorescence, centered at $\sim 185\text{ nm}$, is blue-shifted relative to both pumping wavelengths. In conjunction with appropriate blocking filters and photomultiplier tubes, this blue-shifted fluorescence can be almost entirely discriminated from scattered laser light and emission from other atmospheric species and thereby provides a background-free signal for detection of NO.

7. Current LIF sensors measure NO_2 , NO_x , and NO_y by conversion to NO followed by detection using the two-photon, laser-induced techniques. In the case of NO_2 , this conversion is accomplished by laser photolysis of ambient NO by the output of a 351 nm XeF excimer laser. Since the NO_2 photolytic efficiency can approach unity, total NO_x can be readily detected by this approach. In the case of NO_y , detection of NO follows conversion in a catalytic reactor.
8. Uses a low temperature detector (40–50°C), ^3H electron capture gas chromatograph, $\sim 20 \text{ cm}^3$ (STP) sample collected cryogenically, elution times typically 5 to 6 minutes. (Detection limit can be changed by varying the collection time.)
9. Teflon filter keeps particulate NO_3^- out, but there is some volatilization. The same tailend analysis works for a denuder or annular denuder, which may be better at distinguishing vapor from particulate NO_3^- .
10. Like NO_2 , HONO is detected by near-ultraviolet laser photolysis. In the case of HONO, however, the detectable photofragment is OH, which is detected by a single-photon, laser-induced fluorescence.
11. Metallic molybdenum at $\sim 400^\circ\text{C}$ has been demonstrated to be a quantitative and fast NO_y converter with no NH_3 conversion. The basic reaction is of the form $\text{NO}_y + \text{Mo} \rightarrow \text{O}_x + \text{NO}$. Time response of $< 1 \text{ s}$ for NO_2 and PAN is relatively straightforward. Fast time response for HNO_3 in a system which is stable, drift free, and easily calibrated and zeroed has yet to be developed. (Research is under way at the U. of Denver, but outcome is uncertain.) Major caveat is that the system must be used carefully because molybdenum oxide powder ablates from the converter.
12. A gold tube converter master blaster (Fahey, et al., 1995) with H_2 reductant converts NO_y to NO. The NO is reacted in a quartz tube with O_3 to make NO_2 , which is detected using a Luminescence 3 luminol instrument. The instrument is zeroed by combining the O_3 and sample air just before the detector, bypassing the quartz tube. The O_3 level is kept constant at $\sim 1 \text{ ppmv}$, which eliminates the nonlinearity of the luminol machine. The unit is lightweight and uses little power.
13. Total odd nitrogen reduced to NO with 95% to 100% conversion using gold/CO converter operated at 300 to 325°C.
14. *Tungstic Acid Denuder.* NH_3 is absorbed on the surface of a denuder tube coated with tungstic acid. The NH_3 is desorbed and subsequently converted to NO, which is detected by chemiluminescence. HNO_3 is also collected and desorbed as NO. The NH_3 and HNO_3 are separated by temperature programming desorption or by sequencing the NH_3 conversion process.
15. *Molybdenum Oxide Denuder.* NH_3 is absorbed on the surface of an oxidized (VI oxide) molybdenum tube. After absorption sequence, the tube is heated with a flow of zero air passing through the tube. The NH_3 is partially desorbed ($\sim 30\%$) as NO. The NO is detected by a chemiluminescence detector.
16. Air is drawn through trap containing glass beads impregnated with 1% phosphoric acid. Flow meters are used to monitor flow rate or volume of air through traps. Authors used flow rate of 10 l/min. After air sampling, NH_4^+ is eluted from tap with distilled water and measured with an NH_3 -specific ion electrode.
17. Air is drawn through glass tube coated with oxalic acid. Acid later washed out and NH_4^+ determined with NH_3 -specific ion electrode.
18. NH_3 is currently measured by sequential photofragmentation of NH_3 and its photo-products, first to form NH_2 and then to form metastable $\text{NH}(\text{b})$, by the 193 nm output of an ArF excimer laser. After an appropriate time delay (1 to 5 μs), the $\text{NH}(\text{b})$ is further excited by absorption of an $\sim 450 \text{ nm}$ laser photon that results in intense blue-shifted fluorescence at 326 nm. This fluorescence, although blue-shifted relative to the 450 nm probe wavelength, is not completely background free due to residual fluorescence resulting from the interaction of the 193 nm photolysis beam with the chamber walls. This residual background is, however, very small due to the substantial time delay between the passage of the photolysis and probe laser beams.

The first category also includes instruments for NO_2 and total reactive odd nitrogen (NO_y) based on the detection of NO resulting from the chemical or physical reduction of these species. This conversion can result from photolysis (in the case of NO_2) or chemical conversion on hot surfaces (for both NO_2 and NO_y). These techniques, with their high sensitivities, hold promise for fast-response flux determinations, but laboratory assessments of the overall instrument frequency response are also required. For example, for frequencies larger than about 1–2 Hz, inlet, converter, and reaction memory effects need to be investigated to determine possible filtering of the response. Clearly, the higher mean concentrations of NO_y present a distinct advantage for possible high-frequency measurements. However, as outlined elsewhere in this report, NO_y flux determinations without concurrent flux measurements of other family members are often not particularly useful.

The second category includes instrumentation for NO_2 , PAN, HNO_3 , NH_3^+ , NO_3^- , and HONO. Here, the precision of current measurement techniques is sufficient for gradient methods and certainly for budget or enclosure methods. Instrument comparisons have been conducted for most of these species. There are also long-path absorption methods available for NO_2 and for nighttime NO_3 and HONO (Platt et al., 1984; Platt and Perner, 1980). However, their application to surface exchange measurements needs to be investigated.

It is more difficult to categorize current instrumentation for NH_3 and HNO_3 . Techniques for both species are available, but the results of instrument comparison studies for HNO_3 (and planned for NH_3) are not yet generally available. The reluctance of the community to accept these methods is mainly associated with sampling difficulties rather than detection. These species are notoriously difficult to transport unperturbed through inlets, and losses through sample handling can be severe. These factors can also make calibration difficult. A novel alternative for NH_3 , involving a vane-mounted sampler that measures fluxes directly (with some surface-layer structure assumptions), may prove useful (Leuning et al., 1985).

The third category is obvious from a cursory examination of Table 3.1. For example, no measurement techniques are currently available for N_2O_5 , HO_2NO_2 , or many organic nitrates (other than PAN or PPN).

In summary, there are a variety of measurement schemes for odd nitrogen species, many of which are based on the sensitive detection of NO (O_3/NO chemiluminescence or two-photon laser induced fluorescence) or NO_2 (luminol). Other species of NO_y are detected either by heterogeneous chemical conversion or by photolytic conversion. The exceptions to this general detection scheme are the TDL and

the filterpack methods. All of these provide detection limits in the low pptv range, although the integration times required to attain this level range from one second to tens of minutes for the chemiluminescence, TDL, LIF, and filter pack methods, in roughly that order. Most of these instruments have been developed for high sensitivity with little consideration of frequency response. Moreover, the difficulty in sampling "sticky" gases like HNO_3 , HONO, and NH_3 through an inlet system limits the time response of many instruments. Open path absorption methods may alleviate many of these problems and provide higher frequency response for such species.

Carbon Monoxide, Methane, and Nonmethane Hydrocarbon Sensors

Most of our knowledge about the atmospheric distributions of the carbon species CO, CH_4 , and non-methane hydrocarbons (NMHC) has been obtained by gas chromatographic analyses using flame ionization detection. This detection technique can be used with continuous sampling systems, but it is most often used for grab samples, often processed a considerable time after sampling. Quite recently, however, tunable laser techniques have been developed that allow real-time and fast-response measurements of CO and CH_4 . These techniques are discussed in further detail below and summarized in Table 3.2.

Fast-Response Sensors for CO and CH_4

Gas sensors using semiconductor TDLs have the potential for making measurements of many important atmospheric gas species. The wide applicability of TDL-based sensors is due to the availability of lead-salt TDLs, which may be composition tuned to operate near a particular wavelength in the spectral region between 3 and 30 μm , where most atmospheric species have absorption bands. Other semiconductor laser sources fabricated from III-V compounds are also available in the near-infrared spectral region. The ease of wavelength modulation of TDLs (simply by modulating the laser injection current) enables highly sensitive differential absorption ($1:10^4$ to $1:10^5$) detection of many gas species.

A fast-response TDL sensor has been developed to measure CO from an aircraft (Sachse et al., 1987a; 1987b; 1988). A TDL lasing in the 4.7 μm spectral region is used to detect ambient CO in a White cell containing a 12.5 m absorption path. Instrument response time depends on the air sampling rate; consequently, a low-volume White cell and a vacuum pump with a high pumping speed are important factors in achieving the rapid response required for airborne eddy-flux measurements. A high performance air sampling system has been developed using a venturi air jet ejector vacuum pump that is driven by bleed air from an aircraft engine compressor (Sachse et al.,

1987b). This TDL sensor has achieved a $1/e$ response time of 70 ms using a 1.5 liter White cell volume and a $2,500 \text{ l min}^{-1}$ pumping speed (at 100 torr). Substantial reductions (by a factor of three or more) in White cell volume are readily achievable and will result in further improvements in the time response of TDL gas sensors.

Recent modifications of this instrument have enabled it to make simultaneous, fast-response measurements of CO and CH₄ during the ABLE-3A expedition to Alaska. Methane detection is accomplished using an additional TDL lasing in the $7.6 \mu\text{m}$ spectral region. By beam combining the radiation from the $4.7 \mu\text{m}$ and $7.6 \mu\text{m}$ TDLs using a dichromic beam splitter, the two laser beams follow a common path through the White cell, permitting simultaneous differential absorption measurement of CO and CH₄. A "two-color" detector consisting of a sandwich structure of InSb on HgCdTe enables independent detection of the differential absorption signals occurring at the two wavelengths.

While TDLs are extremely versatile, they require careful handling and significant talent to operate. Furthermore, they consume considerable power, especially if the laser must operate at below 77 K (liquid nitrogen temperature). Many of these problems can be avoided if a gas laser can be substituted for the TDL.

Rare gas laser infrared absorption detectors rely on accidental close coincidences between an atomic line of the lasing medium and an appropriate molecular transition. Such coincidences occur for HeNe and CH₄ ($2,947.9 \text{ cm}^{-1}$), and HeXe and N₂O ($2,467.4 \text{ cm}^{-1}$), among others. Zeeman splitting of the laser gain line over a portion of the plasma column provides three possible emission wavelengths, which are scanned by modulating the cavity length to sense differential absorption (Kolb et al., 1986; McManus et al., 1989). Depending on the nature of the laser power control loop, the instruments can be configured to detect either absolute concentration or, with increased sensitivity, small concentration fluctuations as needed for eddy correlation. The lasers are small and rugged, and can be coupled to either open- or closed-path multipass absorption cells. Detection levels are similar to those obtainable with TDL systems, since similar differential absorption signal processing is involved.

A unique fast-response method that has been used for CH₄ chamber flux measurements utilizes a gas-filter-correlation IR absorption analyzer coupled to either a closed or an open sampling chamber (Sebacher, 1978; Sebacher and Harriss, 1982; Harriss et al., 1982; Harriss et al., 1985). This technique provides continuous sampling and analysis of the air in the chamber, with high precision (± 10 ppb for CH₄) and a response time of 1 s, enabling CH₄ fluxes as small as $10^{-12} \text{ kg CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ to be measured in a 15-minute sampling and analysis period. The continuous measurement of CH₄ in the chamber

allows variations in the flux rate during the sampling period to be readily identified. The rapid response of the technique, combined with the chamber design, allow any disturbances to natural systems during flux measurements to be kept to a minimum.

Slow-Response Methods for Hydrocarbons

Currently, fast response sensors for NMHCs are not available. Measurement of species such as ethylene, propene, isoprene, and the monoterpenes requires collection of discrete samples of sufficient volume to permit quantification by gas chromatography. Consequently, enclosure and tower (gradient) procedures are applicable to the measurement of NMHC fluxes but eddy-correlation methods currently are not. Table 1.11 lists the ranges for ambient hydrocarbon concentrations observed in various environments. Concentrations of many NMHCs in clean oceanic air masses may be as low as 0.1 ppbv (Bonsang et al., 1988), which is close to the detection limit of current methods. In contrast, ambient isoprene concentrations, which fall in the ppbv range in the vicinity of hardwood forests on hot summer afternoons, can be measured with certainty.

Grab-sample methods for NMHC and CH₄ measurements have existed for several years (Steele et al., 1987; Sexton and Westberg, 1979; Roberts et al., 1983; Rudolph et al., 1981; Singh et al., 1985). Whole-air samples are collected in either glass or electropolished stainless steel containers. Analysis is by gas chromatography (GC) with flame-ionization detection. Preconcentration by cryogenic trapping of the NMHC is normally necessary prior to injection into the chromatograph. The sample collection method readily allows for sampling at different heights on a tower or aircraft. Tethered balloon sampling can be accomplished by collection into teflon bags (Zimmerman et al., 1988).

Techniques for carbonyl species sampling include high-pressure liquid chromatography (HPLC) of samples collected on impregnated cartridges (Kuntz et al., 1980) and cryogenic collection into glass loops followed by analysis with a flame ionization detector (FID)-equipped gas chromatograph (Snider and Dawson, 1985). The cartridge method collects carbonyl compounds by passing air through silica cartridges impregnated with 2,4-dinitrophenylhydrazine. Samples are then eluted from the cartridges and analyzed by high-pressure liquid chromatography (HPLC). The GC technique provides measurement of many C₂-C₅ carbonyls with detection limits in the lower ppt range. Both of these methods are appropriate for measurements on towers as well as aircraft.

Several methods exist or are under development to measure organic acids. These include condensation sampling (Farmer and Dawson, 1982), a mist chamber (Talbot et al., 1988), denuder tubes (Norton,

1986), and impregnated filters. Results from an intercomparison of these methods during June 1986 showed agreement between all systems except for the impregnated filters (Keene et al., 1989). Most of the existing data have been collected by the use of the condensation method—cooling a highly polished, clean surface below the dew point temperature so that a film of water collects on the surface. Highly soluble gases are collected with essentially unit efficiency. Ion chromatography or ion exclusion chromatography provides measurement of organic acid concentrations in the condensate. These concentrations are then used to calculate gas-phase levels of the acids. Tower and aircraft measurements are possible with all current systems with the exception of those that use the condensation technique.

Sulfur Species Chemical Sensors

As discussed in Chapter 1, the mixing ratios of sulfur species in the atmosphere, in almost all regions free of industrial pollution, are < 1 ppbv. The measurement of such low concentrations of reactive and labile sulfur compounds of interest, such as H_2S , CH_3SH , SO_2 , and CH_3SCH_3 (DMS), and even the more stable species COS and CS_2 , has been a serious challenge and the most significant motivation for the development of sulfur-specific detectors. Those detectors currently available or known to be under development are listed in Table 3.3, together with the sulfur species for which they are applicable, estimated sensitivities, and sampling-related information.

Detectors Sensitive to a Variety of Sulfur Compounds

The oldest (~ 20 years) of the listed detection techniques is the flame photometric detector, or FPD. Its sensitivity to sulfur compounds relies on thermal decomposition of the compounds in an oxy-hydrogen flame with the subsequent occasional formation of an electronically excited S_2 molecule that can radiate in the near UV. The detection of photons from those molecules that escape collisional de-excitation is the signal-producing mechanism. Since the FPD relies upon the formation of an S_2 molecule, its sulfur response is inherently nonlinear. Recently, a number of workers (D'Ottavio et al., 1981; Goldan et al., 1987) have lowered the detection limit of the FPD and circumvented this nonlinearity by intentionally adding some convenient volatile sulfur species to the flame combustion gases. If the detected sulfur species concentrations are small compared to the added species (commonly SF_6), the differential response is quasi-linear.

A number of chemiluminescent sulfur detectors that have recently been developed are also included in Table 3.3. These depend upon the reaction of a specific class of sulfur compounds with a gas-phase chemical reagent to produce electronically or vibrationally

excited species whose subsequent radiation can serve as a detection mechanism. Spurlin and Yeung (1982) claim a detection limit of 3 ppbv for H_2S by using its reaction with ClO_2 . Kelly et al. (1983) observed the chemiluminescent reaction of a number of sulfur-bearing compounds with O_3 and showed a detection of DMS in the low ppbv range, with higher sensitivity for CH_3SH and much lower sensitivity for H_2S . Perhaps the most promising of the chemiluminescent detection techniques is that described by Nelson et al. (1983), in which sulfur compounds react with F_2 . Recent work with this type of detector shows promise of achieving detection limits of ~ 1 $\mu\text{g S}$ per sample, somewhat lower than that achieved with an SF_6 doped FPD. Since this response to different sulfur compounds varies a great deal (negligible response to SO_2 , COS , H_2S , and CS_2 was reported), its use in the measurement of sulfur fluxes in the atmosphere appears limited.

A recent development in sulfur gas detection is the use of an electron capture detector (ECD); (Johnson and Lovelock, 1988). Sulfur-bearing compounds may be converted to SF_6 at moderate temperatures ($\sim 200^\circ\text{C}$) by reacting them with AgF_2 . Since the resulting SF_6 has a large electron capture cross section, it may be readily detected with an ECD, thereby taking advantage of that detector's extremely high sensitivity. The AgF_2 is replenished by supplying a small amount of fluorine gas to the sample stream. Since the ECD is also sensitive to F_2 , the excess F_2 must be removed by reacting it with H_2 on a hot palladium catalyst. Although this technique is in its infancy, the procedure is fraught with technical difficulties, and its application is likely to be limited to skilled practitioners, it offers great promise. The method should yield a detection limit some hundred times lower than even the doped FPD.

Application to Total Sulfur Measurements

Since both the FPD- and ECD-based detection schemes described above are sensitive to all sulfur-bearing compounds, either may be used as a total sulfur detector, as well as in systems where the sulfur compounds are speciated. The undoped FPD is capable of detecting changes in sulfur flow of approximately 3×10^{11} molecules s^{-1} and the doped FPD of approximately 4×10^{10} molecules s^{-1} under optimum circumstances. Since typical sample flows may be made as high as 0.2 l min^{-1} STP, these correspond to mixing ratios of approximately 3 ppbv and 0.5 ppbv, respectively. Thus, the FPD has sufficient sensitivity for total sulfur measurements, at least in somewhat polluted environments, and much of the deposition flux work to date has utilized an FPD-based system. By minimizing sample throughput times, response times of the order of a second (or slightly less) can be achieved, but the FPD remains inherently noisy, even for levels of sulfur gases (predominantly SO_2)

found in moderately polluted air. Pressure fluctuations affecting the flame and collisional quenching by other minor atmospheric species (such as CO_2 and H_2O) present operational problems that were difficult to overcome in early applications of FPD techniques in eddy-flux studies, and which remain the sources of continuing concern. FPD detectors optimized for fast response have been utilized for eddy-correlation measurements of total sulfur deposition in many studies in moderately polluted environments (e.g., Hicks et al., 1986a).

The inherently greater sensitivity of an ECD-based system holds greater promise in that regard. Its detection limit, estimated to fall in the range of 5×10^8 to 10^9 molecules s^{-1} , coupled with a sample flow rate of $\sim 20 \text{ cm}^3 \text{ min}^{-1}$, results in a detection limit of 50 to 100 pptv. Detector time constants $< 1 \text{ s}$ can be achieved by increasing the sample flow rate and decreasing the detector volume with some loss of sensitivity. Since such a system would be compatible with the requirements of micrometeorological techniques, its development would appear highly desirable. Using either an FPD or ECD detector-based system for the measurement of volatile sulfur gas fluxes requires, of course, the removal of SO_4^- aerosols prior to analysis and dealing with the problems associated with different sensitivities for different sulfur compounds.

Species-Specific Detectors — Fast Response

Table 3.3 also lists several laser and nonlaser spectral techniques that can be used to monitor specific sulfur compounds with detection limits expected to fall in the 0.2 to 1 ppbv range. Of these, two new techniques show promise for the sensitive, rapid, real-time detection necessary for eddy-correlation flux measurements. The first of these uses differential optical absorption of TDL radiation in either an open, atmospheric pressure multipass region (Kolb et al., 1986; Anderson and Zahniser, 1988), or a closed, lower pressure, multipass absorption cell (Edwards et al., 1984; Edwards and Orgram, 1986). This technique, which is expected to have a detection limit near 1 ppbv for SO_2 , is currently under development for eddy-correlation flux measurements.

The second approach is the vacuum UV flash photolysis/laser-induced fluorescence (VUV-FP/LIF)

technique. In this method, a parent sulfur species (SO_2 , H_2S , or CS_2) is photodissociated by 193 nm photons from a pulsed ArF excimer laser. The resulting molecular fragments (SO, HS, or CS) are then detected by induced fluorescence from a tunable dye laser. This innovative technique is estimated to be capable of a detection limit of ~ 150 pptv but is more equipment intensive than the TDL approach.

Both of these techniques exploit the specificity of spectral detection, along with the high sensitivity and temporal resolution often possible with sophisticated laser techniques. It should be recognized, however, that lasers are expensive and frequently difficult to incorporate in field instrumentation, and usually require advanced skills to operate successfully.

Species-Specific Detectors — Slow Response

No species-specific detectors with sufficient sensitivity to measure ambient levels of biogenically produced sulfur compounds on time scales suitable for eddy-correlation flux measurements are currently available. The measurement of such compounds (most notably DMS) requires some type of sample concentration followed by analysis, with the possible exception of the ECD-based scheme described above. If the concentration step is species specific, it may be followed directly by detection. More generally, however, the concentration step is followed by species separation by some type of chromatography with subsequent individual species quantification. Such batch or grab sample processing techniques typically have time scales ranging from several minutes to several tens of minutes. Thus, flux measurements for these species will be restricted to gradient techniques.

Currently available analysis techniques of this type are also summarized in Table 3.3. The sample concentration techniques utilized in the measurements referred to are summarized in Table 3.4. Some of these sample concentration techniques are amenable to subsequent species-specific detection and some only to classes of sulfur compounds as noted in the table. Those techniques that utilize liquid extraction are generally amenable only to ion chromatographic analysis and lead to much higher ($\sim 10^3$) detection limits. The flash vaporization technique results in a nonspecific "total sulfur" sample.

Table 3.2 Current Species Measurement Technologies — Carbon Monoxide, Methane, Nonmethane Hydrocarbons, and Organics

Species	Technique	Sampling Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
CO	Closed path laser differential absorption	Continuous	.05 s to minutes	10 ppbv	~ 1%	Flight demonstrated	Sachse et al., 1987a,b; Sachse et al., 1988
	Mercuric oxide detector after GC separation	Batch	Seconds to minutes	~ 1 ppbv	Not applicable	Commercially available	
CH ₄	Diode laser differential absorption	Continuous or direct	.05 s to minutes	10 ppbv	~ 1%	Flight demonstrated during ABLE-3A	
	IR rate gas laser absorption	Continuous or direct	.05 s to minutes	10 ppbv	To be evaluated	Under development. Field tested during ABLE-3A	Kolb et al., 1986 McManus et al., 1988
	Gas-filter-correlation IR absorption, with sampling	Continuous	1 s	10 ppbv	Negligible drift over a normal 15-min. sampling period	Minimum detectable flux of 3×10^{-11} kg CH ₄ m ⁻² s ⁻¹ over a 15-min. sampling period	Sebacher and Harriss, 1982; Harriss et al., 1985
NMHC	Gas chromatography with flame ionization detector	Batch	Seconds to minutes	10 ppbv	Not applicable	Detector is linear over wide range of concentrations	Steele et al., 1987
	Gas chromatography with flame ionization detector	Batch	Seconds to minutes	50 pptv	Not applicable	Samples may require concentration before analysis	Sexton and Westoerg, 1979; Roberts et al., 1983; Singh et al., 1985

continued

Table 3.2 (Page 2)

Species	Technique	Sampling Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
Organic acids	Condensation sampling	Batch	> 10 min.	10 pptv	Not applicable		Dawson and Farmer, 1988
	Mist chamber	Batch	30 min.	Not known	Not applicable		Cofer et al., 1985; Cofer and Edahl, 1986; Andreas et al., 1988a
	Denuder tubes	Batch	60 min.	Not known	Not applicable		Norton, 1986
	Impregnated filters	Batch	60 min.	Not known	Not applicable	Known interferences	Keene et al., 1989
Carbonyls	2, 4-DNPH impregnated cartridge followed by HPLC	Batch	120 min.	Not known	Not applicable		Kuntz et al., 1980; Grosjean and Fung, 1982
	Condensation sampling followed by gas chromatography with flame ionization detector	Batch	60-120 min.	1-10 pptv	Not applicable		Snider and Dawson 1985

Table 3.3 Current Species Measurement Technologies — Sulfur Chemical Species

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
Total sulfur	Flame photometric detection	Continuous sampled or batch	~ 0.5 sec.	0.5 ppb @ 0.02 l/min (~ 2 pg S s ⁻¹)	1-2%	SF ₆ doped FPD. Careful flow control required on all flows. Sensitivity is species dependent. Hydrocarbon interferences	D'Ottavio et al, 1981
	Conversion to SF ₆ /electron capture detection	Continuous sampled or batch	~ 10 min.	3 pg S/sample 2 pptv/1 l sample	~ 1%		
	Metal foil collection/flash vaporization/flame photometric detection	Batch	~ 0.5 sec. ~ 10 min.	~ 50 pptv @ 20 cm ³ /min. ~ 0.2 pg S s ⁻¹ ~ .03 pg S/sample	? ?	Estimates from GC application below. Conversion to SF ₆ followed by F ₂ removal by catalysis	New technique See GC application below
			~ 10 min.	~ 20 pF S/sample	?	Collects predominantly reduced sulfur. Non-speciated flash vaporization from arbitrarily large sample. Some H ₂ O interference	Kagel and Farwell, 1986

continued

Table 3.3 (Page 2)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References	
SO ₂	UV-fluorescence	Continuous sampled	1 min. and up	~ 3 ppbv	~ 30%	Elimination of H ₂ O interference requires teflon cell	Schwarz et al., 1974	
	Chemiluminescence	Batch	> 10 min.	~ 4 ng S/batch ~ 3 ppb/ 1L sample	~ 2%	Impregnated filters, wet chemical handling, capable of large samples	Meixner & Jaeschke 1984	
	Laser-induced fluorescence	Direct, no sampling	3-5 s	200 pptv	~ 10%	Near maximum achievable sensitivity	Bradshaw et al., 1985	
	Vacuum UV flash photolysis/laser-induced fluorescence	Direct, no sampling	0.1-2000 s	150 pptv	10-20%	Under development	Bradshaw et al., 1988	
	Differential UV absorption	Continuous	> 1.0 s	~ 20 ppbv		Has been used for eddy-correlation measurements in very polluted regions (H. Nestler, Heidelberg U.). Sensitivity of 0.01 ppbv for sampling sensitivity times of ~ 20 min.	Platt and Perner, 1980	
	Tunable diode laser	Direct, no sampling or continuous	0.1-100 s	~ 1 ppbv (closed cell) ~ ppbv (open cell)	1%	Under development; may be improved by a factor of 20 with astigmatic off-axis resonator	Edwards & Ogram, 1986; Hastie et al., 1983; Kolb et al., 1986	
	SO ₄ ⁻	Ion chromatography	Batch	> 10 min.	~ 5 pptv	Not appli-	Requires a large sample. Requires column separation	Andreae et al., 1987

continued

Table 3.3 (Page 3)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
Dimethyl-sulfide	Gas chromatography flame photometric detection	Batch	~ 10 min.	3 pg S/sample ~ pptv/ 1 l sample	~ 1%	Requires GC separation SF ₆ doped FPD. Very important O ₃ interference	Goldan et al., 1987 Andreae et al., 1985
	Chemiluminescent detection	Continuous sampled or batch	~ 1 s 10 min.	~ 200 pptv ~ pptv/ 1 l sample	?	Interferences from other reduced sulfur compounds or requires GC separation. New technique. Little experience	Nelson et al., 1983
	Gold wool collection/thermal desorption/flame photometric detection	Batch	~ 10 min.	20 pg S/sample	~ 2%	Requires CG separation. Large O ₃ interference	Bernard, 1982
H ₂ S	Conversion to SF ₆ electron capture detection	Batch	~ 10 min.	~ 0.03 pg S/sample	?	Requires GC separation conversion to SF ₆ with F ₂ catalytic removal of excess F ₂ . New technique	Johnson and Lovelock, 1988
	Gas chromatography flame photometric detection	(Same as for dimethyl sulfide using same technique as described above.)			GC separation	No significant O ₃ interference. Requires	
	Conversion to SF ₆ electron capture detection	(Same as for dimethyl sulfide using same technique as described above.)				Requires GC separation	

continued

Table 3.3 (Page 4)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
	Filter collection FMA fluorescence quenching	Batch	10-60 min.	~ 3 ng S/sample	~50% @ 5 ppt	Large filter-to-filter background variability	Natusch et al., 1972
	Gold collection/ flame photometric detection	Batch	10-100 min.	10 pg S/sample	?	Large chance for vari- ability of H ₂ S collection efficiency. Requires SO ₂ removal. Interference from other reduced sulfur compounds	Braman et al., 1978
OCS	Gas chromatography flame photometric detection	(Same as for dimethyl sulfide using same technique as described above)				No O ₃ interference. Requires GC separation	
	Conversion to SF ₆ electron capture detection	(Same as for dimethyl sulfide using same technique as described above)				Requires GC separation	
CS ₂	Gas chromatography Flame photometric detection	(Same as for dimethyl sulfide using same technique as described above)				Requires GC separation. Small O ₃ interference	
	Conversion to SF ₆ electron capture detection	(Same as for dimethyl sulfide using same technique as described above)				Requires GC separation	

continued

Table 3.3 (Page 5)

Species	Technique	Sample Method	Sampling Time (Range)	Detection Limit	Stability	Comments	References
	Vacuum UV flash photolysis/laser-induced fluorescence	Direct, no sampling	0.1-2000 s	150 pptv	10-15%	Under development	Rodgers et al., 1986
CH ₃ SH	Gas chromatography/flame photometric detection	(Same as dimethylsulfide but less ozone interference)					
Methane sulfonic acid	Ion chromatography	(Similar to SO ₄ ²⁻ aerosols as listed above)					
Dimethyl sulfoxide and dimethyl sulfonic acid	Gas chromatography/flame photometric detection	Batch	2-30 min.	Similar to dimethyl sulfide	~ 1%	Requires silica gel preconcentration	Harvey and Lang, 1986

Table 3.4
Concentration Techniques for Sulfur Species

Species	Technique	Recovery	References
H ₂ S	Impregnated filter	Liquid extraction	Natusch et al., 1972 Jaeschke & Herman, 1981
SO ₂	Impregnated filter	Liquid extraction	Meixner & Jaeschke, 1984 Ockelmann & Georgii, 1984
Reduced sulfur compounds	Palladium foil	Flash evaporation	Kagel & Farwell, 1986
Reduced sulfur compounds	Gold or wool	Nondestructive thermal desorption	Barnard et al., 1982 Ammons, 1980
COS, CS ₂	Tenax GC	Nondestructive thermal desorption	Stuedler & Kijowski, 1984
All	Glass, bead bed/ cryogenic enrichment	Nondestructive thermal desorption	Farwell et al., 1979 Farwell & Gluck, 1980
All	Open tubular/ cryogenic enrichment	Nondestructive thermal desorption	Goldan et al., 1987

Aerosol Detectors

Aerosols are involved in the atmospheric cycles of several trace gases with important consequences on rates of deposition, as well as potential climatic effects. Many trace species have solid phases in the atmosphere (e.g., SO₄²⁻), with straightforward consequences. In other cases (e.g., chemical composition changes associated with aging sea salt aerosol), the involvement is more complex. For some, such as mineral and organic particles suspended and transported by the wind, the interactions may be more subtle. There is a need to define the surface emission fluxes of primary aerosols, surface deposition of both primary and secondary aerosols, and the flux divergence due to gas-to-particle conversion.

The definition of aerosol fluxes is intrinsically more complex than that for gases, as the definition must generally include information on both the size distribution and composition of the aerosols. In recent years, fast, high-resolution particle detectors have been developed. The most commonly used is a laser-optical particle counter. Electric charge devices have also been used for covariance measurements (Wesely et al., 1977). Flame photometric devices are capable of accurate measurement of some elements contained in aerosols (e.g., S and Na). These devices are generally fast and accurate enough for flux measurements (Hicks

et al., 1988).

Additional intricacy arises when the aerosol size distribution is itself modified by the mean humidity profile, or when the aerosol fall velocity approaches the friction velocity. Fairall (1984) has addressed the effects of the humidity profile, as well as other aerosol flux measurement techniques. Lenschow and Kristensen (1985) have addressed the effects of a finite number of particles in estimating a particle flux.

The critical questions requiring aerosol flux measurements to address the role of aerosols in the atmospheric cycles of trace species and their potential for climate change are:

- What is the deposition efficiency of different vegetated surfaces as a function of atmospheric and plant conditions?
- What is the potential for wind-generated emission flux for different areas of the earth's surface as a function of seasonal and climate conditions? What is the potential for long-range transport of these particles?
- What are the emission and deposition fluxes of sea salt under various weather conditions, and what sort of chemical fractionation can occur within the sea salt aerosol due to gas-particle interactions?

We strongly recommend that any ocean-atmosphere flux experiment include a particle flux component.

4 FLUX MEASUREMENT PROGRAM PLAN

C. E. Kolb, F. C. Fehsenfeld, L. P. Steele, and P. D. Goldan

The previous chapters review current understanding of the sources, sinks, and distributions of many of the trace atmospheric species of global interest, and of the techniques that can be used for measuring vertical fluxes of these trace species. The next step is to outline and order important experiments for advancing our understanding of the chemical behavior of the atmosphere, taking into account the limited sensing capabilities and field resources currently available to carry out such experiments. As discussed in Chapter 3, one of the major limitations to research in this area is the lack of reliable, sensitive detectors that can be coupled with micrometeorological techniques to measure fluxes. Therefore, for many species, the first recommendation is that further development of instrumentation take place before questions relating to sources and sinks are addressed. In other cases, experiments have already been conducted, and further proposed research largely uses the available technology in new locations and situations.

One general requirement for flux measurement programs is a capability for periodic comparisons to verify the performance of new sensors and measurement techniques. To optimize the utility of the data obtained, whenever appropriate such comparison studies should be conducted with complete micrometeorological capabilities. Facilities such as the NCAR Atmosphere-Surface Turbulent Exchange Research (ASTER) facility offer considerable attractions in this regard. ASTER, now under development, is a tower-based portable micrometeorological facility designed to be operated under a variety of conditions. It is planned to be available to the scientific community after mid-1989. The facility is designed to be used with a wide range of chemical and meteorological sensors, depending on experimental requirements. It will measure fluxes of momentum, moisture, and temperature, along with fluxes from user-supplied instrumentation. The utility of this approach has been well demonstrated elsewhere; periodic comparisons of sensing techniques and of alternative flux-measuring methods have been conducted routinely as part of earlier programs of this kind, as components of research on the delivery of air pollutants to land surfaces (e.g., Hicks et al., 1986b, 1989).

Nitrogen and Ozone Group

Ozone

Ozone is one of the few species for which practical and reliable fast-response sensors are available for direct eddy-correlation flux measurements at atmospheric concentrations.

The existing set of ozone deposition data consists largely of spot measurements of a few categories of surfaces, predominantly in the mid-latitudes. These include several agricultural surfaces, forests, rangeland, and coastal waters of the U.S. Both extensive geographic surveys and intensive site measurements have been made; there are no major disagreements between the results of these two types of measurement. Only a very few of these measurements extend over different seasons. A somewhat larger number include diurnal variability.

Future experiments should be planned for surfaces of importance to the global ozone budget. These include tropical and boreal forests, tundra, taiga, and agricultural croplands such as rice paddies that cover large areas. In addition, it is not clear that diurnal and seasonal changes are sufficiently well understood even over more commonly studied surfaces. To facilitate use of the data, the results of deposition studies should be reported as surface resistances, which remove at least part of the dependency of deposition on local micrometeorological conditions.

Two situations deserve priority treatment because of their potential importance to the global ozone budget and because of the fact that few measurements have been made. The first of these is wintertime measurements over the continents, with particular emphasis on areas with snow cover, partial snow cover, and partial vegetative cover, over as wide a range of meteorological conditions as possible. Both site-intensive tower measurements and wider-area aircraft measurements should be planned. Measurements should be taken throughout the boundary layer so that fluxes at the surface and the top of the boundary layer can be obtained by linear extrapolation, and so that a mean concentration budget can be evaluated.

The second category is measurements over open oceans. It is particularly important to obtain data from

areas with differing biological productivity as a function of meteorological conditions and season. It is expected that the primary platform for measurements over ocean will be aircraft. Existing aircraft measurements demonstrate that it is feasible to measure the surface resistances, but only a few data points have thus far been obtained. Measurements over the tropical oceans and in high wind conditions are of particular importance.

Because of its relatively slow reaction time (except in highly polluted areas), ozone can also be a very useful tracer for micrometeorological processes. In this respect, it is comparable to water vapor, with the advantages that no phase changes occur and that it has no effect on the buoyancy of the air. In addition, it is not appreciably soluble in clouds and hence can be used as a conservative tracer for entrainment and mixing processes involving clouds.

Since the flux and gradient are readily measured, the ozone diffusivity (i.e., the ratio of the flux to the local gradient) can be obtained, which can then be used to estimate fluxes of other trace gases from gradient measurements with slow-response instrumentation. Similarly, the ratio of the flux at the top of the mixed layer, which can be obtained by extrapolation from the flux measured at several levels within the boundary layer, to the change in concentration across the top of the boundary layer is a direct measure of the velocity of entrainment of air from the upper troposphere into the mixed layer. Once this entrainment velocity is known, it can be used to estimate fluxes of other species through the top of the boundary layer. This information is of enormous practical significance since most trace species can be measured only with slow-response instrumentation.

Remote sensors for tropospheric ozone concentration profiles are largely limited to IR and UV DIAL systems. Both kinds of system have undergone extensive development in recent years (see, for example, Browell et al., 1983), with the IR sensors offering somewhat greater spatial resolution at the expense of greatly reduced range. UV DIAL systems have been used to obtain ozone profile measurements (50 m resolution) through the complete troposphere. It is tempting to consider the possibility of combining remote species measurements with remote wind profiling measurements (Hogg et al., 1983) to measure fluxes remotely. The exact performance of an ozone DIAL system is, however, more dependent upon atmospheric conditions than is the case for the wind profilers. Ozone concentration, temperature, aerosol distributions, and the spatial and temporal resolution requirements all affect the measurements. Although the diversity of operational parameters makes evaluating "typical" performance characteristics difficult, their temporal and spatial resolution appear to equal or exceed that of currently available wind profilers for ranges greater than about

300 m. This resolution may be sufficient to be useful for measurement of eddy flux of ozone in the upper part of the convective PBL.

Hydrogen Peroxide

The gas-phase oxidation processes of the odd hydrogen free radicals are terminated by radical-radical reactions that form hydrogen peroxide and organic peroxide. The peroxides thus formed can be taken up by aqueous aerosols, cloud water, and surface deposition. The peroxides in the atmosphere, particularly in aerosols and cloud water, are an important oxidant, notably responsible for the conversion of SO_2 to SO_4^- .

Because of the importance of the peroxides, there has been considerable effort directed toward the development of instruments to measure H_2O_2 in the troposphere, including the gas phase, on aerosols, and in cloud water (Heikes et al., 1982, 1987; Kelly et al., 1985). To date, however, there are no measurements published on the surface exchange or flux divergence of H_2O_2 .

Instruments that are currently available do not have sufficient sensitivity to measure either H_2O_2 deposition or flux divergence by eddy correlation. Moreover, the capability of available techniques, i.e. enzymatic fluorimetry (EF) and tunable diode laser absorption spectrometry (TDLAS), to quantitatively sample H_2O_2 or to distinguish between H_2O_2 in the gas phase and in aerosols has not yet been established. For this reason, present technology should be aimed at improving and verifying these techniques and at their subsequent utilization to measure H_2O_2 deposition using gradient techniques near the surface. In addition, the use of these methods in aircraft studies to determine the tropospheric distribution of H_2O_2 as a function of altitude, season, and latitude would provide important information on the processes regulating the production, loss, and redistribution of H_2O_2 in the troposphere.

Reactive Nitrogen Oxides and Ammonia

According to our present understanding, NO_y compounds are introduced into the atmosphere as NO_x , which can then be converted to PAN and HNO_y by chemical processes. Combustion and soil emissions of NO_x are the principal sources in the PBL. Lightning, aircraft, and transport of NO_y from the stratosphere are the known significant sources in the free troposphere. The NO_y is removed from the PBL by both dry and wet deposition. A critical factor regulating the lifetime of NO_y compounds in the atmosphere and, hence, the influence of NO_y on tropospheric photochemistry is the exchange of NO_y between the boundary layer and the free troposphere.

Nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$) are both emitted from and deposited to the earth's surface. For the most part, however, emission dominates,

and emissions from soils are recognized as being a significant source of atmospheric NO_x (Logan, 1983). However, the magnitude of this source is subject to considerable uncertainty. For example, Hahn and Crutzen (1982) estimate that soil may represent between 0% and 20% of the total global source. Stedman and Shetter (1983) indicate a soil source of NO_x that is between 13% and 50% of the global total, while Logan (1983) estimates that between 7% and 30% of the global total NO_x originates from microbial activity in soils.

Much of this work was based on only one set of soil NO_x emission data (Galbally and Roy, 1978). Since then, several other studies have been conducted in different areas and under a wide variety of climatic and soil conditions (Johansson, 1984; Johansson and Granat, 1984; Slemr and Seiler, 1984; Delany et al., 1986; Anderson and Levine, 1987; Williams et al., 1987). The results demonstrate that there is considerable variability and uncertainty in NO_x soil emission estimates.

In order to refine the estimates, emission rates must be related to soil properties such as temperature, type, moisture, pH, percent organic matter, and nitrate and ammonium concentrations. Knowing the dependence of NO_x emission on these factors gives insights into the biogenic mechanisms responsible for the NO_x generation. Because of the variability of these factors in nature and the complexity of the biogenic response to them, additional detailed field studies covering all seasons, as well as investigations under controlled laboratory conditions, are required. Ancillary atmospheric measurements should include ambient air, dew point, and soil temperatures, wind speed and direction, pressure, solar radiation, and precipitation.

Since NO is both emitted and deposited at the surface, and fast-response, sensitive detectors are currently available to measure its flux, NO is useful for undertaking a systematic evaluation of several of the methods currently used for flux measurement. Therefore, NO would be an excellent candidate for field comparison of enclosure, gradient, and eddy-correlation techniques. The site for such a study needs to be carefully considered, since obtaining a uniform known surface flux of NO is difficult. The area must be accessible and horizontally uniform with respect to both NO emission and micrometeorological quantities. This is critical when using different techniques because of the intrinsic differences in the sample area to which the different techniques respond. It is especially challenging for NO , since its surface flux is known to be extremely variable, both spatially and temporally. The choice of the specific biome (natural grassland, scrubland, cropland, short or tall vegetation, etc.) needs to be carefully considered, and the soil, microbe, and vegetation parameters need to be carefully documented. The intercomparison should extend over

a range of seasons and environmental conditions, throughout the diurnal cycle and, if possible, before, during, and after precipitation.

Under certain conditions, rapid reactions may convert odd nitrogen from one species into another. An example of this is the $\text{NO-NO}_2\text{-O}_3$ triad, which has a reaction rate of the order of a minute. Measurements of the surface flux of a single species may therefore be much less meaningful than simultaneous flux measurements of the entire family of odd nitrogen compounds. By measuring fluxes of the entire suite, we can ensure that we have not missed an important part of the total odd nitrogen emission or deposition flux. On the other hand, Lenschow and Delany (1987) have shown that for two species for which the chemical reaction time is much shorter than the diffusion time from their source, the ratio of the fluxes is equal to the ratio of the concentrations. Therefore, it is only necessary to measure the flux of one of the species concurrently with the mean concentrations of both to obtain the fluxes of both species.

There are virtually no existing data on the deposition of PAN; there are limited measurements of NO_2 and HNO_3 dry surface fluxes. Nitric acid fluxes have been estimated over a few surfaces using gradient techniques (Huebert and Rob ert, 1985; Huebert et al., 1988), but the coverage is by no means representative. Artifact-free NO_2 flux measurements are also rare, but some do exist. We know of no measurements of the flux of NO_y , although this valuable measurement would help us place bounds on all the other odd nitrogen fluxes.

For each of these species, measurements over a much broader range of biomes than has currently been reported is essential in order to estimate fluxes to significant portions of the globe. Whenever possible, these measurements should be obtained concurrently with measurements of the other significant odd nitrogen species. We recognize two ramifications of this recommendation: (1) few laboratories are expert at all these techniques, so that multigroup cooperation will often be required, and (2) the limited availability of state-of-the-art measuring systems will make it necessary to plan practical experiments that may not be as complete as ideal ones.

A desirable experimental format would include gradient measurements of ammonia/nitrate and PAN, coupled with eddy-correlation measurements of NO , NO_2 , and NO_y fluxes. Figure 4.1 shows a schematic of a proposed experiment. Although the precision available for measuring PAN may be marginal for flux measurement (assuming a deposition velocity in the range of a few tenths of a cm s^{-1}), it may be adequate to establish an upper limit to the PAN flux. The NO_y measurements would also be useful for estimating the total surface flux of odd nitrogen species.

It is obvious, from the discussion in Chapter 1, that there is still much scope for research into the

sources and sinks of NH_3 at the surface. Even the best documented sources have uncertainties of 100%. Because of the many processes that can generate NH_3 , aircraft measurements of NH_3 inputs over large areas, as described by Lenhard and Gravenhorst (1980), for example, seem to offer much promise. Emissions from biomass burning and natural fields obviously need better quantification.

Most NH_3 cycling in the atmosphere is thought to occur close to the earth's surface (involving aerosol formation, incorporation in cloud water, and deposition), and a preponderance of gas-phase NH_3 is thought to be located in the planetary boundary layer. However, this supposition has yet to be confirmed by measurements. Thus, measurements of ambient NH_3 levels are needed in order to understand the processes that control NH_3 exchange and the tropospheric NH_3 distribution.

Such measurements are relatively scarce, however, due to a variety of experimental difficulties. Ammonia forms strong hydrogen bonds and adheres tenaciously to any unheated surface. This often leads to memory effects and sample losses, a particularly serious problem for optical techniques that require absorption or excitation cells, and leads to high background levels in filter packs, bubblers, and acid-coated denuder tubes, which necessitates long collecting times. Hydration of NH_3 by atmospheric water vapor at high relative humidities further limits the usefulness of highly specific spectroscopic techniques. Nevertheless, several techniques have been proposed to measure gas-phase NH_3 . In order to establish the ability of these techniques to quantify tropospheric NH_3 levels, a thorough test of NH_3 measuring techniques is required.

Although present sensors do not have response times fast enough for eddy-correlation flux measurements, they are sufficiently sensitive to determine NH_3 levels throughout much of the earth's troposphere. Measurements of NH_3 levels as a function of altitude, season, and latitude would constitute an important first step in placing limits on the exchange mechanisms and chemical processes that regulate this distribution. These measurements should be accompanied, where possible, by measurements of HNO_3 and aerosol NH_4^+ , NO_3^- , and SO_4^{2-} .

Measuring fluxes of the HNO_3/NH_3 couple presents some unique problems. When the product of the HNO_3 and NH_3 concentrations exceeds a particular value, a fraction of these gases will condense to form ammonium nitrate aerosol (Haeberl et al., 1988; Brost et al., 1988). Under these conditions, the flux of nitrate is carried both by HNO_3 vapor and by nitrate aerosol; similarly, the total NH_3 flux is transported by NH_3 vapor and ammonium aerosol. The total nitrate and

NH_3 flux is conserved, but the individual species fluxes may not be. The vapor species diffuses and adheres to the surface as a phase change near the surface supplies fresh vapor to the depleted laminar sublayer.

To obtain the most realistic picture of nitrate and NH_3 fluxes, therefore, all four species should be measured concurrently. The rapid adjustment time of this equilibrium between phases makes it difficult to make rigorous statements about the distribution of material between phases, but it is relatively easy to measure the total nitrate and total ammonium gradients with filter packs, from which the total flux can be estimated.

Most of these experiments appear to be feasible in the very near future, although not all the necessary instrument development has been completed. For example, the response times of NO_y detectors need to be demonstrated before we can confidently use them for eddy correlation. The precision of PAN instruments needs to be improved in order to measure vertical gradients. Development work should continue on fast interference-free NO_2 and NO_x instruments. Filter measurements of nitrate and ammonia should be supplemented with denuders whenever appropriate.

Since all of these developments seem achievable in the near future, experiments could be planned immediately. An example of such an experiment was carried out in the Amazon Basin as part of the NASA/GTE/ABLE-2A (during the dry season) and ABLE-2B (during the wet season). Preliminary results from ABLE-2A are discussed in a special issue of *J. Geophys. Res.*, 93, 1349-1624. Advective transport of chemical species from surrounding pollution sources and agricultural land posed a problem for the experiment. Detailed mesoscale meteorological information was useful for identifying pollution sources. Large-scale mean concentrations measured by the aircraft were critical to establishing that the distribution patterns of chemical species observed at the micrometeorological tower site were characteristic of the regional forest environment.

A similar experimental design was tested during the summer of 1988 in the Yukon Delta region of Alaska during the NASA/GTE/ABLE-3A. This region was well suited for the experiment due to relatively persistent meteorological patterns over an extensive flat tundra. Particular attention was paid to spatial scale factors involving biogenic source distribution. Enclosures, towers, and aircraft were used to measure concentrations and fluxes of NO over a broad spectrum of spatial scales. Tower and aircraft measurements of NO , NO_2 , NO_y , O_3 , CO_2 , CH_4 , H_2O , winds, temperature, and humidity addressed spatial and temporal scales of variability, and serial launches of free balloons provided measurements of boundary-layer height through the experimental period.

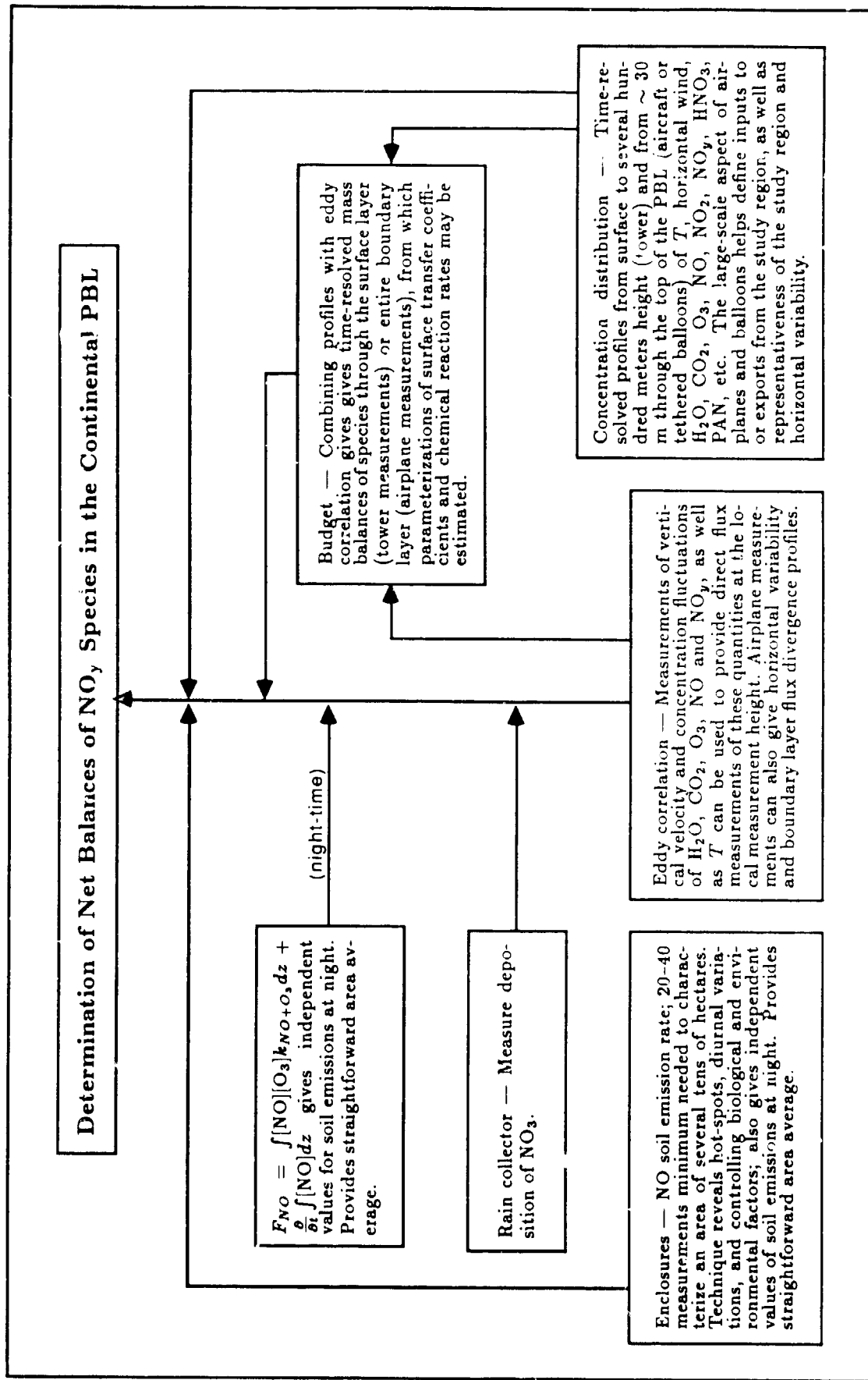


Figure 4.1. Diagram of integrated NO_x/NO_y field experiment. The goal of the experiment is to define the net balances of NO_y species in the PBL over important continental regions. Detailed local experiments are to be carried out using a ground site with a micrometeorological tower, and results will be placed in a regional context using an aircraft.

Sulfur Group

The recommendations discussed here outline in greater detail the specific types of research needed to characterize surface exchange of sulfur species. The plan for trace sulfur species studies suggests a focus on six important research areas, which share a number of considerations. First, the emphasis must be on exchange, so that both deposition and emission fluxes are addressed. While studies at any one area might well focus on a particular flux-generating process, the interpretation of acquired data must be incorporated into a more complete characterization of the global surface exchange. Second, studies are suggested for a variety of continental and oceanic biomes, the particular regional focus of any given research topic being based upon either existing data or knowledgeable estimates of the potential global significance of that region. Third, whereas several trace sulfur gases are estimated to be of highest priority based upon the currently available data, other trace sulfur species should not be dismissed without justification based on defensible data.

Fourth, there is a need for interdisciplinary research that incorporates a mix of expertise and methodologies in any attempt to characterize a given flux. This is necessary not only to determine the flux per se of a given species from a particular biome, but also to provide the basis for predictive capabilities that can often come only from in-depth understanding and appropriately designed process-level studies. Consequently, the plan calls for a combination of field and laboratory studies, with the mix depending on the question being examined.

One further major recommendation is the need to interface, both physically and conceptually, the study of sulfur gas exchange with studies being planned for other classes of trace gases (i.e., NO_x , ozone, and hydrocarbons). This is especially important since many surface exchange issues are common to all classes of compounds, and any one experiment could greatly benefit from efforts expended to characterize fluxes of other trace species and from shared experimental platforms and technologies.

The specific suggested experiments are summarized in Table 4.1. For each of the six critical areas identified, specific studies are suggested to address either process level studies or flux measurements. The critical areas focus on the general issues that require resolution in order to accurately estimate global exchange rates. As such, the descriptions are phrased in a general, rather than a highly specific, way. The experimental approaches deemed necessary to address the critical areas are briefly described as either process-level or flux measurements in the appropriate column. Process-level studies may be conducted under controlled laboratory conditions and are intended to elucidate basic production, uptake, or transformation

mechanisms, whereas flux determination is biome-specific and requires in situ measurements as well as appropriate sulfur compound speciation.

Air-Sea Gas Exchange Rates: Process-Level Study

While large fluxes of volatile sulfur gases have been observed coming from some plant species in terrestrial and near-shore aquatic environments, it is thought that the majority of biogenic sulfur input into the troposphere occurs from the open ocean. An increasing body of data indicates that supersaturation of DMS exists in the ocean and that transport into the atmosphere may be responsible for fluxes significant on a global scale. While measurements of atmospheric mixing rates of DMS support this view and are in general agreement with estimated transport rates, the transport of DMS across the air-sea interface and its dependence upon physical variables such as wind speed are poorly understood. For these reasons, studying this transport as a globally significant process is highly recommended.

Since detection of DMS at the observed 100 pptv level currently requires sample preconcentration and analysis on a time scale of ~ 30 minutes, such flux measurements appear to be approachable only by means of the vertical gradient technique. Such measurements would require the use of towers in an open water environment under a variety of atmospheric and sea-surface conditions. The coincident measurement of a suite of atmospheric trace gases, some of which are amenable to measurement by eddy-correlation techniques, would aid considerably in the interpretation of results and would be highly desirable. While deep ocean measurements would ultimately be desirable, more modest platforms in shallower waters would yield important results.

Oceanic Production of Volatile Sulfur Species

In order to extend the site-specific sulfur trace gas exchange rates from oceanic systems, derived from studies such as discussed above, to global estimates of net production, it is necessary to identify the principal biota involved and the major controlling environmental factors and then to integrate the results into a predictive model. Process-level studies are necessary to characterize the taxonomy of the important sulfur emitting species, followed by studies that address the role of environmental factors in modulating both their emission rates and geographic distribution. The second phase of this process-based approach would be the development of a model to predict exchange rates for specific sulfur gases under a variety of naturally occurring conditions.

This modeling effort would require field validation. Flux measurements in selected biomes with appropriate geographic and temporal scales, as suggested by the model, should be undertaken. The underlying focus

Table 4.1

Critical Areas	Process-Level Studies	Flux and Sulfur Speciation Studies
1. Determination of trace sulfur gas (such as DMS) air/sea exchange rates	Tower-based flux and vertical profile measurements of a suite of trace gases, including DMS, as a function of atmospheric and sea-surface conditions. The suite of gases should include those amenable to measurement by eddy-correlation techniques	
2. Characterization of the rate of sulfate aerosol formation from biogenically produced volatile sulfur gases	Laboratory and modeling studies of biogenic sulfur gas oxidation reaction pathways and mechanisms of aerosol formation	Coupled measurements of volatile sulfur gas source and product species as a function of geographic and temporal scales. (Some significant efforts are already under way.)
3. Development of a predictive capability for the oceanic production of volatile sulfur species	Experimental determination of sulfur gas evolution by micro-organisms as a function of taxonomic and environmental conditions	
	Development of a model relating the geographic distribution of the important sulfur-producing species to relevant oceanic and atmospheric conditions (e.g., temperature, salinity, sunlight)	Field measurement of the geographic distribution of the important species of volatile sulfur gas producers. Field validation of relevant distribution models
4. Characterization of SO ₂ deposition fluxes to continental and oceanic surfaces	Laboratory measurement of SO ₂ uptake resistances as a function of controlling environmental chemical and biological factors	Systematic measurements of SO ₂ and SO ₄ ⁻ wet and dry deposition in ecologically representative biomes. Studies must include biologically and geographically representative spatial and temporal scales
	Tower, enclosure, and aircraft-based SO ₂ deposition studies to key environmental surfaces. Enclosure methodologies should be coupled to eddy-correlation and vertical profile techniques	

Table 4.1, continued

Critical Areas	Process-Level Studies	Flux and Sulfur Speciation Studies
5. Characterization of SO_4^- deposition fluxes to continental and oceanic surfaces	Aircraft and mountain station studies of processes controlling the scavenging and/or production of SO_4^- in clouds and its subsequent deposition to the earth's surface	See above under SO_2 fluxes
6. More extensive characterization of volatile sulfur gas emissions from continental biomes. Development of a global predictive capability	Laboratory measurement of volatile sulfur gas emissions from a representative selection of plants and soils as a function of environmental, physiological, and taxonomic variables. (Some work on agriculturally important crops has already been undertaken.)	Survey measurements of sulfur gas emissions in previously unexplored biomes (e.g., Arctic tundra, boreal rain forests, dry tropics). Speciated measurements of sulfur gas fluxes in well-characterized areas to validate predictive models.

should be the development of predictive capabilities rather than an exhaustive inventory of all biomes.

Aerosol Formation from Volatile Sulfur Compounds

The emission of volatile sulfur compounds into the troposphere leads ultimately to the formation of sulfate aerosols. These aerosols may be the dominant form of sulfur deposition in remote regions of the globe and may also be the predominant source of condensation nuclei responsible for cloud formation in marine environments. The processes leading to the formation of sulfate aerosol from DMS emitted by marine biota are very poorly understood, as is the global and temporal distribution of the aerosol. Consequently, both process-level and survey measurements are recommended to understand this problem.

Process-level experiments would involve modeling and laboratory studies of the mechanisms, reaction pathways and rates of formation of sulfate aerosols through the oxidation of reduced volatile sulfur gases of biogenic origin. While not limited to DMS, such studies should initially focus on DMS, as it is thought to be of prime importance. In addition, field determination of the spatial and temporal distribution of both the subsurface sources and the atmospheric distribution of volatile sulfur species are necessary. While some such field measurements have been made, considerably more coupled data of precursor and aerosol atmospheric concentrations would be of great value in understanding this interaction between the troposphere and the underlying biologic community.

SO₂ Fluxes to Continental and Ocean Surfaces

Although many measurements of SO₂ fluxes have been made, many important questions involving the rates and processes governing these exchanges need to be resolved. One pressing question relates to the role of scaling point measurements of SO₂ fluxes to larger areas, associated with model grids or ecosystems used in budget computations. Difficulties arise due to spatial variation in surface vegetation and terrain complexity; thus, areally averaged fluxes over a complex topographic mosaic of underlying surfaces may or may not equal the weighted average based on the individual components of the surface mosaic. Experiments coupling aircraft flux measurements with a spatial average of tower-based SO₂ flux measurements are required to address this problem.

A theoretical framework exists for describing the process governing the transfer of SO₂ to vegetated surfaces. Unfortunately, some of the pathways postulated in this framework are not well quantified. Particular attention needs to be paid to factors governing SO₂ deposition to soils, detritus, and moist canopies. Many questions remain about the effects of surface wetness resulting from dew, rain, or snow on

SO₂ deposition rates; since the pH of such a liquid film may be expected to decrease as SO₂ absorption proceeds, uptake may change dramatically with time, and laboratory experiments are required to address this question.

Analogous questions apply to oceanic systems. Studies are needed to determine the factors controlling SO₂ uptake to ocean waters with different wave, and, therefore, surface characteristics.

Sulfate Deposition to Continental and Oceanic Surfaces

Sulfate exists in the atmosphere in both particulate and aqueous forms, as well as in gaseous form. Consequently, processes governing the sulfate SO₄²⁻ deposition must be distinguished from those associated with SO₂ deposition. Data pertaining to the magnitudes of both dry and wet SO₄²⁻ deposition to different biomes and ocean surfaces is needed. Unfortunately, deposition rate measurements of sulfate particles are difficult. Since deposition velocities are a function of particle size, deposition rates are a complicated function of particle size distributions. Significant improvements in methods used to measure sulfate particle fluxes appear to be needed.

Sulfate deposition to sites adjacent to significant orographic features poses a special problem. SO₄²⁻ is deposited not only by dry processes and precipitation but also by cloud impaction on mountainous terrain and vegetation. Studies are further burdened by complicated airflow patterns in such terrain. It would appear that aircraft and mountaintop studies would have to be closely coupled to address the problem. Studies of cloud scavenging and transformation would have to be performed, since both affect the SO₄²⁻ deposited by clouds. Concentrations of oxidants such as H₂O₂ are expected to play a major role in this regard.

From a biogeochemical standpoint, fluxes of both SO₂ and SO₄²⁻ are needed to construct a global sulfur budget. Variations in temporal and spatial scales of both of these important species need to be better characterized. Data from existing monitoring networks may be utilized, but these networks are inadequate for extension to a global scale. Additional monitoring stations in representative continental and oceanic sites, providing data on chemical concentrations, meteorology, and surface characteristics, are sorely needed.

Volatile Sulfur Gas Emissions from Continental Biomes

Several previously completed field measurement programs indicate that soils and vegetation in both intertidal and upland regimes contribute significantly to the production of reduced trace sulfur gases. These observations are, however, very sparse. Thus, it is difficult to extend these measurements to a

global scale with any degree of certainty. It is important to extend such measurements to other continental regions of suspected interest in order to develop reliable predictions for a variety of sites and environmental conditions. This task requires attention both to flux measurement per se and to the chemical characterization of the sulfur species being released.

For several biomes that are potentially significant on a global scale, few or no sulfur gas flux measurements have been performed. These include tundra, wet and dry tropics, and boreal rain forests. Surveys in these areas are recommended in order to assess their contribution to the global sulfur budget.

Process-level studies are also recommended to examine both vegetation and soils as emission sources under controlled laboratory and field conditions. These efforts should identify taxonomical, and physiological and environmental variables affecting sulfur gas emissions. Some studies of this type have already been undertaken but were restricted to agricultural crops; a considerable broadening of scope is required. The principal methodology used in such studies to date has been enclosure systems. These should be augmented with other micrometeorological approaches as soon as the requisite sensitivity and temporal resolution have been developed.

This research must result in a capability to predict fluxes and to account for the considerable spatial and temporal (i.e. diurnal, seasonal, and annual) variability in emissions from continental biomes. In order to fully validate this predictive capability, additional studies in some well-characterized source region should be useful.

Carbon Group

Methane

Of all the hydrocarbon species found in the atmosphere, currently methane is the best understood. The growth of methane concentrations in the atmosphere has been demonstrated by direct measurements on atmospheric samples over the past decade (Blake and Rowland, 1988; Rasmussen and Khalil, 1986; Fraser et al., 1986a), spectroscopic measurements of the total column amount of methane (Rinsland et al., 1985), and by the measurement of air bubbles extracted from polar ice cores (Etheridge et al., 1988; Pearman et al., 1986; Stauffer et al., 1985; Rasmussen and Khalil, 1984). The increase in methane has been occurring for the past two centuries, over which time the concentrations have more than doubled from a preindustrial level of about 700 ppbv to the present value of about 1650 ppbv. Recently the ice-core record for methane has been extended back to 160,000 years BP by Raynaud et al. (1988) and to 100,000 years BP (Stauffer et al., 1988). Both investigations showed that during glacial times the methane concentrations were about half of those found in interglacial periods. The present atmospheric burden of methane is known to

be about 4,300 Tg; the distribution of methane in the troposphere has been measured by Steele et al. (1987). By using estimates of the average concentration of hydroxyl radical in the atmosphere, Prinn et al. (1987) deduced the average atmospheric lifetime of methane to be 9.6 (+2.2, -1.5) years, where the uncertainties refer to one standard deviation. While most of the long-term increase in methane is probably due to an increase in the magnitude of the sources, the close chemical coupling between CH₄, CO, and OH in the atmosphere means that increasing levels of CO in the atmosphere can also lead to an increase in the level of methane (Thompson and Cicerone, 1986).

While we may have compiled considerable information about atmospheric methane, there still exist significant uncertainties in our knowledge of the sources of methane. There is a growing consensus that the magnitude of the annual release to the atmosphere is in the range 400 to 600 Tg (e.g., Bingemer and Crutzen, 1987; Cicerone and Oremland, 1988), but the relative contributions from known sources is far from settled. In a recent paper, Lowe et al. (1988) interpreted ¹⁴C/¹²C ratios in atmospheric methane to deduce that about 77% of this trace gas derives from fossil carbon sources. This percentage is much higher than had been suggested previously. A consequence of the uncertainty is that it is still not possible to quantitatively account for the observed long-term increase.

A determination of the uncertainties in the various methane sources will not be easy. Success will almost certainly have to depend on a combination of several activities: atmospheric measurements of mean concentrations; direct flux measurements over known or suspected source regions; process studies to better quantify total and isotopic releases from known sources; measurements of the different isotopic species of methane, both as carbon and hydrogen; and atmospheric modeling studies to aid in the integration and interpretation of our knowledge about methane. Many of these activities are already under way but may have to be expanded or augmented. Most of the atmospheric measurements of methane are currently taken in the boundary layer. Regular determinations of vertical profiles in the troposphere at a number of locations would aid considerably in constraining model calculations. Direct flux measurements have usually been carried out for relatively brief periods of time. It would be desirable to measure fluxes at some locations for at least a year. This would provide information about possible seasonal variations in fluxes and help to reduce uncertainties when estimating annual releases. Such an exercise would probably require that the fluxes be measured by a noninvasive technique such as eddy correlation.

The measurement of the isotopic composition of atmospheric methane is potentially very valuable in understanding the sources of methane, because

different sources may release isotopically distinct methane (Stevens and Engelke, 1988). The contribution of fossil methane to the total budget can, in theory, be deduced by measurements of $^{14}\text{C}/^{12}\text{C}$ ratios in atmospheric methane, but as Lowe et al. (1988) point out, the continuing production of $^{14}\text{CH}_4$ from nuclear power plants will complicate the issue in coming years. One area that has received relatively little attention is the hydrogen isotopic composition of methane. Such measurements could impose valuable constraints on the relative magnitudes of various sources in the global methane budget. Process studies can elucidate the mechanisms of methane production and release and the factors that can influence those mechanisms (Martens et al., 1986; Blair et al., 1987).

The compilation of high-resolution global data bases for methane emissions from natural wetlands (Matthews and Fung, 1987) and from animals (Lerner et al., 1988) is a very positive development, since they can be used as inputs to three-dimensional tracer transport models of the atmosphere to test hypotheses about the source terms in the global methane budget. Unpublished simulations of various methane sources with such a model by Fung and coworkers at NASA/GISS show that some methane sources are large enough to raise the annual mean concentration over large regions by tens of parts per billion. These model results could be readily tested by routine measurements of methane concentrations at appropriate locations within or near to the source regions.

Carbon Monoxide

As mentioned earlier in the report, perhaps 50% of the sources of carbon monoxide are in tropical regions. This estimate is not based upon direct measurements of fluxes. Using airborne eddy-correlation techniques and the fast-response CO sensor described by Sachse et al. (1987b), it should now be feasible to test directly the estimates of carbon monoxide production in the tropics. This would require measurements of the eddy flux and the mean CO concentrations at different heights in the boundary layer over a tropical forest, as well as CO concentrations in the free troposphere above the boundary layer. It would be desirable, but not absolutely necessary, to measure the CO levels and the CO flux at the ground while the aircraft measurements were being made. Since much of the CO in the tropics is thought to derive from oxidation of NMHCs, it would also be desirable to measure the vertical gradient of the NMHCs in the boundary layer as part of the experiment. Observations of this type have already been carried out over the Amazon Basin as part of NASA/GTE/ABLE-2A and 2B, as reported for ABLE-2A in the *J. Geophys. Res.*, 93, 1349-1624, and have demonstrated that the technology is at hand to address this question.

Nonmethane Hydrocarbons and Organics

At present there are no fast-response sensors for NMHCs and organics. Their presence in the atmosphere at concentrations of about 1 ppbv or less makes the development of fast-response sensors a daunting task. Therefore, for the foreseeable future, fluxes of NMHCs will be estimated by gradient or budget techniques, which require only measurements of mean concentration or concentration differences. Because of the large number of species in this class, any effort to develop fast-response sensors should perhaps focus on isoprene, since from the point of view of atmospheric chemistry, it is arguably the most important member of this class. Since the production of isoprene by plants is known to be related to photosynthesis, further studies of plant metabolism may yield critical information that can be used to predict isoprene emissions to the atmosphere.

Species Concentration Budget Experiment

Under certain circumstances, the emissive flux from an important source region can be derived by making measurements of the elevated mixing ratio of a given species in the downwind plume from the region. Concentrations measured in the air downwind of the source reflect (1) the original composition of the air, (2) the addition of species from local sources to the near-surface layer, (3) the amount of entrainment/mixing with the background air, and (4) photochemical evolution in the air parcel. A well-designed experiment would include spatially/temporally correlated measurements of a number of chemical species both upwind and downwind of a major source region; it would allow for the empirical calculation of relative fluxes, including those such as ozone that are evolved as the plume of NO_x and hydrocarbons ages and mixes with the environment.

The time scales involved would fall in the range of 0-5 days, and thus conserved tracers would include CFCs, CO_2 , CH_4 , CO, N_2O , SF_6 , black carbon, and alkanes; whereas the chemically evolving species would include O_3 , NO, NO_x , PAN, NO_y , H_2O_2 , SO_2 , and shorter-lived hydrocarbons. The calibration of absolute flux can be based on (1) a conserved tracer with a known rate of emission, or (2) meteorological analysis of the growth and mixing of the plume. Similarly, the photochemical time scale for aging of the parcel (e.g., NO_x/NO_y ratio) could be based on (1) a species with a known decay rate or (2) the meteorology. In either case, the background environment (or air upwind of the region) must have a well-characterized composition and low variances for species mixing ratios. It may be possible (and necessary) to consider two different mixes of background air, such as boundary layer air and free

tropospheric air, each with a characteristic composition.

An important requirement is that the spatial/temporal correlations be resolved in order to eliminate high-frequency variations that may be caused by separation of source or instrumental noise. Relative enhancements would not be derived by the cross-covariance of two species at zero lag but rather by their values at some lagged time that would be representative of some fraction of the integral scale. There is a need to sample far enough downwind so that different point sources in the region have had a chance to mix partially. Empirical definition of the integral scales is needed for specific cases.

The multivariate statistics resulting from such an experiment could be used in conjunction with simple quasi-Lagrangian models of the chemical evolution of emissions as they mix and evolve with the background air. They could be used to define what happens chemically to such emissions as they pass from the boundary layer into the free atmosphere by convective processes and how much ozone is produced in the open troposphere as these layers disperse. The more species that are measured simultaneously, the greater the number of constraints with regard to absolute fluxes and photochemical age could be applied to reduce the uncertainty of the results.

Exchange between the PBL and the Free Troposphere

A key issue is the rate of exchange of chemical species between the PBL and the free troposphere. Meteorologists usually divide this exchange into two separate processes: "entrainment," where free tropospheric air is brought into the PBL by small-scale turbulence processes (i.e., spatial extent less than a few hundred meters) across a clearly defined density discontinuity, and "cloud venting," where large organized convective elements, powered by latent-heat induced buoyancy, transport substantial amounts of PBL air throughout the troposphere (as high as the tropopause for deep convection). Both processes have received considerable attention from meteorologists because of the obvious importance of the vertical transport of momentum, sensible heat, and moisture. The entrainment process has been studied most extensively for the clear and stratocumulus-topped convective PBL. The entrainment rate for marine stratocumulus is typically in the range of 0.05 to 1.0 cm s^{-1} , while in the clear, continental PBL it may be as large as several tens of centimeters per second near midday.

Cloud transport has been studied in a variety of large field programs (e.g., the Global Atmospheric Research Program Atlantic Tropical Experiment [GATE] and the Cumulus Cloud and Precipitation Experiment

[CCOPE]). A major goal of these programs was to develop parameterizations for the formation, extent, and impact of cumulus convection. Although these parameterizations are an essential ingredient in mesoscale and global scale atmospheric models, they are still very crude, case specific, and only loosely based on the underlying physics. More recently, cloud transport of chemical species was estimated over the Amazon region during the rainy season in ABLE-2B.

Many of the previous atmospheric studies of convection have emphasized the internal dynamics of the process rather than the effective transport properties of a field of cloud elements. From a chemical perspective, Ritter (1984), Ching et al. (1985), and Greenhut (1986) have investigated the transport by cumulus clouds between the mixed layer (subcloud base) and a capping inversion at cloudtop using aircraft, surface-based measurements, and tracers.

It is now clear that a study of these processes should be undertaken using a combination of aircraft and ground-based remote sensors, in addition to the direct sensing capabilities mentioned above. The remote sensors should include the complementary pairing of a chemical measuring (DIAL or Raman) lidar with a vertical velocity Doppler lidar or radar profiling system. Such an experiment would be integrated with a high-resolution satellite cloud map (e.g., from LANDSAT), which would allow extrapolation to model grid scales.

We propose that future experiments of this type be done in two phases. The first phase would be in dry convective conditions (few or no clouds), in which the flux divergence of specific species within the PBL would be related to the characteristics of the transition (inversion) layer as a function of synoptic conditions. Data from such a study will enable top-down and bottom-up diffusion theories (Wyngaard and Brost, 1984) for the vertical profiles of scalar fluxes to be evaluated and related to larger-scale conditions.

The second phase would occur in an active convective cloud field. Airborne fast-response instruments would be used below and within the cloud layer to determine updraft/downdraft statistics and the transport of chemical species within the clouds and in the region between clouds. Vertical mean concentration profiles within and above the PBL to determine the concentration jump at the inversion are important for understanding the observed cloud transport. These can be determined from aircraft ascents and descents and by ground-based profiling techniques.

Satellite data obtained simultaneously would be used to determine the representativeness of the cloud field sampled by the aircraft over a larger region, thus making a connection between the flux divergence of species within the PBL to the larger synoptic scale.

Modeling and Parameterization

The objective of field experiments is the quantification of chemical budgets over particular areas and times. Modeling is essential to provide an interpretive framework for flux measurements that are often fragmentary and unrepresentative in space and time, even in experiments that include a broad spectrum of measurements from enclosures, towers, and aircraft in carefully chosen test areas. Models that are specific to the experimental region cannot only fill in the sampling gaps, but also help to develop empirical parameterizations that can then be used for global scale chemical transport models which, as emphasized in *GTC-Plans for the U.S. Research Effort* (UCAR, 1986), are essential tools for understanding and predicting changes in the earth's chemical system.

Role of Models in Experimental Design and Analysis

Models that relate concentrations and fluxes are essential complements to experiments. Their role is twofold: to help plan future measurement strategies and to interpret observations. On the scale of a given experiment, models are used to test assumptions about processes and mechanisms affecting trace species distributions. Both observational and modeling studies are conducted to evaluate budgets of species concentration, as given by (2.6) or by an integrated form of this equation. Basically, these relations equate the time rate of change of concentration to the sum of horizontal advection, vertical flux divergence, and chemical sources and sinks. For a chemically inert gas (e.g., CO₂), chemical sources and sinks are negligible. Therefore, fluxes can be measured by either enclosure methods or, if a sufficiently fast-response high-resolution sensor is available, from towers or aircraft.

For species that are chemically reactive on a time scale comparable to the transport and mixing time scales of the atmosphere, enclosure methods may not be feasible, and flux divergence may be appreciable in the surface layer, which greatly complicates the use of micrometeorological techniques for flux measurement. In this situation, modeling may play an important role in estimating terms in the budget equation and evaluating observational strategies. Sometimes, although individual trace species may not be conserved, the sum of several species may be (e.g., NO_x).

An important problem in determining chemical budgets from field studies concerns the inherent variability of the atmosphere. A predictable or systematic variability due to seasonal and diurnal changes can be dealt with by a combination of field studies and modeling. Random variability presents greater difficulty (e.g., convective turbulence that can cause large intermittent fluxes of material over small areas, or precipitation that can quickly deplete the atmosphere's soluble gases and aerosols in a small

region). The need to consider the consequences of random variability in the atmosphere requires a more statistical description of processes in model calculations. One way to do this is to develop stochastic descriptions of selected processes for incorporation into a coupled transport-chemical model (Stewart et al., 1988). Observations are used as a basis for the statistical description of the phenomenon to be studied (e.g., wind statistics for turbulence or advection fluxes), and repetitive model simulations are carried out, each one with a different but statistically equivalent scenario of individual events to calculate means and variances.

Parameterization Experiments

A major goal for field research is the development of parameterizations that can then be used in modeling studies on a variety of temporal and spatial scales from local to global, and from a few hours to thousands of years. Some of the most difficult problems in this area deal with parameterizing fluxes over real-world surfaces, such as forests, hills, and oceans.

Development of methodologies for examining air-surface exchange within and above deep vegetative canopies should be continued. This includes evaluation of micrometeorological approaches, testing the adequacy of measurements from single towers, development of site-specific, simplified sampling strategies, and fundamental studies of exchange among different portions of the canopy and underlying surface. For example, standard turbulence flux-gradient approaches inside canopies are usually not successful, which implies that resistance models of exchanges within the canopy are not realistic.

Development and extensive testing of flux measurement techniques over hilly terrain are also needed. Likewise, the influence of isolated surface irregularities (e.g., windbreaks) needs to be evaluated. These and related problems of scale are best investigated with a combination of measurements from towers and aircraft, with additional contributions from enclosure studies.

Estimates of air-sea exchange rates of many trace chemical species are necessary. Water surface skin conductance needs to be studied, particularly for wind speeds greater than about 15 m s⁻¹. Although initial studies may be profitably carried out in shallow-water areas, extension to the open sea, where the parameterizations have to be applied, will eventually be required.

Development of Techniques

Research on fundamental aspects of the properties of turbulence involving chemical species is necessary to advance the state of the art of micrometeorological techniques. For example, further studies to accurately determine the Kolmogorov inertial subrange constant

for trace species will lead to better accuracy of the dissipation technique (Fairall and Larsen, 1986), which can be used on moving platforms such as ships. Studies of the influence of rapid chemical reactions on both mean and turbulence variables obtained from chemical species, including flux-profile relationships, statistical quantities such as variances, covariances, skewness, and other higher-order moments, and spectra and cospectra of chemical species and related variables (e.g., velocity components, temperature, and humidity) should improve our understanding of the limitations of flux measurement techniques and yield useful new approaches to flux measurement.

Statistical measures such as the integral scale or spectral shapes of trace species fluctuations should be investigated as tracers for PBL entrainment and for advection associated with nonuniformities in surface exchange. As well-defined situations are examined and documented, derived statistical measures of behavior could be applied to chemical species whose vertical exchange characteristics are still poorly understood. Application of saturation-point theory developed by Betts (see Boers and Betts [1988] and references therein) may give useful information for estimating PBL entrainment rates.

Work should continue on developing eddy-accumulation techniques into operational flux-measuring tools. Further refinements are necessary to obtain precision comparable to established micrometeorological techniques; in particular, flow control must be improved or parameterizations based on micrometeorological concepts developed to allow alternative realizations of the eddy-accumulation technique utilizing simpler fluid flow principles.

The criteria for use of path-averaged concentrations, such as obtained by optical absorption measurements over tens of meters, need to be established for gradient techniques. It appears that the required area of horizontally uniform conditions would increase as the path length increases. Certainly, criteria concerning siting and accuracy of measurements cannot be relaxed, as compared to traditional gradient methods. For example, refined understanding is needed of the way in which uncertainty in the height difference between any two horizontal averaging paths affects the accuracy of the eddy flux computed from them, and of the consequences of operating too near the zero-plane displacement height.

In addition to the need for chemical sensors

with improved performance, other improvements to instrumentation are needed. Sensors that are smaller, reliable, easy to operate, and more durable would be useful for working in vegetative canopies. The application of remote-sensing techniques to measure profiles of vertical fluxes should be pursued. Tethered balloons and blimps offer some advantages as well. Inertial platforms might be deployed on ships so that eddy correlation could be applied at sea without rigid platforms.

Some major facilities need to be developed or exploited. Existing tall towers (heights of 100 to 300 m) should be utilized when appropriate; worldwide inventory of their locations, surroundings, and availability should be taken so that they may be considered when needed. Construction of a major sea platform should be considered. Possibilities include a deep-sea spar buoy and jack up platforms, with space and facilities adequate for operation of sophisticated chemical instrumentation.

Although remote measurement of trace species fluxes seems feasible, to date we know of no such attempts. We mention the possibility because of the potential importance of being able to measure flux profiles from either the ground or an aircraft. This would obviate the need for tall towers, eliminate flow distortion errors, and permit low-level flux measurements from aircraft. Range-resolved remote measurements of both wind fields and trace gas concentrations have been carried out, although not concurrently. Remote measurements of ozone concentration have been discussed previously. In the case of wind profiling systems, several types of sensors are in various stages of development and application. These systems include conventional acoustic sounders (SODARs), higher-frequency "mini" acoustic sounders, phased-array clear-air UHF (400 MHz) radar systems, and Doppler lidars. Conventional acoustic sounders have vertical range resolution on the order of 50 m for a three-minute integration over a range of about 100 to 500 m. The resolution of the UHF radar system is range-dependent with 100 m resolution over the range from 300 to 2600 m typical for a two-minute integration period. Over an extended range of 600 to 7,000 m, a similar two-minute integration would typically provide a range resolution of about 300 m. Doppler lidars offer the promise of even better performance at extended ranges than the UHF radar, although they are at a much earlier stage of development.

5 NEW OPPORTUNITIES FOR FLUX MEASUREMENT

B. B. Hicks, C. E. Kolb, and D. H. Lenschow

The preceding discussion indicates that the status of instrumentation for measuring species concentration varies greatly for different species. On the one hand, for some species such as ozone and NO, current instruments can be used to measure flux by eddy correlation and other techniques. At the other extreme, for many species no foreseeable development appear likely to provide means for flux measurement. Between these extremes, for many species techniques on the horizon offer considerable potential. Generally, no single method promises to be a breakthrough for large numbers of species. Therefore, research aimed at improved chemical species sensors needs to be carefully considered on a species-by-species basis; in some cases, small improvements in existing techniques may be sufficient to provide flux measurement; in other cases, completely new technology will be necessary.

Advances in tunable laser sources can be expected to lead to significant improvements in detection techniques using differential absorption or laser-induced fluorescence spectroscopy. Similarly, incremental improvement in both sample handling and detection technologies for chemiluminescent and chromatographic instruments are also clearly possible.

Beyond incremental improvements in existing technology, it is important to identify and pursue opportunities for improvements of an order of magnitude or more in sensitivity or responsivity. It is also critical to identify new detection technologies that may have been demonstrated in laboratory use but have not yet been evaluated for field use.

While it is difficult to predict where the next breakthroughs in sensor technology will occur, it is possible to cite a few examples from current laboratory work that hold great promise. Other novel detection techniques for the priority species discussed in earlier chapters are certainly possible, and research into a wide variety of new detection schemes should be encouraged.

Improvements in Chemical Sensing

IR Absorption Sensor Breakthroughs

Multipass optical paths, whether inside closed sampling cells or open to the atmosphere, are an

important component of many spectral detection techniques, especially those utilizing tunable lasers for differential absorption measurements. Most such devices currently use traditional White-cell geometries that typically allow 20 to 40 passes. Recently, researchers at Aerodyne Research, Inc. have begun to utilize off-axis resonator cells, which were originally developed as optical delay lines for early computer applications (Herriott and Schulte, 1965), to increase the number of passes.

Such off-axis resonators can theoretically be configured in an "astigmatic" manner, which should allow an increase of 10 to 30 in the number of passes and therefore in the absorption path length and the sensitivity for a given size sample cell. Such an advance would make either airborne or ground-based eddy correlation or gradient measurements with tunable laser absorption techniques possible for a much larger number of gases.

The sensitivity of most tunable laser absorption field measurements is limited to differential absorptions ($\Delta I/I$, where I is the laser intensity on the detector) of 10^{-3} to 10^{-4} . Differential absorptions in the 10^{-6} range have been reliably measured in the laboratory but are often difficult to achieve because of the presence of Fabry-Perot interference fringes (etalons) generated by multiple-beam interferences in the optical path.

Several signal processing techniques are currently being developed, particularly for tunable diode laser systems, which promise to allow routine measurements of $\Delta I/I$ in the 10^{-5} to 10^{-7} range, greatly increasing the sensitivity of TDL-based instruments. These new techniques include the two-tone optical heterodyne or two-tone frequency modulation method under development at IBM, SRI International, and NASA (Gehrtz, et al., 1986; Cooper and Warren, 1987; Chou and Sachse, 1987); the sweep integration techniques for fringe subtraction developed at McMaster University (Cassidy and Reid, 1982; Beckwith et al., 1987); and the Brewster-plate spoiler technique for fringe reduction developed at the Jet Propulsion Laboratory (Webster, 1985). Coupling one or more of these fringe reduction techniques with the lower-magnitude

fringes typically found in the off-axis resonator mirror geometries noted above should greatly extend the capability of TDL and related tunable laser instruments.

Sensor Breakthroughs for Sulfur Species

Chromatographic separation is an important technique for many high-priority but low concentration trace species—particularly volatile sulfur species. Because of the current low detection capability for standard flame photometric detection (FPD), as outlined in Chapter 3, many species can be quantified only by lengthy batch concentration techniques. Even gradient flux measurement methods require a much more efficient detection system for sulfur compounds.

At least two laboratories are currently investigating techniques that promise at least a factor of 100 increase in sensitivity for gaseous sulfur species. Investigators at Denver University are developing a hydrogen flame technique for converting sulfur species to SO, followed by chemiluminescent detection of SO₂, formed by reaction of SO with O₃.

Investigators at the Georgia Institute of Technology are attempting to adapt a microwave-induced plasma/emission spectroscopy (MIP/ES) technique to high-efficiency sulfur detection. A plasma consisting of atoms and ions of the sample gas is produced by a microwave generator, and the plasma emission is monitored by a photomultiplier at a wavelength that is specific for the sample gas. The advantage of MIP/ES over conventional FPD is the relatively high excitation energy, which creates a well-defined plasma; by comparison, flame excitation produces a variety of atoms, molecules, and radicals at different energy levels, which are strong functions of the flame characteristics. Another advantage of MIP is that plasma emission is much stronger than flame emission and therefore promises a substantially lower detection limit, possibly down to levels that make the real-time monitoring of sulfur and other gases in the atmosphere possible.

Laser Ionization Sensors

Spectral detection techniques have an enormous value, since they can often be designed to display very high specificity for the target species. On the other hand, the collection and detection of photons can be relatively inefficient. Individual ions at low pressure can, however, be reliably detected. The combination of spectral specificity (exploiting currently available laser technology) and unit detectivity can currently be combined in laboratory studies in the technique of resonance-enhanced multiphoton ionization (REMPI). In REMPI, one or more relatively high-powered, tunable lasers are used to photoionize the target species via absorption of two or more photons through an intermediate excited electronic state.

Applications of this technique for molecular species have been reviewed by Johnson and Otis (1981), while extensions to free radical species have recently been reviewed by Hudgens (1987). At sufficiently low pressure, the technique can be coupled to mass spectrometric detection, providing a second level of specificity (Schlag and Neusser, 1983; Bernstein, 1982). This technique, with or without mass spectrometric ion selection, may eventually be useful for flux measurement.

Detection technologies that can measure a number of species simultaneously are clearly desirable. Fourier transform infrared (FTIR) instruments have often been used in quantifying infrared-active gas mixtures in laboratory studies, heavily polluted atmospheres, and industrial process streams (Griffiths, 1983; Theophanides, 1984); they have also been used in field infrared emission analyses of hot gas sources (Wormhoudt et al., 1985), and in the upper atmosphere (Kunde et al., 1987). Significant advances are now being made in engineering small, rugged, and highly sensitive FTIR instruments. Furthermore, the advent of microprocessors allows real-time calculation of Fourier transforms and data display, even under field conditions. It may be possible to couple FTIR sensors with other multispecies sensing capabilities and to use novel multipass or long path cells to allow simultaneous gradient measurements of several species.

Flux Measurement Technology

For the most part, the micrometeorological technology necessary for flux measurement is available and relatively mature compared with chemical sensor technology. Therefore, we feel that the atmospheric chemistry community need not direct a great deal of attention to improvements in this area. Clearly, the greatest impact on the capabilities for flux measurement will come from development of high-speed, high-resolution chemical sensors that are adequate for eddy-correlation flux measurements, and from very accurate high-resolution sensors for mean measurements that are needed for flux measurement by the gradient technique and by budget techniques. Since the most fundamental and direct technique is eddy correlation, we feel that if there seems some hope of developing sensors capable of eddy-correlation flux measurement, this is the preferred course to pursue. This development is especially important for flux measurement from aircraft, because of the impracticality of flying sufficiently close to the surface to use surface layer similarity methods (e.g., the surface layer flux-gradient relationship) for estimating the flux.

There are, however, a few areas where improvements in airplane technology for flux measurement are desirable—and anticipated. The Global Positioning System (GPS), a satellite-based radio navigation system, can provide more accurate aircraft position

and velocity than the currently used inertial navigation system (INS). On the other hand, INS has better time response and can make accurate measurements of airplane attitude angles that are required for accurate measurements of vertical air velocity. The combination of GPS and INS will improve the accuracy of mean wind measurements and, to a lesser extent, of velocity fluctuations. The most pressing need in species concentration measurement from aircraft is a reliable and robust low-drift, fast-response humidity sensor. This is an active area of technological exploration. The solution has been just around the corner for the past 20 years. We still believe that within a few years, the promise will be realized with new optical humidity detectors (infrared or ultraviolet). Recently, several commercial IR hygrometers have become available and a UV hygrometer has been under development, but these have not yet been thoroughly tested by the meteorological community, nor have they been designed for aircraft use. A UV hygrometer for aircraft use is now under development at NCAR.

An important consideration for chemical species flux measurements from aircraft is the error that can be introduced into the measured eddy-correlation flux by flow distortion and air density fluctuations if species density is measured (as is the case for radiation absorption or emission sensors). As Wyngaard (1988a) points out, this error is potentially significant, particularly if the species measurement is in a strongly distorted flow region such as near the aircraft fuselage. There is no error, however, if instead species mixing ratio is measured. As pointed out earlier, measuring mixing ratio with respect to dry air also obviates the need for correcting for mass fluxes resulting from sensible and latent heat fluxes. Therefore, it is highly

desirable to develop sensors that measure mixing ratio—particularly for aircraft but also for ground-based flux measurements.

In the more distant future, development of airborne remote sensors has the potential of revolutionizing the use of aircraft as a mesoscale measuring platform. Airborne DIAL has already been developed and used for profiling mean ozone and humidity structure in the atmosphere. Raman techniques also offer some potential for remote species measurement in the atmosphere. Ground-based and airborne Doppler lidars have been developed. It is conceivable that eventually they can be combined with remote species measurements and provide a remote eddy-correlation flux measurement capability, both from the ground and from aircraft. In this way, flux profiles might be measured remotely, without the need of multiple measurement levels.

Obviously, other new developments to improve flux measurement not even anticipated at this time are certain to emerge. Because of this, it is important to monitor developments in instrumentation not immediately applicable to flux measurement that may sometime provide a key for further advancement. Inertial navigation systems, for example, were developed for self-contained military guidance and navigation applications. Without this application, the technology would likely never have become available to the scientific community. Yet they provided the key for accurate eddy-correlation flux measurement from aircraft. Similarly, there are likely other technological breakthroughs that may someday give us capabilities that are now just imagined. We hope that this report is of some help in summarizing the current state-of-the-art and encouraging developments in flux technology.

APPENDIX

Acronyms and Abbreviations

ABLE	Atmospheric (or Amazon or Arctic) Boundary Layer Experiment	ISLSCP	International Satellite Land-Surface Climatology Project
ASTER	Atmospheric Surface Turbulent Exchange Research (Facility)	LANDSAT	Land Remote Sensing Satellite
BP	Before Present	LIF	Laser-Induced Fluorescence
CBL	Convective Boundary Layer	MIP/ES	Microwave-Induced Plasma/Emission Spectroscopy
CCOPE	Cooperative Convective Precipitation Experiment	NASA	National Aeronautics and Space Administration
CITE	Chemistry Instrumentation Test Experiment	NBL	Nocturnal Boundary Layer
DACOM	Differential Absorption CO Measurement	NCAR	National Center for Atmospheric Research
DIAL	Differential Absorption Lidar	NOAA	National Oceanic and Atmospheric Administration
ECD	Electron Capture Detector	NSF	National Science Foundation
EF	Enzymatic Fluorometry	PAM	Portable Automated Mesonet
FID	Flame Ionization Detector	PBL	Planetary Boundary Layer
FIFE	First ISLSCP Field Experiment	RASTER	Remote ASTER stations
FPD	Flame Photometric Detection	REMPI	Resonance-Enhanced MultiPhoton Ionization
FTIR	Fourier Transform Infrared	SODAR	Acoustic (SONIC) RaDAR
GARP	Global Atmospheric Research Program	STP	Standard (Atmospheric) Temperature and Pressure
GATE	GARP Atlantic Tropical Experiment	TDL	Tunable Diode Laser
GC	Gas Chromatography	TDLAS	Tunable Diode Laser Absorption Spectrometry
GISS	Goddard Institute for Space Studies	UCAR	University Corporation for Atmospheric Research
GTCP	Global Tropospheric Chemistry Program	UV	Ultraviolet
GTE	Global Tropospheric Experiment	VUV-FP/LIF	Vacuum UV Flash Photolysis/Laser-Induced Fluorescence
HPLC	High Pressure Liquid Chromatography	WMO	World Meteorological Organization
INS	Inertial Navigation System		
IR	Infrared		

Chemical Symbols

AgF ₂	Silver Fluoride	H ₂ S	Hydrogen Sulfide
ArF	Argon Fluoride	HgCdTe	Mercury Cadmium Telluride
CFC	Chlorofluorocarbon	InSb	Indium Antimonide
CH ₄	Methane	NH ₃	Ammonia
CO	Carbon Monoxide	NH ₄ ⁺	Ammonium Ion
CO ₂	Carbon Dioxide	NMHCs	Nonmethane Hydrocarbons
CH ₂ O	Formaldehyde	N ₂ O	Nitrous Oxide
CH ₃ CHO	Acetaldehyde	N ₂ O ₅	Dinitrogen Pentoxide
CH ₃ COOH	Acetic Acid	NO	Nitric Oxide
(CH ₃) ₂ CO	Acetone	NO ₂	Nitrogen Dioxide
CH ₃ Cl	Methyl Chloride	NO ₃ ⁻	Nitrate Ion
CH ₃ SH	Methylmercaptan	NO _x	Nitrogen Oxides (NO + NO ₂)
CH ₃ SCH ₃	Dimethylsulfide (DMS)	NO _y	Total Odd Nitrogen Compounds
COS	Carbonyl Sulfide	O ₃	Ozone
CS ₂	Carbon Disulfide	OH	Hydroxyl Radical
ClO ₂	Chlorine Dioxide	PAN	Peroxyacetyl Nitrate
DMDS	Dimethyldisulfide	POPHA	p-Hydroxyphenylacetic Acid
DMS	Dimethylsulfide	PPN	Peroxypropenyl Nitrate
HCOOH	Formic Acid	Rn	Radon
HNO ₂	Nitrous Acid	RONO ₂	Organic Nitrate
HNO ₃	Nitric Acid	R'ONO ₂	Organic Nitrate
HNO _y	Nitrogen Acids	ROOH	Organic Peroxide
HONO	Nitrous Acid	SF ₆	Sulfur Hexafluoride
HO ₂ NO ₂	Pernitric Acid	SO ₂	Sulfur Dioxide
H ₂ O	Water	SO ₄ ⁼	Sulfate Ion
H ₂ O ₂	Hydrogen Peroxide		

Mathematical Symbols

$C \equiv C + c$	Total instantaneous value of scalar	n	Dimensionless frequency ($= fz/U$)
C	Mean value of scalar	T	Averaging time
c	Fluctuation from mean of scalar	t	Time
C_{xy}	Cospectral density of variables x and y	t_c	Time constant
d	Distance separating sensors	Δt	Maximum allowable sampling interval
F_c	Vertical flux of c	U	Wind speed
f	Frequency	u_*	Friction velocity ($= \overline{uw}$) ^{1/2}
F_r	Correction to flux density	v_d	Deposition velocity
f^*	Numerical coefficient	w	Vertical wind speed component
H	Henry's law constant	\overline{wc}	Vertical flux of c
I	Laser intensity at the detector	w_*	Convective velocity ($= \frac{g}{T} \overline{wT} z_i$) ^{1/3}
k	von Kármán constant (~ 0.4); also surface-to-air transfer coefficient	z	Height
K	Eddy diffusivity	z_i	Height of PBL
		ρ	Density
		ψ	Adjustment for atmospheric stability

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LIST OF PARTICIPANTS

Dr. Stuart Anderson
Aerodyne Research
45 Manning Road
Billerica, MA 01821
(508) 663-9500 x231

Dr. M. O. Andreae
Max Planck Institute for Chemistry
Biochemistry Dept.
Postfach 3000
D-6500 Mainz 1
Federal Republic of Germany
49-6131-305420

Dr. Dennis Baldocchi
NOAA
Atmospheric Turbulence and
Diffusion Division
P.O. Box 2456
Oak Ridge, TN 37831
(615) 576-1232

Dr. Joost A. Businger
National Center for Atmospheric Research
P.O. Box 3000
Boulder, CO 80307-3000
(303) 497-8838

Dr. Anthony C. Delany
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307-3000
(303) 497-8776

Dr. O. T. Denmead
Division of Environmental Mechanics
CSIRO
P.O. Box 821
Canberra, A.C.T. 2601
AUSTRALIA

Dr. Ray Desjardins
Agrometeorology Section
Land Resource Research Institute
Central Experimental Farm, Bldg. 74
Ottawa, Ontario
CANADA K1A 0C6
(613) 995-5011, ext. 255

Dr. Chris W. Fairall
Meteorology Department
506 Walker Building
Pennsylvania State University
University Park, PA 16802
(814) 863-3934

Dr. Carl Farmer
Laboratory for Atmospheric Research
Washington State University
Pullman, WA 99164-2730
(509) 335-1526

Dr. Fred Fehsenfeld
R/E/AL6
NOAA
325 Broadway
Boulder, CO 80303
(303) 497-5819

Dr. David Fitzjarrald
Atmospheric Sciences Research Center
State University of New York at Albany
100 Fuller Road
Albany, NY 12205
(518) 442-3838

Dr. Inez Fung
Goddard Institute for Space Studies
2880 Broadway
New York, NY 10025
(212) 678-5590

Dr. Paul D. Goldan
R/E/AL7
NOAA
325 Broadway
Boulder, CO 80303
(303) 497-3814

Dr. Gary Greenhut
R/E2
325 Broadway
Boulder, CO 80303
(303) 497-6165

Dr. Gerald L. Gregory
Mail Stop 483
NASA/Langley Research Center
Hampton, VA 23665
(804) 864-4341

Dr. Robert Harriss
 Institute for the Study of Earth, Oceans and Space
 Science and Engineering Research Bldg.
 University of New Hampshire
 Durham, NH 03824
 (603) 862-3875

Mr. Bruce Hicks
 NOAA/ATDD
 P.O. Box 2456
 Oak Ridge, TN 37831
 (615) 576-1232

Prof. Barry J. Huebert
 Center for Atmospheric Studies
 Graduate School of Oceanography
 University of Rhode Island
 Narragansett, RI 02882-1197
 (401) 792-6616

Dr. Charles E. Kolb
 President
 Aerodyne Research, Inc.
 45 Manning Road
 Billerica, MA 01821
 (508) 663-9500 x290

Dr. Donald Lenschow
 National Center for Atmospheric Research
 P.O. Box 3000
 Boulder, CO 80307
 (303) 497-8903

Dr. Shaw C. Liu
 R/E/AL4
 NOAA/ERL/Aeronomy Laboratory
 325 Broadway
 Boulder, CO 80303
 (303) 497-3356

Dr. Jennifer Logan
 Center for Earth & Planetary Physics
 Pierce Hall, Harvard University
 29 Oxford Street
 Cambridge, MA 02138
 (617) 495-4582

Dr. Chris Martens
 CB 3300, Marine Sciences Program
 University of North Carolina
 Chapel Hill, NC 27514
 (919) 962-1252

Dr. Robert J. McNeal
 Code EEU
 National Aeronautics and Space Admin.
 Washington, D.C. 20546
 (202) 453-1681

Dr. Jarvis Moyers
 National Science Foundation
 Atmospheric Sciences Division
 Washington, D.C. 20550
 (202) 357-9657

Dr. Richard Pearson, Jr.
 NASA/AMES Research Center
 Mail Stop 245-5
 Moffet Field, CA 94035
 (415) 694-4388

Dr. Michael Prather
 Goddard Institute for Space Studies
 2880 Broadway
 New York, NY 10025
 (212) 678-5625

Dr. Brian Ridley
 National Center for Atmospheric Research
 P. O. Box 3000
 Boulder, CO 80307-3000
 (303) 497-1420

Dr. John Ritter
 Mail Stop 401B
 NASA/Langley Research Center
 Hampton, VA 23665-5225
 (804) 864-5693

Dr. Michael O. Rodgers
 School of Geophysical Sciences
 Room 107, Baker Building
 Georgia Institute of Technology
 Atlanta, GA 30332
 (404) 894-3895

Dr. Glen Sachse
 Mail Stop 468
 NASA/Langley Research Center
 Hampton, VA 23665
 (804) 864-1566

Dr. William Shaw
 Department of Meteorology
 Naval Postgraduate School
 Monterey, CA 93940
 (408) 646-2411

Dr. Donald H. Stedman
 Chemistry Department
 University of Denver
 Denver, CO 80208-0179
 (303) 871-3530

Dr. L. Paul Steele
 CIRES/NOAA
 Campus Box 216
 University of Colorado
 Boulder, CO 80309-0216
 (303) 497-6228

Dr. George E. Taylor
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831-036
(615) 574-7353

Dr. Anne Thompson
Code 616
NASA/Goddard Space Flight Center
Greenbelt, MD 20771
(301) 286-2629

Dr. Marvin Wesely
Environmental Research Division
Argonne National Laboratory
Bldg. 203
Argonne, IL 80439
(312) 972-5827

Dr. Hal Westberg
Laboratory for Atmospheric Research
Washington State University
Pullman, WA 99164
(509) 335-1526

Dr. Steven C. Wofsy
Harvard University
Pierce Hall, 29 Oxford Street
Cambridge, MA 02138
(617) 495-4566

Dr. Rod Zika
University of Miami
Rosensteil School of Marine and
Atmospheric Science
4600 Rickenbacker Causeway
Miami, FL 33149-1098
(305) 361-4715