ATMOSPHERIC SCIENCES REVIEW SUB GROUP
WORK GROUP 2

UNITED STATES — CANADA

MEMORANDUM OF INTENT
ON
TRANSBOUNDARY AIR POLLUTION

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WORK GROUP 2

ATMOSPHERIC SCIENCES AND ANALYSIS

FINAL REPORT
TECHNICAL BASIS

Monitoring and Interpretation
Subgroup Report

Subgroup Co-Chairmen

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Submitted to Work Group 2 in fulfillment of the requirements of the Memorandum of Intent on Transboundary Air Pollution signed by Canada and the United States on August 5, 1980.

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Dear Mr. Ferguson and Dr. Machta:

We are pleased to transmit under cover of this letter the final report of the Monitoring and Interpretation Subgroup of Working Group 2, Atmospheric Sciences and Analysis, as provided for in the Work Plan. We believe that this report satisfies in a scientifically responsible manner (to the extent possible within the severe time constraints) our terms of reference.

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PREFACE

During Phase II, strong emphasis was placed on the use of atmospheric modeling in addressing the transboundary long-range transport and acid deposition issue. Monitoring data on ambient atmospheric levels and deposition rates clearly play a major role in the development, intercomparison and validation of these models. But in addition, these data can be used, independently of the models, to document the existence of transboundary air pollution problems and to provide another tool to assist in developing appropriate remedial actions.

During the latter part of Phase II, a need to evaluate monitoring was recognized, and a start was made by including a first summary of monitoring results as Chapter 3 in the Working Group 2 Interim Working Paper 2-15. In formulating the Phase III work plan it was decided to give this topic higher priority and a Subgroup on Monitoring and Interpretation was accordingly formed. The following is the report of this Subgroup. It forms the basic background documents for the appropriate chapters and sections in the full Working Group Report No. 2-F.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary

In the overall analysis of the issue of long-range transport of acidic and alkaline materials in the atmosphere, measurement of the final amounts deposited is an important part of the research. Past efforts to establish viable monitoring programs have generally achieved only limited success. In the last five years, the precipitation chemistry networks in North America have begun to produce high quality data sets. Though much has been done, there is still a need for closer cooperation between Canada and the United States so that a uniform precipitation chemistry data record can be developed to address questions about trends in acidic deposition and what changes would result from any control action that might be taken to limit, or reduce, acid precursor emissions.

Most of the efforts to date have been directed toward establishing monitoring systems to measure wet deposition on a routine basis. Advances have been made in network design, collection methods, and analysis techniques, but establishing a more rigorous quality assurance program should still be a goal of the North American monitoring networks.

The second part of the atmospheric deposition process is dry deposition, but there is, as yet, no simple method available to measure the dry component of the deposition. Several possible candidate techniques are discussed in this report. Understanding of the dry deposition process is vital to evaluating the overall question of atmospheric deposition.

Whatever the limitations of past and present data sets, it is important that they be evaluated for their potential value in modeling and control strategy. This report attempts to list what considerations must be taken into account when assessing data sets--such factors as representativeness of the values, uniform collection and analysis techniques, temporal resolution, and others. A summary list of active networks is provided.

The next step beyond the monitoring network and data recording is the initial interpretation of these data. A number of approaches are used in analyzing existing data sets. These include: plotting of spatial variations, evaluation of temporal fluctuations, single-station trajectory analysis, and mass budgets on a broad scale. Spatial depiction of monitoring data is a common method of showing chemical deposition over periods of a month to a year. The evaluation of temporal variations can be useful in identifying trends in precipitation chemistry, variability due to meteorological factors, and cyclic processes. Other methods of study are explained in the report.

In addition to acidic and alkaline materials, certain potentially injurious substances may be subject to long-range transport and deposition. They can be grouped into three important classes--oxidants, organics, and heavy metals. Each class is briefly discussed in the report.

Monitoring of atmospheric deposition and interpretation of the data is one of the key areas providing ground truth for atmospheric transport models and an initial understanding of deposition through statistical analyses of the data. Long-term commitments to monitoring networks and the interpretation of their data are vital in describing and evaluating the acid deposition problem.

Conclusions

Monitoring data in North America show a strong geographical correspondence between a large contiguous region of precipitation having low pH (i.e., less than 4.5) and the region of most intense emissions. The region with low pH also corresponds closely with areas having the highest concentrations of SO_4^{2-} in the precipitation, and in both cases the maxima are at or immediately downwind of the major source region. By referring to the maps of sensitive ecosystems produced by Working Group 1, it is immediately apparent that this region of high deposition covers fortuitously extensive sensitive areas in both eastern Canada and the eastern United States. On a global basis, there is at least one other large region of low precipitation pH and this is also associated with the major industrial regions of Europe. In addition, the presence of occasional, very acidic rains in remote areas suggests that natural and/or distant anthropogenic sources of sulfur can possibly contribute to the acidity and sulfate content of rain in these locations. The main acids in these places are either sulfuric or organic acids. The role that such natural or distant anthropogenic sources of sulfur play in eastern North America, although likely to be small, remains to be clarified. On the other hand, the role that natural sources of nitrogen oxides play is unknown.

Monitoring data at individual stations can be classified according to wind direction or air parcel origin and comparison then made between various sectors. Several stations in the eastern United States and Canada, and Bermuda clearly have more acidic precipitation when the air is arriving from the region of strongest emissions. This average concentration of acidic species in these sectors is typically a factor of 5 higher than for the sectors when the air is arriving from low emission zones. Although useful as a tool to identify sectors of origin of the pollutant, this technique cannot distinguish between nearby and more distant sources.

Gross budget studies over large regions such as eastern Canada and the eastern U.S. can look at the major input (including natural) and output terms for sulfur on an annual basis. Three such studies using monitoring data, together with simple climatological wind flow across boundaries, indicate that man-made sulfur emissions in eastern North America exceed natural areas by a factor of 10 to 20. Further, in eastern North America, the three removal terms--wet deposition, dry deposition and out-flow into the Atlantic--are roughly equal. The latter is corroborated by the low pH values observed in Bermuda during northwesterly winds. This analysis also indicates that an average of about three to five times as much total sulfur flows north from the U.S. to Canada as in the other direction.

In addition to using modeling tools, a possible means of estimating the changes in pollutant deposition from changes in upwind emissions would compare deposition during past periods of different-than-present emission rates with concurrently monitored deposition rates. As noted, this opportunity is severly hampered by the poor quality and limited quantity of past measurements. With this caveat, however, one may note that, in the eastern U.S., a) the lack of a noticeable trend in wet sulfate deposition during the past five years is consistent with small changes in SO_x emissions, and b) an upward trend in wet nitrate deposition qualitatively agrees with a similar upward trend in NO_x emissions. But in northern Europe, the pentade (five-year average) to pentade sulfur deposition between 1955 and 1975 did not follow the trends in SO_x emissions.

Although acidic and alkaline deposition is emphasized in this report, it must be recognized that there are potentially injurious pollutants that may participate in long-distant transport. Ozone, organics, and heavy metals were identified as possible substances of concern. Of these, it is shown that ozone has received the most study and its behavior and effects best documented. The transport and deposition of organics and heavy metals are less well-known and more emphasis should be placed on understanding their atmospheric cycles.

Recommendations

In some of the sections of this report, a few explicit recommendations are made, but several others are only implicit in the discussions scattered throughout the text. Here these recommendations are compiled and are followed by a brief rationale for each.

The difficulties in both the collection and interpretation of air and precipitation monitoring data are self-evident from reading the following report. While many advances have been made in monitoring techniques and our understanding of the long-range transport phenomenon has increased substantially in recent years, there is still considerable room for improvement. The following general recommendations are made with this in mind. Detailed "how to do it" recommendations are not appropriate here, but the subgroup feels strongly that the Memorandum of Intent and any subsequent agreement should provide a framework in which to set up a joint U.S.-Canada mechanism to implement the recommendations. These recommendations apply to monitoring on regional, national, and global scales and are not necessarily in order of priority.

A. A strong commitment is required from the appropriate agencies in the U.S. and Canada to continue, on a long-term basis, ground-based routine monitoring networks for air and precipitation chemistry.

Such networks are required to provide a data base for the following, not necessarily in order of priority:

- atmospheric model developments; intercomparison and verification,
- research on atmospheric chemistry processes,
- input to assessment and research on the effects to aquatic and terrestrial systems of long-range transport of air pollutants and their deposition,
- establishing the existence of long-term trends, and
- monitoring the effectiveness of any agreements made under the MOI to limit or cut back on emissions.

B. The operation of networks needs to be closely coordinated among agencies within each country, as well as between each country, to ensure reliable data output.

This coordination is required to ensure that, as far as possible, common (or at least compatible) monitoring techniques and siting criteria are used. The data should be in a compatible format so that common, readily accessible data banks can be established. Most important is a well-designed and rigorously applied quality assurance program so that the users have a high degree of confidence in the data sets.

C. A system is required to produce official North American data listings and documentation and also concentration and deposition maps on a routine basis by the main agencies responsible for the data base.

With the rapid proliferation of networks and users of the data, many maps are now being generated. These are not always consistent because of many factors, including different time periods used, different averaging methods selected, and the inclusion or exclusion of certain data. Such differences create confusion for the users (decision-makers, politicians, lobby groups, effects research scientists, etc.). The work group feels it is essential that the agencies preparing such maps be fully acquainted with the monitoring and quality control procedures. The data banks and maps must be prepared on a rapid turnaround (approx. six months) basis with reports published regularly (quarterly and annually) in much the same way as for other meteorological data.

Documentation of networks is presently quite variable and should be standardized. Users need to know whether or not there is a good quality assurance program in place, the criteria for rejection of data, and when changes in methodology are instituted by the network.

D. Existing data sets for air and precipitation chemistry need to be critically evaluated for reliability as soon as possible.

The existing data sets are being utilized by a wide variety of users for a wide variety of purposes. This use is sometimes quite indiscriminate, with little regard for known problems, either because of lack of understanding of the problems or simply because the necessary information does not exist. It was initially the hope that this sub-group could carry out such an evaluation of the data sets. However, it soon became evident that this was a very large task well beyond the resources and time available. Chapter 3 of the report, therefore, discusses the potentially useful data sets available and suggests the factors to be considered in such an evaluation. The objective would be to produce data sets in which one would have maximum confidence, together with quantitative estimates of the uncertainty for each parameter of interest. In addition, this evaluation would provide valuable advice to those about to set up new networks, as well as to those responsible for existing networks, and prevent the perpetuation of incorrect procedures and the continued generation of questionable data.

E. <u>More observations are required of the vertical variations of air, cloud, and precipitation chemistry using mountainside and mountaintop sites, as well as instrumented aircraft, in coordinated joint studies.</u>

Limited information, so far available from a few mountain sites (e.g., Whiteface Mt., Mauna Loa, Colorado Rockies) and aircraft studies (e.g., OSCAR, PEPE, NEROS), has forced a re-examination of hypotheses proposed on the basis of ground-monitoring only.

Such observations are important for:

- providing a better understanding of atmospheric chemistry processes and the factors controlling the eventual composition, and hence pH, of precipitation reaching the ground;
- evaluating the importance of special types of deposition such as dew, frost, and fog;
- improving the parameterization of these processes (especially in-cloud) in models; and
- addressing the issues related to saturation effects and non-linearity of long-range transport chemistry.

Several mountain sites in Canada and the U.S. offer the potential for routine observatories. Also, several well-equipped aircraft in the U.S. and Canada should be utilized in joint studies where the use of multiple aircraft is essential to produce combined data sets that are much more valuable than those from just a single aircraft.

F. More monitoring at remote sites (oceanic and polar) is strongly encouraged in order to better document and understand the global distribution of air and precipitation chemistry.

Some of the existing remote stations indicate average rainfall pH below 5.0 and, on infrequent occasions, as low as about 4.0. It is therefore important to continue, and perhaps expand, this type of monitoring with the purpose of establishing the "global background" values of air and precipitation concentrations of various important chemical species. Analyses of these data are urgently required and should help determine the contribution to the observed concentrations from natural sources and ultra long-range transport from upwind anthropogenic sources. Such understanding is necessary in order to interpret the source-receptor relationships in the regions of maximum acidic deposition in the proper context.

G. More information is required on dry deposition. Accelerated research into methods of directly monitoring dry deposition on a routine basis is urgently needed. In the meantime, increased measurements of ambient air concentrations should be made at a larger number of precipitation monitoring sites, so that rates of dry deposition can be estimated.

Over much of eastern North America, dry deposition is estimated to be of comparable importance to wet, yet little routine data are available compared to wet deposition. This lack seriously limits the extent to which atmospheric transport and deposition models can be evaluated, and limits the data available for effects research.

H. <u>The levels of other potentially injurious substances, such as ozone, organics, and heavy metals, must be monitored and evaluated in order to understand their importance in the long-range transport of pollutants.</u>

Though acidic and alkaline deposition is emphasized in this report, it must be recognized that there are other pollutants that may participate in long-range transport. As the environmental effects of these pollutants become better understood, further information must be provided on their transport and deposition in order to make an overall assessment of their potential environmental effect.

LIST OF CONTRIBUTORS

This report was prepared by members of the Work Group 2 Subgroup on Monitoring and Interpretation as listed below. The authors carried the primary responsibility for chapters and in some cases reviewers provided comments on the final drafts. In addition, all those listed provided comments to a greater or lesser degree on various other sections. The Canadian and U.S. subgroup members worked closely and amicably on the preparation of individual chapters of this report, the final review of the complete report, and reviewing of the summary chapters in the full Working Group 2 Final Report 2F. Drs. J. Miller and P. W. Summers as co-chairmen of the work group were responsible for coordinating the report with production assistance from Dr. Nels Laulainen and Mr. B. Niemann.

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Chapter 1

INTRODUCTION

1.1 Terms of Reference of the Subgroup

The following terms of reference for the Subgroup on Monitoring and Interpretation were agreed to by the full Working Group 2 on 18 November 1981:

A. With respect to the atmospheric concentration and deposition rates of the significant chemical components attributable to long-range transport and with special emphasis on the contributions to acidic deposition:

   1. critically examine the instrumentation used, network design, chemical analysis techniques and quality assurance procedures for monitoring;

   2. document, provide a catalogue of, and critically review, the major data sets available from observational networks and special studies operated on regional, national and global bases;

   3. document the existance of transboundary air pollution problems, especially in North America, by interpretation of these data sets in terms of spatial and temporal variations from networks, analyses of special regional studies and analyses of single station observations;

   4. assess the value of the data sets and their analysis for:

      a. providing information for model development, comparison and validation, and

      b. providing techniques as one tool to assist in developing emissions control policy and strategies.

B. Review the analyses of regional visibility patterns and historical trends and critically examine the relationships between these and the long-range transport of air pollutants.*

C. Briefly review the monitoring techniques used, the available data sets and the evidence for the long transport of:

ozone
organic substances
heavy metals

D. Summarize the above for inclusion, where appropriate, in the Work Group 2 Phase III Final Report.

1.2 Layout and Scope

The report layout, as indicated in the Table of Contents, follows naturally from the terms of reference. It has been divided into two parts, with the largest being devoted to the deposition of the major acidic and alkaline components contributing to the final ion balance. This is because the current emphasis under the Memorandum of Intent is being devoted to acidic deposition and its effects. Also, monitoring networks to measure these components of precipitation chemistry have been in operation for considerable lengths of time in Europe and North America. More is known, therefore, about this aspect than for organics and heavy metals. The latter, generally occur in lower concentrations and, because of the extreme care needed to collect and analyze samples, only recently have such measurements been made on any significant scale. Short reviews of what is known about these are given in Part II. Also, atmospheric ozone transport and its effects, both independently of and synergistically with SO_2 and NO_x are being given increasing attention by the Memorandum of Intent. This topic is also addressed in Part II.

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*This was later detected as an objective with the responsibility for this topic to be handled by Working Group 1.

Visibility reduction due to fine particulates will be considered as an effect of long-range transport, and will, therefore, be discussed in the Working Group 1 report.

The summary, conclusions, and recommendations were placed at the front of the report for easy reference.

This report will deal only with those monitoring techniques and the interpretation of data sets related to the long-range transport of pollutants and regional transport across political boundaries. It will, therefore, not consider the large amount of monitoring data available from either urban areas or associated with assessing the nearby impact of large industrial complexes. These latter issues will be addressed in the report of Local/Mesoscale Analysis Subgroup of Working Group 2.

It is becoming increasingly difficult to address some of the long-range transport issues without considering them in the context of the so called "global background" chemistry of the atmosphere. The data base is more limited and much of it is relatively recent. Some of the new concepts emerging with regard to the global transport (this might be considered as ultra long-range transport) based on these data will also be discussed.

CHAPTER 2

MONITORING TECHNIQUES

2.1 Wet Deposition

The interest in the wet and dry deposition of chemicals from the atmosphere onto the earth's surface has become a matter of great concern in the United States and Canada in the past 10 years. This concern has arisen because of the demonstrated deleterious effect of a number of the chemical constituents, particularly the acidic ones. Such deleterious effects have been noted particularly in aquatic ecosystems and in the erosion and corrosion of materials used for construction such as marble, concrete, iron, etc. While effects on the construction materials were noted over 100 years ago (Smith, 1872), the relatively recent documentation of the acidification of lakes in Norway has aroused an even greater degree of concern, particularly in Europe and North America. To understand the extent of the problem, it is necessary to determine the nature of atmospheric chemical deposition both qualitatively and quantitatively as well as determining geographical deposition patterns and temporal trends. Since research has demonstrated that chemicals contributing to acidity are primarily anthropogenic in origin, it is also important to understand the nature of the sources, transport, transformation and removal of these materials from the atmosphere.

The need to understand deposition of these materials from the point of view of environmental effects, as well as the atmospheric chemistry and transport processes, has resulted in the need for atmospheric deposition monitoring networks. While this section deals primarily with wet deposition monitoring, it should be kept in mind that the dry deposition process is one which undoubtedly contributes significantly to the overall total deposition.

As might be expected, the growing concern in recent years has spawned the development of many deposition monitoring studies. A number of networks of varying design in both the United States and Canada have provided data, both qualitative and quantitative, on atmospheric deposition. Summaries listing and describing these networks have been prepared by Kennedy (1978), Niemann et al. (1979), Whelpdale and Barrie (1982), and also in the updated listing in Chapter 3 of this report. While the summaries indicate a great deal of activity in the monitoring of atmospheric chemical deposition, one is cautioned when using data from these previous monitoring programs to consider carefully the context in which the data were acquired. The need for this caution will become evident from the discussions in the following sections on such topics as network design, siting criteria, sampling procedures, etc. The reader will be made aware of the fact that each of these topics relates to the objectives which prompted the development of a specific type of monitoring activity and how the design of that activity may place limitations on the use of the data.

As in any area of scientific endeavor there has been a development of terminology, the definitions of which are unique to the research related to atmospheric deposition and the monitoring. Some widely used terms that relate to deposition monitoring are defined as follows:

pH--The pH is defined as the negative log of the hydrogen ion concentration (the scale ranges from 0 to 14). These numbers indicate the acidity, i.e., the free hydrogen-ion concentration or "activity" in a solution. Each unit of decrease on the pH scale represents a 10-fold increase in acidity. A pH of 7 is neutral, a pH of less than 7 is acidic, and a pH of more than 7 is alkaline. However, for the application to acid precipitation issues, the reference point will be chosen to be 5.6 instead of 7.0 since this is the approximate equilibrium pH of pure water with atmospheric carbon dioxide at 20°C. This reference point is only arbitrary and in no way represents a baseline on background value.

Precipitation--The term will be used as it is in meteorology to denote aqueous materials, in liquid or solid form, that fall from the atmosphere to the ground.

Acid Rain--A popular term generally used to describe precipitation with a pH of less than 5.6. It is sometimes used to include both wet and dry deposition of acid materials.

Acid Precipitation--Water from the atmosphere in the form of rain, sleet, snow, and hail, with a pH of less than 5.6. (This is how scientists typically use the term.)

Wet Deposition--A term that refers to: (a) the amount of material removed from the atmosphere by rain, snow, or other precipitation forms; and (b) the process of transferring gases, liquids, and solids from the atmosphere to the ground during a precipitation event.

Dry Deposition--A term for the amount of all materials deposited from the atmosphere to the earth's atmosphere in the absence of precipitation.

Bulk Deposition--A term describing the estimate of total deposition (both wet and dry) using an open collector.

Atmospheric Deposition--Transfer from the atmosphere to the ground of gases, particles, and precipitation, i.e., the sum of wet and dry deposition. Atmospheric deposition includes many different types of substances, non acidic as well as acidic.

Acid Deposition--The transfered amount of acidic substances from the atmosphere to the ground via wet or dry-deposition processes.

Event Sampling--Collection of a sample for the entire duration of a single precipitation event.

Sequential Sampling--Fractionating a single event into two or more samples usually determined by establishing specific time intervals or sample volume amounts.

Daily, Weekly, or Monthly Sampling--The collection of samples over a predetermined period (day, week, month, etc.) such that the sample represents an accumulation of precipitation of all events during that period.

2.1.1 Network Design

In designing an atmospheric deposition monitoring network, it is critical that one carefully defines the objectives to be met by the monitoring program. Only in this way can one rationally design a network that will provide data of a useful nature. Today most networks are designed to meet one of two general objectives, i.e., providing data for:

1. Research related to atmospheric transport, chemistry and removal processes, and

2. Research related to the effects of atmospheric deposition on the natural environment and man-made structures.

Network design depends on two interrelated factors, namely the spatial scale and density of the network, and the temporal duration and frequency of the sampling. Before defining these variables, a statement of specific objectives must be formulated for the monitoring network. This statement will address such topics as the region of concern (i.e., international, national or regional); the required information (i.e., trends, means or ranges); and the measurement of interest (i.e., concentrations or rates of deposition). A specific objective related to determination of the effects of atmospheric deposition might be as follows:

> "To satisfy national and international needs and commitments for data on the state and trends of regionally representative as well as background precipitation chemical concentrations and rates of deposition within the area of concern."

For the spatial design of the network, the scale is defined by the region of concern, and the density of sampling sites is defined by the required separation to give meaningful spatial resolution. The time variables are the total duration of the sampling period and the frequency of collection for composite sampling within this period.

The generally accepted sampling periods for a regional wet deposition measurement network are monthly, weekly, and daily. For example, a network designed to meet the needs of ecological effects research would require a network of low density--national or regional in scale--collecting samples on a weekly basis, and operating over long periods of time (5 to 10 years) in order to develop geographical and temporal trends in deposition patterns. A number of these factors will be discussed in the following sections, however, it should be kept in mind that there is no single ideal or optimum network design and that the factors discussed in the following sections can only be defined after a careful consideration of objectives and available resources.

2.1.2 Siting Criteria

Monitoring programs related primarily to environmental and ecological effects, such as the NADP program in the U.S. and the CANSAP program in Canada, have developed a consistent set of criteria and examples of these are listed in order to provide the reader with an indication of the kinds of considerations that are important. The NADP and CANSAP networks are designed to measure regional deposition patterns on a scale of approximately 200 to 400 km and thus it is important that the monitoring stations represent a region, usually of a sub-state or sub-province size and not be significantly influenced by local sources. The station density of the networks will be determined by the requirement to adequately represent a given region and by available resources. It should be kept in mind that studies relating atmospheric deposition to most ecological effects usually require long sampling periods of 5 to 10 years in order to determine both temporal and spatial trends. Examples of siting criteria which might be used for such a network include:

a. Within 50 km of the sampler there will be no significant source of pollution such as an industrial plant.

b. Within 1 km of the sampler there will be (i) minimal and preferably no moving sources of pollution such as air, water, and surface transportaion, (ii) no surface storage of sources of pollution such as sewage plants, (iii) no wind activated sources of pollution such as cultivated fields or areas of no vegetation, and (iv) no stationary source of pollution such as a heating vent, furnace exhaust, or chimney.

c. Within 5 meters of the sampler there shall be no object above the height of the sampler.

d. The sampler shall be located in an open area with an undisturbed, preferably flat surface, such as a grassy area surrounded by trees.

e. No object shall be closer to the sampler than a distance of 2.5 times the height of the object.

In addition to the above criteria the following essential requirements for monitoring stations are:

a. availability of a suitably trained operator;

b. availability of a suitable and reliable power source;

c. adequate site security, i.e., site located in a location that allows limited or restricted public access (no unauthorized persons should have access to the monitoring equipment); and

d. all weather accessibility to the site.

2.1.3 Instrumentation

A typical set of criteria would be that the collector:

a. minimize evaporation of the collected precipitation;

b. minimize surface area of collected precipitation exposed to the atmosphere;

c. minimize contamination for the parameters of interest (e.g., from dry deposition, foreign materials, or materials used in construction of the samplers);

d. maximize collection efficiency (i.e., minimize aerodynamic and other effects that would adversely affect the amount of precipitation collected); and

e. be equipped with a sensor capable of (i) responding to the lightest precipitation while not responding to false effects (e.g., dew, fog, etc.), and (ii) closing the lid within a fixed time period after the cessation of precipitation.

The sampling containers for measuring acidity and major ions in precipitation are usually made of plastic, generally polyethylene or polypropylene. For the measurement of heavy metals and organics, such as pesticides, plastic containers may not be a good choice. In this case, other materials such as glass may be more appropriate.

To satisfy the above criteria, the collection vessel could be either an open bucket, a bucket with a plastic bag insert, or a bucket containing a funnel and a collection bottle. It should be exposed only when precipitation is occurring by using a lid activated by an automatic sensor for precipitation. For examples of two samplers in common use in North America, see Figures 2-1a and 2-1b.

Each sampler should be co-located with a standard rain gauge. The standard rain gauge gives a more precise measurement of precipitation amount.

2.1.4 Sampling Procedures

Field sampling procedures are determined to a large extent by the objectives of the program. Frequently, conductivity and pH are measured immediately after the sample is removed from the sampling device. This requires a good quality control program to ensure reliable results. In addition, depending upon the chemical analysis to be performed, different sample handling procedures may be chosen at the site. This will also depend on whether the various chemical analyses are to be performed at the site or whether the sample is to be shipped to some distant laboratory. For example, it is necessary to limit changes in the chemical composition of the sample during storage and shipment time by (a) minimizing the time between collection and analysis, (b) refrigeration, (c) filtering, and (d) addition of preservatives to prevent biological change. These, and many other factors, have to be considered depending on the monitoring program requirements.

The following are some guidelines that may be employed to preserve the integrity of the sample:

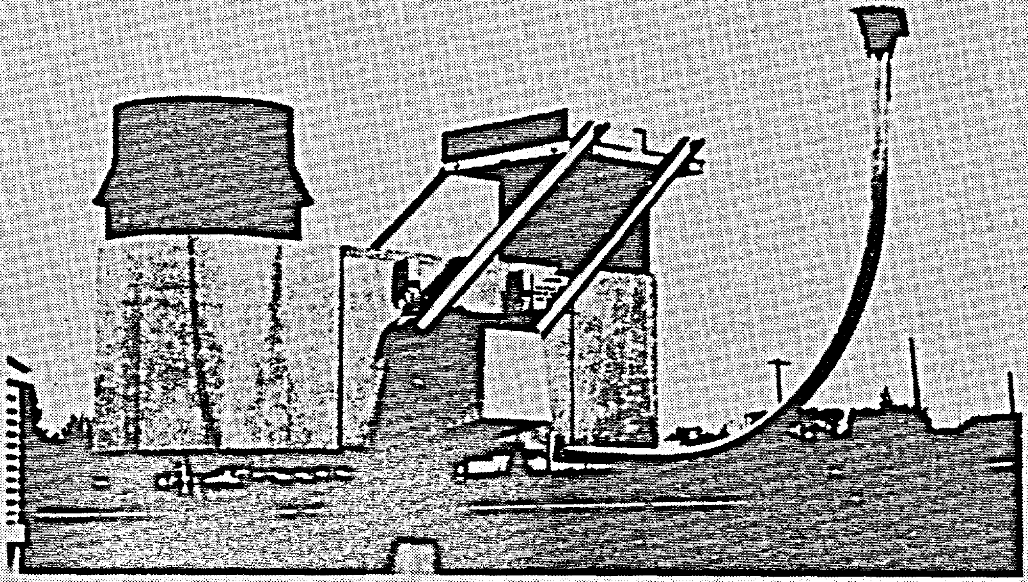

Figure 2-1a Typical Samplers used in North American Networks (This is not to be construed to be an endorsement of this collecter by either government)

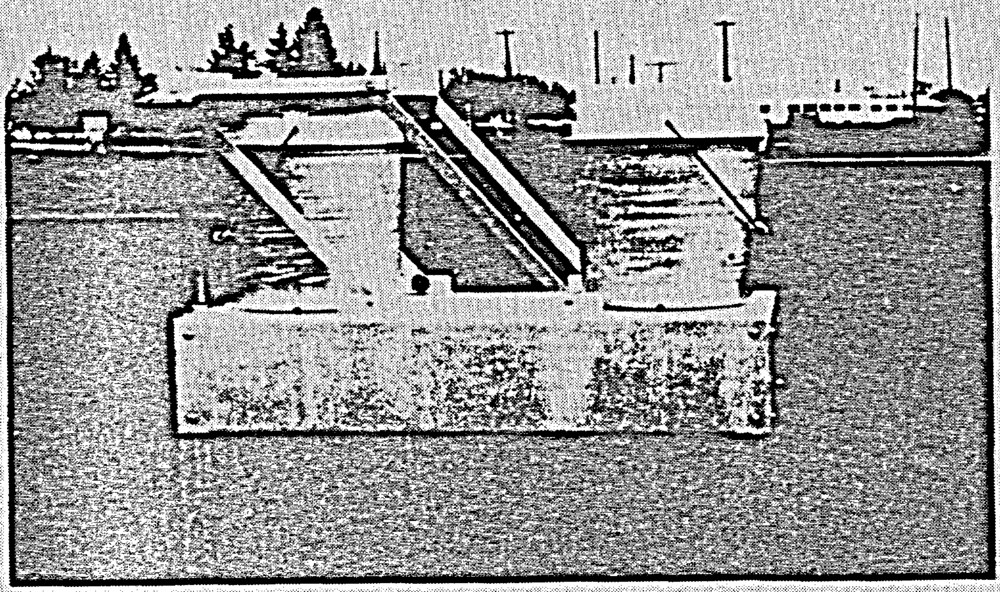

Figure 2-1b Typical Samplers used in North American Networks

a. All containers used for either sample collection or for shipping must be free of detectable levels of the species of interest.
b. Snow or frozen precipitation should be melted at 4°C after collection. All samples should be refrigerated at 4°C while on-site.
c. Collection procedures should minimize the potential for chemical alteration of the sample, including effects from biological activity.
d. The total sample should be shipped to the laboratory.
e. Shipment time in transit should be minimized; coolers may be used where possible.
f. On receipt at the laboratory, samples should be filtered and refrigerated at 4°C. Chemical analysis should be carried out as soon as possible.

To provide a complete data-base, certain relevant information must also be recorded on a sample history form by the operator. This form contains information such as:

a. site identification,
b. operator identification,
c. sampling period,
d. equipment performance and maintenance checklist,
e. sample history (i.e., events during sampling such as blowing dust),
f. observed foreign material in sample (i.e., leaves, insects, particulate matter, etc.),
g. type of precipitation,
h. sample volume collected based on weight measurement, and
i. sample volume measured by co-located standard precipitation amount gauge to determine collection efficiency of the sampler.

The data on this form, together with that added by the analytical laboratory on receipt of the sample, completes the documentation of the sample.

2.1.5 Analytical Techniques

Many current monitoring studies emphasize acidic deposition. Therefore, the chemical analyses normally carried out are for pH and conductivity and the major cations and anions--sulfate, nitrate, chloride, ammonia, calcium, magnesium, sodium, potassium, and sometimes phosphate. Other monitoring programs may emphasize the deposition of heavy metals, pesticides, and other organic compounds. There are a variety of analytical techniques that are suitable to carry out the various analyses, but the application of these techniques will depend upon the laboratory capability and thus the following will discuss only broad categories of methods.

2.1.5.1 Major Cations and Anions

1. pH and Conductivity--pH and conductivity are generally measured by specific equipment that is designed to measure these parameters electrically. The chemical parameter, pH, although deceptively easy to determine with modern equipment requires special care to arrive at accurate results due to the low ionic strength (low conductivity) of rain and snow samples. Frequent checks with low ionic strength reference solutions are required to avoid the frequently found problems of pH electrodes of inadequate quality.

2. Anions--The common anions are generally measured either by automated techniques involving wet chemistry or by the more recently developed methods of ion chromotography. Either procedure is appropriate when carefully controlled.

3. Cations--The major cations can be measured by either flame photometry ion chromatography or atomic absorption or a combination of these three techniques.

2.1.5.2 Heavy Metals

There are several procedures which are used to measure heavy metals. Most of these are of a spectrographic nature. The three most commonly used techniques today involve atomic absorption spectroscopy, neutron activation, and the more recently developed ICP (Inductively Coupled Plasma) spectrographic method. The advantage of the latter two methods is that they permit the analysis of 20 or more heavy metals simultaneously on a single aliquot of the sample.

2.1.5.3 Pesticides and Organics

Pesticides and organics are generally measured by gas chromatography or a combination of gas chromatographic and mass spectrometric methods. These methods are designed for handling samples with a variety of organic contaminants. Other analytical methods are available for specific compounds.

2.1.5.4 Sample Handling

Equally important, and in some cases more important than the specific analytical methods, is the care and procedures used in the handling of the samples and the sampling containers. Precipitation samples are relatively pure compared to other aqueous samples, such as lake or river water, and the materials analyzed more generally occur in the subparts per million level or less. Thus even the slightest contamination in a container, such as a fingerprint, may contribute more to the concentration of a species, such as sodium, than will be found in the uncontaminated precipitation sample. Therefore, extreme care has to be used in handling the sample both in the field and the laboratory and also in the cleaning of the sample containers. The particular procedures to be followed will depend on the chemical analyses to be carried out.

2.1.6 Data Base

Depending on program objectives, the data available from a monitoring program should include the chemical analysis of the precipitation samples; a measure of the precipitation amounts on an event or daily basis; the nature of the precipitation, (rain, snow, hail, etc.); the time that the sample container was in the field (with commencement date and time and termination date and time); and any other information that may be necessary, such as meteorological data.

Information can potentially be removed from the data set at all stages. Examples are: (a) site operators failing to send samples in for analysis when they look unduly contaminated, (b) laboratory personnel deleting data for samples that were not collected in the field according to standard protocol for the network and (c) data analysts applying statistical procedures to remove "outliers" or "unrepresentative" data.

Data as described above are generally made available in two forms, printed and computer stored. The data publication should include chemical data (usually expressed in concentration terms), precipitation amounts, important site characteristics, and other information as described above. Site documentation should include longitude, latitude, elevation, proximity of major sources, vegetation cover, etc.

2.1.7 Quality Assurance

For wet deposition monitoring networks, a greater effort must be put into developing a quality assurance program addressing all of the activities that result in the production of a data base. It is relatively easy to specify quality assurance for the analytical methods. Some of the greatest uncertainties in comparing data from networks involve differences in sampling mode, sample handling, etc. Within a single network it is important to provide for:

1. the use of uniform siting criteria,
2. the use of common or equivalent sampling procedures,
3. the use of common or equivalent analytical procedures,
4. the use of uniform reporting units,

5. the employment of systems audit to ensure that siting criteria are met and that sampling and analytical procedures have equivalency,

6. the employment of performance audits to monitor quality control of sampling, sample analysis and data handling procedures, and

7. the documentation of all aspects of the monitoring processes (i.e., site characteristic, sampling procedures, laboratory analyses, data handling, and quality assurance).

Before comparing data from two different networks, it is necessary to determine whether the two data sets are comparable. Some networks collect weekly samples and others collect monthly samples. Quality assurance reports for the separate networks should contain all the necessary information needed to assess the bias and accuracy of the network data and an evaluation of procedures and equipment used in each. When several networks exist simultaneously, it would be extremely useful to evaluate possible differences in the data sets due to differences in the network methods and equipment. The most direct way of doing this is to have instruments co-located at several network sites having different meteorological and pollution environments. The operation of co-located sites should be continuous rather than a one time endeavor.

2.1.8 Existing Monitoring Program

The reader is referred to references in Section 2.1 and Chapter 3 of this report for a detailed discussion of existing monitoring networks and data bases. Only two deposition monitoring networks exist today in North America that are national scope: the CANSAP network, which consists of 54 sites, has operated since 1977; the NADP network, which consists of over 100 sites, has operated since 1978. The NADP network will be expanded to 125-150 sites in the next several years.

Both of the above networks employ wet/dry collectors and analyze samples for major cations and anions including pH and conductivity. Each network employs a single analytical laboratory, a uniform set of siting criteria and standard sampling procedures and equipment. The NADP network samples weekly and the CANSAP monthly (currently being considered for revision). An assessment of data comparability is currently being carried out with the co-location of samplers at three sites in the U.S. and three sites in Canada. Each of these networks is designed for long-term operation in order to determine long-term spatial and temporal trends in deposition patterns, and the objectives are primarily related to research needs on the effects of atmospheric deposition on the environment.

One of the most direct ways to assess the differences between networks is to have co-located sites. Several sites are required to evaluate the range of differences that may occur under varying meteorological conditions and pollution environments. This type of study must be in place for a period that enables a significant number of data pairs to be evaluated.

One method of comparison uses duplicate samples sent to the various laboratories and then evaluates the analytical results. Various laboratories in North America and Europe have initiated these intercomparisons and the results have been published (Lampe and Puzak, 1981).

2.2 Dry Deposition

There is no "simple" method available to routinely monitor dry deposition of acidic and alkaline species to a natural landscape. There are, however, sophisticated techniques either available or being developed. It is, therefore, recommended that the best approach to dry deposition monitoring is to support intensive research efforts to measure and parameterize dry deposition rates over common natural surfaces (forest, water, cropland, snow) while routinely monitoring ground level air concentrations.

In the context of long-term deposition monitoring, it helps to consider the differences between wet and dry deposition. Studies of the former are simplified considerably by the nature of the phenomenon itself. Material is delivered in liquid samples that can be collected and analyzed relatively easily. However, dry deposition delivers material in gaseous and solid form, and sometimes in liquid (e.g., whenever humidity is sufficiently high that "solid hygroscopic particles are, in fact, wet), without the convenience of an associated natural process (precipitation) to organize and concentrate the delivery.

Almost all ongoing research concedes that such fundamental dissimilarities between wet and dry deposition mechanisms do exist. Rainfall concentrates pollutants from large quantities of air in the lower atmosphere and delivers these pollutants in irregular but relatively intense doses. Precipitation itself is a highly variable phenomenon that is well-studied in its own right. For example, it is well-known that different areas of the world are subject to substantially different kinds of precipitation systems, presumably with different precipitation scavenging characteristics. Dry deposition, on the other hand, is a slow, continuing process that delivers materials to the surface at a rate that is tightly controlled by and proportional to the concentration of the material in the air itself. Thus, it is to be expected that rates of dry deposition will necessarily be highest near sources. Measurements in eastern Canada substantiate this expectation (Barrie, 1982). The highest rates of wet deposition of the same pollutant might be further downwind. Dry deposition is also influenced by the configuration of the source in question--surface emissions are held in contact with the ground considerably more than emissions released at a greater altitude, so that, in the former case, rates of dry deposition would be expected to be much greater.

2.2.1 Measurement Techniques

There are essentially two schools of thought regarding the evaluation of dry deposition on a routine, monitoring basis. The first advocates the use of artificial collecting surfaces (or vessels) and the subsequent careful chemical analysis of material deposited on them. The second school prefers to infer deposition rates from time series analysis of pollutants deposited on natural surfaces such as snow or from measurements of air concentration of the pollutants in question and of appropriate characteristics of the lower atmosphere and of the natural boundary surface in the vicinity of the observation point. The use of collecting vessels gained considerable popularity in studies of radioactive fallout during the 1950s and early 1960s. At those times there was great concern regarding the rate of deposition of radioactive particles to the surface and the subsequent uptake of those particles by foliage and the transmission of radioactivity through the food chain. Large numbers of wet and dry collecting vessels were deployed around the world. These collectors used identical buckets for obtaining samples of rainfall and of so-called dry deposition. In their most highly developed form these collecting devices employed covers that were activitated by a sensor and moved automatically to expose a wet collection bucket at all times when it was raining. Various configurations of this kind of apparatus have been developed and are currently in use in many networks.

The drawbacks of artificial collecting surfaces for obtaining measurements of dry deposition rates are well-known. Not only do these devices fail to measure gaseous deposition, but they fail to provide a realistic simulation of the complicated microscale roughness features of foliage and other natural surfaces. For instance, recent tracer studies with ammonium sulfate particles* have shown that bucket-like collectors preferentially over-collect large supermicron particles of local origin by a factor of two to three and under-collect submicron particles of the size bearing acidic materials from distant sources by a similar factor. However, it must be acknowledged that since the radioactive fallout era, this kind of collection device has been an accepted tool for investigating pollutant deposition, largely as a consequence of two major factors. First, it was found experimentally that the use of a dry collection bucket and a wet collection bucket of the same geometry provided answers that satisfied the global budget of strontium-90 and similar radioactive fallout compounds (Volchok, 1980). It should be remembered, however, that radioactive fallout was injected at high elevations and that, as a consequence, most of the delivery of material to the surface was via rainfall. Depending upon the sampling location, as much as 95% of the total fallout deposition was associated with precipitation. Consequently, an error of a factor of two in the measurement of the residual dry deposition component might not have been

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*This work has been carried out by Ibrahim et al., 1982, and has been submitted for publication in Atmospheric Environment.

detected. However, in the case of present interest, the pollutants with which we are concerned are emitted at far lower altitudes and dry deposition is a correspondingly larger component of the total flux of material from the air to the surface. In this context, a factor of two error in dry deposition evaluation is likely to be far more critical. Second, the use of collection vessels has been tolerated by many, mainly because there is no simple alternative.

The inadequacies of dry deposition sampling techniques (buckets, flat plates, etc.) have been the subject of several recent reports. A workshop on dry deposition methodology (Hicks et al., 1980) concluded that the collection methods developed in studies of close-in radioactive fallout should not be extended to the case of submicron particles, such as are of major importance in considerations of acidic deposition.

The issue has been of special interest to the National Atmospheric Deposition Program of the United States which has authorized a special committee to investigate the interpretation of dry-deposition bucket measurements. A report summarizing the considerations and conclusions of this committee is in preparation. Among other factors, the report draws attention to the frequency of contamination of material collected in dry buckets by local windblown dust and bird droppings.

The limitation of surrogate-surface and deposition-vessel methods for evaluating dry deposition rates of airborne pollutants are sufficient to have generated an active search for alternatives. A detailed summary of possible techniques can be found elsewhere (Hicks et al., 1980). They are described briefly below.

(a) Eddy correlation techniques

The eddy correlation method, or the measurement of the vertical transfer of atmospheric properties and constituents, was first applied to momentum fluxes by scientists in the United Kingdom. Subsequent efforts extended the method to include sensible heat and water vapour. Applications of the method for the measurement of the fluxes of carbon dioxide, ozone, and fine particles have been reported (Jones and Smith, 1977; Wesely et al., 1977). There have been a few recent measurements of sulfur dry deposition rates using eddy correlation methods (Galbally et al., 1979; Hicks and Wesely, 1980).

The eddy correlation method assumes that the atmospheric transport of the property of interest is via turbulent eddies. In the case of SO_2, the technique provides a direct measure of vertical flux by correlating the vertical component of wind speed with the instantaneous concentration at a given measuring point.

This vertical flux is expressed by

$$F = \overline{(\overline{C} + C') \times (\overline{w} + w')} \quad (1)$$

where

F = total flux,
C = concentration,
w = vertical wind speed.

In this equation the bars denote average values and the primed symbols represent the short time deviation from this average.

From (1) the average total flux can be written as:

$$F = \overline{C}\,\overline{w} + \overline{C'w'} \quad (2)$$

If the fluxes are computed across a plane parallel to the local streamline air flow, and if the substance in question is not sedimenting, then it can be assumed that $\overline{w}$ equals zero with the result that the total average flux is equal to the eddy flux as determined by the covariance between w and C.

Applications of this method are limited to locations with a uniform surface over an area of diameter 200 to 400 times the measurement height, to averaging times of about 30 minutes and to situations in which flow conditions and pollutant concentrations do not vary greatly over the averaging time.

(b) Variance method

The variance method is similar to eddy correlation in that the flux is determined from the vertical wind speed and concentration parameters. From the basic definition of a correlation coefficient the deposition flux of a non-sedimenting substance can be written as

$$F_p = R_{wp} \sigma_w \sigma_p \tag{3}$$

where

F_p = flux density of parameter p,
R_{wp} = correlation coefficient between p and vertical wind,
σ_p = standard deviation of parameter p,
σ_w = vertical wind speed standard deviation.

If the correlation coefficient is known, then the flux can be estimated from the variance of w and p; it is not necessary to directly determine the covariance of these parameters. During the daytime, a typical value for R_{wp} is 0.4. A representative value of $\sigma_w/u*$ is 1.3 and hence the flux can be expressed as

$$F_p \simeq 0.5\ u* \ \sigma_p \tag{4}$$

(Here u* is the friction velocity, which is related to the wind speed by a constant of proportionality that depends on the surface roughness and atmospheric stability.)

(c) Eddy accumulation

The development of the eddy accumulation technique has been stimulated by a lack of sensors of adequate time response for scalar quantities measured in eddy correlation methods. The method is similar to eddy correlation except that the need for fast response chemical sensors is avoided by the continuous accumulation of air samples during the measurement period for later analysis. The method was first seriously considered in the middle 1960s but successful application for gases has not been reported.

The theoretical basis for the method has been described by Desjardins (1977). It is assumed that the dominant mechanism of atmospheric transport to the ground is through turbulent eddies. High frequency vertical velocity fluctuations are detected and air samples are taken and accumulated with a sampling rate proportional to w. Air samples associated with up and down drafts are directed to separate containers and are analyzed at the conclusion of each experiment. The flux density is then given by:

$$F = N\,(m\uparrow - m\downarrow)/t \tag{5}$$

where

F = flux density,
$m\uparrow$ = mass of pollutant collected during up drafts,
$m\downarrow$ = mass of pollutant collected during down drafts,
t = elapsed time during the experiment, and
N = the ratio of up or down air movement distance to volume sampled during each period.

Assuming no net movement of air in the vertical direction [i.e., $\bar{w}$ = 0 as in equation (2)], then the observed flux is equivalent to

$$F = \overline{Cw'} = \overline{C'w'} \qquad (6)$$

(d) Flux - gradient method

The gradient method of estimating vertical fluxes of atmospheric quantities is based on analogies between turbulent transport in air through eddy diffusivity and molecular diffusivity in the kinetic theory of gases. As the large-scale fluxes are associated with vertical gradients of atmospheric properties, this technique has also been referred to as the concentration gradient or profile method. Gradients of temperature, velocity, or other atmospheric quantities can be measured and eddy diffusivities appropriate for the pollutant in question can be estimated (usually as being equal to that for heat).

Vertical profiles of heat and water vapour have been used to determine fluxes of sensible and latent heat in energy budget studies. Research into crop growth and productivity have applied measurements of carbon dioxide concentration profiles to study gross physiological processes occurring in the vegetated portion of surface boundary layer. As a method for evaluating dry deposition of pollutants to the ground, the gradient measurement technique apparently began with Regener's (1957) measurements of ozone depletion. This method has been subsequently applied to other trace gases such as sulfur dioxide (e.g., Whelpdale and Shaw, 1974; Shepherd, 1974; Garland, 1977).

By extending the similarity between molecular diffusion in the kinetic theory of gases and the more or less random eddy motion of atmospheric turbulent flow, the flux of a molecular property associated with a concentration gradient is usually written as a variant of Fick's Law:

$$F = -K\nabla C \qquad (7)$$

In the atmospheric boundary layer, K is the appropriate eddy diffusivity often estimated by measuring vertical profiles of temperature (or sometimes water vapour) and of horizontal wind speed. If the pollutant concentration profile is measured simultaneously, then the deposition rate can be determined from equation (7).

The flux-gradient method is restricted by the same limitations as the other micrometeorological techniques mentioned above, but has the further limitations that sources and sinks of the properties involved must be co-located. Thus, application of this method over forest canopies could be rather misleading, for example.

(e) Tracers

Tracer methods can also be used to study the processes that control the dry deposition of a pollutant. Deposition of sulfur dioxide or particulate sulfate can be measured using isotopes of sulfur released for brief periods upwind of the surface of interest, for example. The amounts of material deposited on soil and vegetation from test releases can be distinguished from the naturally occurring background concentrations, and gives a method of evaluating the dry deposition directly.

While other radioactive isotopes such as iodine-131 and lead-212 have been used to study the general transport of gases from the atmosphere to the ground (Chamberlain, 1966; Chamberlain and Chadwick, 1966), some workers have used sulfur isotopes in SO_2 deposition measurements (e.g., Garland, 1977; Garland and Branson, 1977; Owers and Powell, 1974).

One application of the method is to use radioactive ^{35}S as the tracer. Amounts in the order of 20 to 30 mCi are released over a test area from which samples of vegetation and soil are extracted for analysis. Simultaneous measurements of air concentrations may also be made to evaluate flux values to the ground. The collected samples then have the sulfur extracted for analysis to determine the radioactive sulfur content. The preferred method of ^{35}S detection is by liquid scintillation counting to measure the low energy beta particles emitted (Willis *et al.*, 1970).

An alternative to radioactive ^{35}S as a tracer could be to use the sulfur already in the release material as a self-tracer (Krouse, 1977). In this method, one examines the ratios of naturally occurring stable isotopes, usually that of ^{34}S to ^{32}S. The release material must again have a $^{34}S/^{32}S$ ratio difference from the natural background. Changes in the relative concentration of $^{34}S/^{32}S$ in the test plot are interpreted to be a result of the flux of material from the test release.

(f) Mass balance technique

A mass balance approach towards the measurement of dry deposition is an indirect method that infers deposition velocities required to balance a sulfur budget through measurement of known inflow and outflow rates over the system of interest. Mass balances can be performed on two different closed systems that include the air-surface interface; the atmosphere or a terrestrial-aquatic ecosystem. In either case atmospheric dry deposition can be obtained by balancing a mass budget of the system. The biggest limitation of this technique is that it involves a differencing calculation that characteristically has high errors associated with it.

The importance of dry deposition processes in removing atmospheric sulfur compounds has been assessed by several studies. Recent sulfur budget analyses (Galloway and Whelpdale, 1980) and modeling estimates (Shannon, 1981) suggest that wet and dry mechanisms are roughly of equal importance in eastern North America as a whole. However, there is considerable uncertainty in this estimate and, thus, there is a continuing need to investigate and assess dry deposition removal.

2.3 Biomonitoring

Biomonitoring provides data on the temporal and spatial trends in concentrations of contaminants in biological tissue. Biomonitoring results can be used for the following:

a. determining the distribution and concentrations of identified substances and problems (effects) associated with these substances;
b. assessing conformity with environmental quality objectives and compliance with environmental protection requirements;
c. evaluating the effectiveness of environmental protection and management decisions and actions; and
d. identifying new, previously unidentified, problem substances.

Indicators chosen as biological monitors should attempt to meet five criteria. The ideal monitoring species should:

a. have an ubiquitous distribution in the area of concern;
b. maintain a physiological and physical condition unchanged by season and seasonal movements;
c. be easy and inexpensive to sample, well-studied and without significant limitations in terms of migratory activity; population size and reproductive potential;
d. have accumulation and loss mechanisms which are sufficiently understood to allow for qualitative and quantitative estimates of source identification and source strength;
e. be capable of taking up the contaminants of concern and accumulating them or their degradation products to concentrations in the body greater than that of the food they consume or the substrate within which they live.

The species recommended may be used to provide data on the effectiveness of and compliance with federal or provincial-state pollution control regulations, help identify point sources of toxic substances, establish the effects of toxic substances, provide baseline data on pollutant levels in the environment, and make possible the identification of new and unrecognized toxic substances in the biota.

Biomonitoring can be further resolved into (a) describing the levels of a given contaminant to determine temporal and spatial trends in concentration and (b) assessing the biological changes that occur within the indicator species as a result of the contaminant. Both types of monitoring provide information needed for the assessment of environmental hazards. Ideally, both effects and levels monitoring should be conducted simultaneously (but not necessarily in the same species) because a good "levels monitoring species" may not be a suitable "effects monitoring species" and because many chemicals may produce toxic effects but leave no measurable residues.

This review outlines the applicability of biomonitoring to the LRTAP problem, and it is not intended to be a comprehensive review of all aspects of biomonitoring.

The value of vegetation as air pollution monitors is in their ability to (a) recognize the presence of airborne contaminants, (b) determine the distribution of pollutants, (c) estimate the level of pollution, (d) provide a passive system for collection of pollutants for later chemical analysis, and (e) directly identify different air pollutants on the basis of (1) type of injury and (2) plant species injured.

The balance of this section will concentrate on the use of plants to determine the distribution of pollutants.

Vegetation has been used extensively to monitor the dispersion and deposition of atmospheric pollutants. Most studies have dealt with plants as biomonitors of inorganic substances around point or area sources of the elements in question. Seed plants have been used as monitors of emissions from (a) the combusion of leaded gasoline (Page et al., 1971; Martinez et al., 1971), (b) smelters (Little and Martin, 1972; Buchauer, 1973), and (c) urban areas (Smith, 1973). The use of seed plants as monitor organisms is subject to several difficulties. For example, data interpretation is complicated because these plants depend primarily on root uptake for the majority of their mineral nutrients though foliar uptake occurs to a variable degree. Subsequent translocation of mineral nutrients serves to further complicate the situation. Hence, element concentrations in seed plants will depend upon several factors other than atmospheric input including such variables as substrate type and leaching rates.

The extensive use of cryptogams such as bryophytes and lichens for monitoring deposition is the result of certain characteristics of these groups. Lichens, because they do not have roots, are dependent for their mineral nutrients on substances deposited to the plant surface as the result of wet and dry deposition. Lichens, again unlike higher plants, do not have a well-developed cuticle and this feature contributes to the ability of lichens to accumulate elements such as sulfur to levels far greater than their expected physiological needs. Also, lichens are perennial and hence can be considered as long-term integrators of atmospheric deposition. However, while seeming well-suited to being used as biological monitors of deposition, the interpretation of data obtained by using bryophytes and lichens is also subject to confounding influences such as the substrate contributions and biological lifetime of elements within the lichen thallus.

Several studies have attempted to use cryptogams to monitor the long-range transport of air pollutants. The earliest indication that remote anthropogenic sources were contributing to bryophyte element levels was reported by Ruhling and Tyler (1968). High lead concentrations were found in bryophytes in southwestern Sweden and lower lead concentrations were observed in more northern areas. Subsequently, well-defined gradients for copper, lead, and nickel were seen in bryophytes with the highest values being seen in the southern half of Sweden (Ruhling and Tyler, 1971). The possible role of precipitation differences in different geographical areas was considered in the interpretation of the data as were other factors such as the marine aerosol input, differing weathering rates of the substrate and differing plant productivity. The authors concluded that the observed gradients were the result of atmospheric transport of emissions from both neighbouring and remote sources. There were no major industrial sources of the elements in question in the area showing the highest concentrations but Ruhling and Tyler (1971) made no estimate of the contribution from the remote source regions.

Similar studies have been completed in Norway and Denmark (Steinnes, 1977; Pilegaard <u>et al</u>., 1979). Several element distribution patterns, as reflected by the metal concentrations in <u>Hylocomium splendens</u> were described by Steinnes (1977). For some elements (e.g., lead), the highest concentrations were found in southern areas. Some elements showed a distribution interpreted to be governed by supply from the marine aerosol while other elements showed a fairly even distribution over the entire sampling area. The element concentrations in moss showed some linkage with precipitation amount and, except for three sites, no evidence of contributions from local sources was apparent. The lack of obvious sources of lead, cadmium, and vanadium in southern Norway indicated that source regions outside Norway were responsible for the high moss element concentrations. This interpretation is supported by the data of Hansen _et al_. (1980) who indicated that the highest atmospheric concentrations of the elements studied were associated with air masses whose trajectories were from the south and southwest. In addition, it should be noted that this pattern of high metal concentrations in bryophytes from southern regions has been seen in Finland by Pakarinen and Tolonen (1976) who used _Sphagnum spp_. as their bio-indicator. However, Pilegaard _et al_. (1979), while showing regional patterns in metal deposition as reflected by moss and lichen species, conclude that local pollution was more responsible for the high plant concentrations in Denmark.

In North America, biomonitoring over large areas has not been fully exploited. Grout (1976) studied the element concentration in bryophytes from northeastern USA. Highest metal concentrations were found in the southern, more highly industrialized parts of New England and a trend of decreasing concentrations was seen with increasing distance from New York City. There were relatively high metal concentrations in the more isolated areas of New England but the extent to which these concentrations are maintained by emissions originating outside of New England was not examined. Percy (1982) has described a survey of the element concentrations in _Sphagnum spp_. collected throughout the Maritime provinces of Canada. No marked regional patterns were observed but the variation in the deposition over the area studied may not have been large enough to be reflected in the biomonitors. The element concentrations were not correlated with precipitation amounts, either on a seasonal or annual basis, or with altitude. Some sites were enriched as the result of local anthropogenic emissions but, overall, the mean values for the elements in question were significantly lower than those reported for Northern Ontario and Southern Sweden.

Lichens have been used extensively to map pollution distribution around point sources but have not been used to examine relative air concentrations over large areas. However, comparison of the lead and sulfur concentrations in the lichen Cladina rangiferina from the Northwest Territories and Eastern Canada showed that these element levels were considerably higher in Eastern Canada (Puckett, unpublished data). The other metals studied (chromium, iron, nickel, titanium, and vanadium) showed no difference between the two geographical areas. Regional differences were also seen within Eastern Canada with the highest values for lead and sulfur being found in the Muskoka/Haliburton area of Ontario and in southern Quebec. A good correlation was found between the lichen sulfur content and the total sulfur deposition predicted from models (Olson et al., 1982). These preliminary observations are based on a limited data set but a more extensive data base (approximately 90 sites in Eastern Canada) is currently being prepared. Sulfur levels in C. rangiferina collected from remote areas (New Brunswick, Nova Scotia) are double those levels found in the Northwest Territories. The sites in the Maritime provinces are remote from local sources and the substrate contribution is limited by using lichens, which are colonizing ombrotrophic peat bogs. The question of the origin of this excess sulfur is not resolved and contributions from source regions outside of the Maritime provinces cannot be dismissed.

Chapter 3

REVIEW OF AVAILABLE DATA SETS

The original objectives of this chapter were:

a. to document, provide a catalogue of, and critically review the major data sets available from observational networks and special studies operated on regional, national and global scales; and

b. to assess the value of these data sets for model development, comparison, and verification, as well as for evaluation of the effectiveness of emission control strategies.

It soon became evident, however, that the above objective could not be met in the limited timeframe available because to do so would require a considerable amount of manpower and funding. Instead, it was decided to list the data sets thought to be of potential value for mathematical modeling and control strategy evaluation, and then to consider the factors that should be taken into account when assessing these data sets with the objective of producing a unified deposition database.

3.1 Data Sets of Potential Value

In the selection of those data sets to be included, special emphasis was given to the monitoring of those chemical components that relate to acid deposition--i.e., the sulfur and nitrogen compounds. To qualify for inclusion, wet deposition measurements had to be made using equipment that exposes the collector vessel only when precipitation is falling. However, bulk deposition was also included, if it was known that (a) the sample was collected every day, (b) the equipment was washed every day, and (c) the sampling locations were in general suitable (e.g., good ground cover around the sampler). Most of the networks considered operate on a regional scale. Nevertheless, some source-oriented networks (identified as such in Appendix 2) were also included as potential sources of useful data for episode studies.

As was described in the last chapter, no direct measurements of the dry deposition rate are available, for purposes of model validation. Methods suitable for routine field monitoring do not exist: the use of "bucket" techniques, or other artificial surfaces, is generally not thought to be an acceptable alternative. The most promising approach seems to be that of inferring dry deposition rates from the ambient concentration, using a "deposition velocity" (Hicks et al., 1980). Therefore, our discussion of dry deposition will be confined to networks that are making regionally representative measurements of the gaseous and particulate SO_x and NO_x compounds, from which dry deposition rates can be estimated.

Appendix 2* lists the available data sets in North America, Europe, and on a global scale, under the following headings: (1) name of network, (2) sponsoring agency, (3) number of stations, (4) area monitored, (5) sampling interval, (6) start/end dates of the network, (7) chemical constituents measured, (8) analytical laboratory used, (9) data storage format, and (10) comments. Under the "Comments" heading are addressed (if information was available) such questions as: is there a quality control program; are any data rejection criteria applied prior to publication of the results; have there been any changes in sampling or analysis procedures during the life of the network; is the network source-oriented; and, are any additional meteorological or air quality measurements taken at the sites?

3.2 Considerations for Assessment of Data Sets

A distinction should be made at the outset between what modellers would ideally like to see in a set of data for model testing, and the kind of information that could and should be made available from the existing networks.

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*The North American information in Appendix 2 is based largely on "A Summary of Wet Deposition Monitoring Networks Operating in Canada and the United States as of March, 1981," Concord Scientific Corp., March 31, 1981, and updates of this report made in December, 1981. See also Miller (1981) and Whelpdale and Barrie (1982).

3.2.1 The Ideal Data-Base

The requirements of the ideal data-base would include the following:

- o regionally representative values, together with estimates of uncertainty, of the precipitation concentration and deposition of the major ions and dissolved SO_2;
- o use of either uniform, or very well cross-checked, methodologies of collection and laboratory analyses across the modelled region;
- o reporting of precipitation type;
- o spatial resolution of about 50 km;
- o temporal resolution of at least one month, together with the extreme values and standard deviation, but event data are preferable;
- o at least five years of data from which to deduce year-to-year variability and trends (see, for example, Section 4.2);
- o direct measurements of dry deposition of the sulfur and nitrogen species of relevance to acid rain, or, pending the development of suitable instrumentation, their air concentrations;
- o rapid dissemination of the data.

3.2.2 Existing Data-Bases

As far as the existing networks are concerned, several features are considered to be necessary:

a. The data set sould be sufficiently complete for the intended use. The completeness of the sampling record depends on the parameter of interest, its observed variability, and the user's acceptable level of uncertainty in the data and the model application. For example, because of the spatial and temporal variability inherent in wet deposition data, it is estimated that about five to 10 years of observations may be needed to evaluate statistical models (U.S.-Canada MOI Work Group 2, 1981). Episodic models (i.e., short-term models simulating a few days) on the other hand would require a shorter data record, involving several episodes, probably with a higher spatial density of measurements. Also, if a model validation is to be made for a particular year, then the data recovery should be such that all seasons are equally represented.

b. The data should be well documented with information on sampling and chemical analysis protocols, local sources of contamination around each sampler, etc., so that a judgement can be made by the user about the usefulness of the data for regional model validation, and the comparability of the data from one network with those from another (i.e., are the two networks "measuring the same thing?"). It is essential that these judgements be made with more information than just visual site inspection (for example, a careful inspection of the precipitation chemistry, especially with regard to soil-originated substances, should also be undertaken). Most of the networks are reasonably well documented for overall procedures. However, specific site documentation has not been vigorously conducted. This documentation is essential for interpretation of data. It is also important not to neglect information of the type listed in the Appendix, on procedural changes, quality control (if at all possible, also including a quantitative assessment of the QC program), data rejection criteria, etc.

c. After a number of monitoring stations have been selected (for example, on the basis of being suitably sited for LRTAP studies, and having a sufficiently complete data set), an estimate should be made of the uncertainty of the measured value at each station. For example, if a LRTAP model can predict the wet deposition of sulfates at a particular location within a factor of 2 of the observed value, while the accuracy of the monitoring data at that location is no better than within a factor of 2, then further tuning of the model parameters, to bring observed and predicted values together, is not justified.

3.2.3 Error Determination

The determination of error limits on concentration and deposition measurements is very difficult, and none of the available data bases fully satisfy the requirements necessary to enable such determinations to be made. There are several factors contributing to the uncertainty in a particular datum:

a. Random errors in sampling and chemical analysis, primarily the former (Galloway and Likens, 1976, 1978), although the latter have been shown to be very significant in some cases (for example, Patterson, 1975). These errors can be estimated by precision measurements, i.e., by operating several samplers at each site. This is being done by some networks in North America (EPRI, Ontario Ministry of the Environment). It may not be necessary to do precision measurements at every site, but rather, at a number of "representative locations" (e.g., farmland, forested area, etc.) for each network. The 95%, or some other confidence limits on a datum, determined by precision measurements, should be regarded as the minimum bounds of uncertainty on that value, as there are additional factors which will also contribute (see further below).

b. Systematic errors in sampling and chemical analysis. These are extremely difficult to estimate, although some idea of their magnitude can be obtained by network intercomparisons (i.e., side-by-side sampling, at a number of "representative" locations, using different collection, sample handling and chemical analysis techniques). Some work along these lines is in progress. A more rigorous examination of systematic errors should be designed, funded, and implemented.

   Systematic errors in concentration and wet deposition measurements involve such factors as poor collector efficiency, sample evaporation after collection, sample contamination by handling or dry deposition due to poor collector design, and chemical deterioration of the sample (especially the nitrogen compounds) between collection periods and analysis. For example, Parkhurst et al. (1980), using some commercially available wet deposition monitors, estimate that the error in wet deposition caused by extraneous contamination between precipitation periods, and handling and analysis variability, could be 20% or more for many of the commonly measured precipitation parameters. (Errors for SO_4^{2-} and NO_3^- were estimated to be less than 20%).

Systematic errors are also possible in dry deposition, i.e., ambient concentration measurements. For example, sulfates can be formed from SO_2 if the filter medium is not chosen properly (Pierson et al., 1976), and the sampling of nitric acid and particulate nitrates is a problem that is still far from being solved (Spicer and Schumacher, 1979; Appel et al., 1981). However, it is probably fair to say that the uncertainty of the value to be used for the deposition velocity (especially for particulates) is currently much larger than that in the measured concentration (Sehmel, 1980). Therefore, effort should be concentrated in narrowing down the confidence limits on deposition velocities for gases and particles, over different surfaces, and for different seasons and meteorological conditions.

c. Uncertainties about regional representativeness of a datum. There are at least two questions to be considered here. First, although a site may have passed the preliminary screening test (i.e., absence of immediately local sources), in eastern North America it is difficult to find a location that is accessible and has electrical power, yet at the same time does not have an area or point source (e.g., urban area, power plant) within some tens of kilometers. How important is the local source interference as compared to the background deposition? An assessment of the magnitude of this contribution will have to be made on a site-by-site basis. Enough information is probably available for a reasonable estimate to be made (see Mesoscale Effects subgroup report 2F-L), at least for long-term data. This has not yet been done in any systematic way for any of the networks.

The second source of uncertainty is that resulting from interpolation between a number of network stations. Interstation interpolation is necessary in order to derive area-wide averages, as well as to estimate values at individual points. Even if models are being validated only at existing measurement points, it is desirable that the predicted spatial pattern be compared with the pattern derived from the measured data. This will help avoid fortuitous agreement or unexplained disagreement between model and data in areas of steep concentration gradients.

The interpolation problem is discussed by a number of authors (see, for example, Granat, 1975, 1977; Gatz, 1978; Finkelstein and Seilkop, 1981). The error involved depends on such factors as network density, sampling period under consideration, variable of interest, and characteristics of the general area of interest (e.g., rural central Sweden would have a much smaller uncertainty due to interpolation between sites than would an urban area such as St. Louis, U.S.A.). This error can be estimated, but requires special experiments using intensified sampling around regular network sites. Probably a few "representative" sites can be selected: every single site need not be considered. The Ontario Ministry of the Environment, and EPRI's Lake Acidification Study in the Adirondacks, are the only ongoing North American studies known to be doing this kind of work.

Many of the considerations to be borne in mind when assessing the usefulness of the available (as well as any future) data sets for mathematical model development also apply for evaluation of emission control strategies. Any data used for the latter purpose should be of the highest possible quality. Since we are here primarily interested in the evaluation of temporal trends, data will be required over a long period of time at a number of selected locations, where conditions surrounding the site (e.g., land usage, industrial activities) have not changed significantly in the past or are not expected to in the future. Good information will be required, at the minimum, on the precision of the sampling method (ideally the data should be accompanied by accuracy estimates as well, although this may not be possible for some of the historical data). A consistency of sampling and chemical analysis procedures over the period of interest will also be required: if they have changed, then an evaluation of how the changes may affect the deposition results must be performed.

3.3 Conclusions and Recommendations

This first overall review of the available monitoring data sets leads to the following four major conclusions:

3.3.1 Conclusions

a. A number of wet deposition data sets of potential value for mathematical model and emission control strategy evaluation have been identified and are listed in Appendix 2. In North America, only the BAPMoN and USGS Upstate New York networks are known to have been operated for a sufficiently long time to provide data for statistical model evaluation, but the quality of the data generated by these networks requires further scrutiny before they can be recommended for use (see, for example, the recent assessment of the CANSAP network by Barrie and Sirois, 1982). In addition, there are several European data sets of potential value for statistical model and control strategy evaluation, and a number of North American networks which could be used for episodic, seasonal or annual studies.

b. Due to time constraints, it was not possible to do a critical evaluation of these data sets. Much more work, involving considerations of the type discussed in Section 3.2, is needed to fully assess their usefulness. A careful examination of the data will be required--for example, there is evidence (Patterson, 1975) that certain chemical constituents have not been accurately measured by some of the European networks (due to errors resulting from poor sampler location, sampling methods, or analytical procedures). It will be especially important to develop, and then apply, methods to estimate the accuracy of the data from all of the current networks. To do this, it will probably be necessary to undertake special studies with intercomparisons of results from different networks and measurements of network precision (a limited amount of work along these lines is already underway).

c. Most of the existing networks are reasonably well documented for overall procedures. However, specific site documentation, use of precipitation chemistry data (e.g., soil-related elements to assess possible sample contamination due to sampler malfunction, etc.) for evaluating sites, quantitative assessments of the quality assurance program (if any), and other information of relevance, is generally lacking.

d. At present, there are no methods suitable for the direct routine monitoring of the dry deposition rate, nor is it likely that such methods will become available in the near future. The most promising approach of immediate usefulness seems to be the estimation of dry deposition rates from measured ambient concentrations and estimated deposition velocities (Hicks et al., 1980). However, much more data are needed on both concentrations and deposition velocities for most of the species related to acidic deposition.

3.3.2 Recommendations

In order to maximize the usefulness of the existing data sets and to ensure more reliable monitoring data in the future, the following three recommendations are made:

a. It is strongly recommended that the necessary manpower and funding be made available to critically evaluate, within the next year, the data from the existing deposition monitoring networks. The objective should be the production of a unified deposition data base for

North America and Europe, with uncertainty estimates for each parameter of interest (and probably for several time-scales, e.g., long-term, annual, seasonal, and event). This work could possibly be done by scientists with expertise in the fields of both deposition monitoring and mathematical modeling. In addition, special research studies--such as network intercomparisons, operation of two or more samplers at a single site, and sample degradation studies--should be encouraged to provide information to assess the data errors.

b. The documentation of most of the networks should be improved. Information is particularly desired by the modelers on whether or not there is a quality assurance program (as well as details about the program, including a quantitative assessment), rejection criteria for excluding outliers, changes in methodology during the network's lifetime, and (if available) quantitative uncertainties in the data.

c. Pending the advent of routine monitors for direct dry deposition measurement, efforts should be increased to measure ambient concentrations for the gaseous and particulate sulfur and nitrogen compounds of relevance to acidic deposition, by the addition of suitable air monitoring equipment at appropriate sites. Also, additional experimental determinations of dry deposition velocities over various types of surfaces are badly needed, especially for sulfates, nitrates (including nitric acid) and ammonia. This work should receive a high priority, since over much of eastern North America, dry deposition is estimated to be of comparable importance to wet deposition (Galloway and Whelpdale, 1980), but adequate information on the former is lacking.

Chapter 4

PRELIMINARY DATA INTERPRETATION

4.1 Spatial Variations

The geographical variations of the concentration in air and precipitation of a particular pollutant is determined by several factors, the most important of which are:

a. the residence time in the atmosphere for the pollutant, which, in turn, is determined by removal processes (chemical transformation, precipitation scavenging, dry deposition);

b. the configuration of sources of the pollutant;

c. the meteorological wind fields that transport and disperse the pollutant;

d. the precipitation fields (temporal and spatial distributions) and storm type in the vicinity and downwind of source regions.

Spatial variations can be viewed on a range of scales from local (1-10 km) to regional (10-1000 km) to global (1000-10,000 km). Substances that affect the acidity of precipitation and the total deposition of acid to the earth's surface are involved in all of these scales. Oxides of sulfur and nitrogen, ammonia and calcium/magnesium compounds in windblown dust are the major species of concern. While considering precipitation chemistry in this chapter, it is useful to bear in mind the general sequence of events that influence the acidity of precipitation. It is represented schematically in Figure 4-1. The sequence of events that contribute to the final acidity of precipitation involve both in-cloud and below-cloud processes (see for instance Hales, 1982). These processes are:

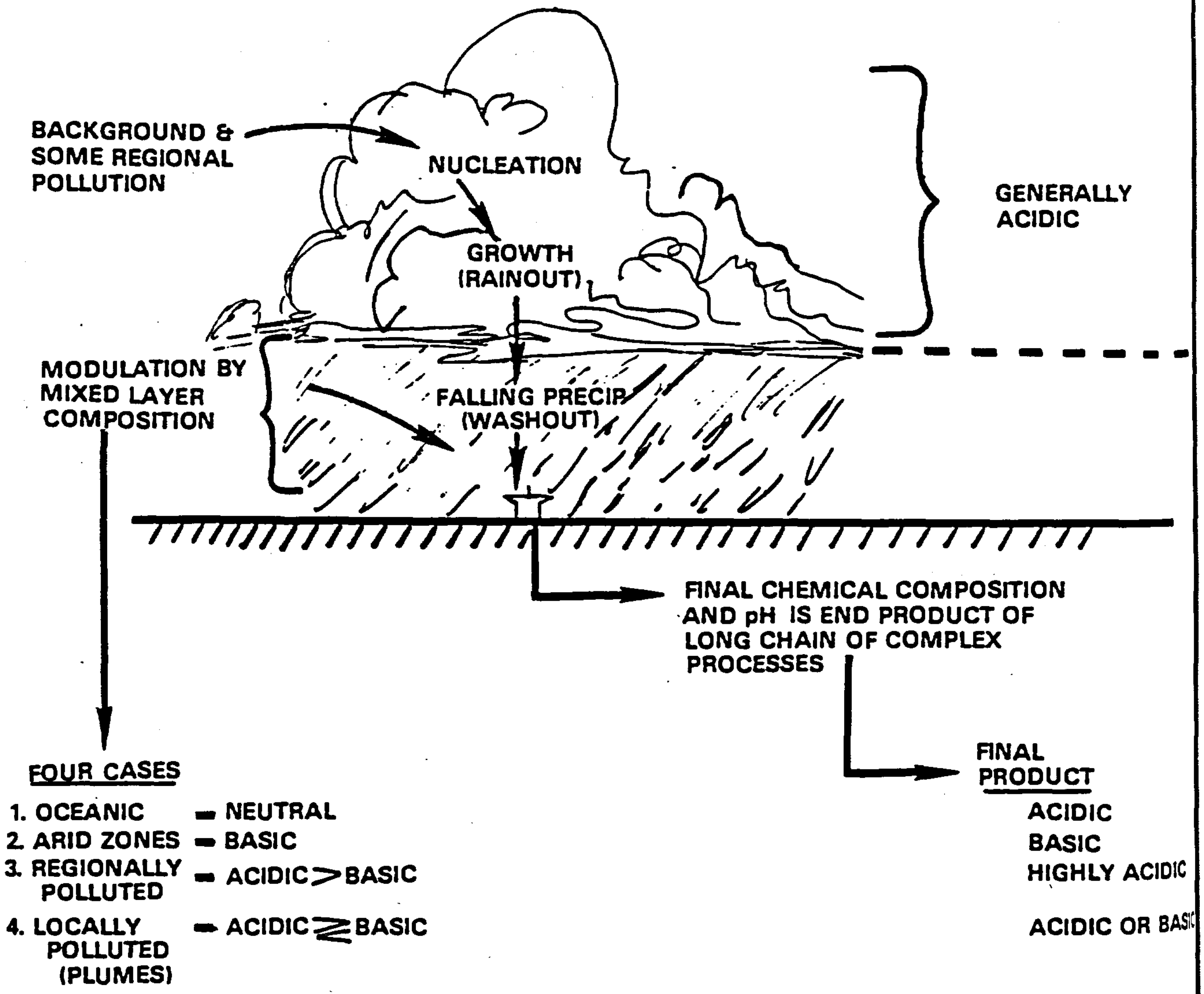


Figure 4-1 Factors Controlling the pH of Precipitation

In-cloud

- o scavenging of particles by condensation,
- o formation of acids by the oxidation of the oxides of sulfur and nitrogen,
- o neutralization of acids by absorption of ammonia gas, and
- o the formation of precipitation from cloud water and ice; and

Below-cloud

- o evaporation of rain to concentrate pollutants,
- o irreversible scavenging of particles,
- o reversible scavenging of gases such as SO_2, NH_3, etc., and
- o oxidation of oxides of nitrogen and sulfur in falling rain.

Whether in-cloud or below-cloud processes dominate the final chemical composition of precipitation depends on the relative concentration of pollutants in the sub-cloud layer and in the air at the inflow regions of the cloud. Away from large industrial or urban areas, in-cloud scavenging processes tend to dominate over those below-cloud ones.

The complexity of processes that control the acidity of natural rainwater have recently been discussed by Charlson and Rodhe (1982), who correctly point out that only in the total absence of all acids and bases other than CO_2 is the pH of precipitation 5.4 to 5.6 (the range of values for distilled water in equilibrium with atmospheric CO_2). The presence of alkaline materials, such as ammonia or alkaline windblown dust, can cause deviations upward from this pH (Sequeira, 1982), while acidic particles and gases can cause deviations downward. For instance, cloud water pHs of 3.7 to 5.1 can be caused by a background concentration of 1 $\mu g\ m^{-3}$ SO_4^{2-} and 0.29 $\mu g\ m^{-3}$ SO_2 depending on the cloud's liquid water content.

4.1.1 The Global Distribution of Acidity

The distribution of mean precipitation pH in the northern hemisphere is approximately that shown in Figure 4-2 (Gravenhorst et al., 1980). The pattern depicted here is highly schematic. It summarizes the results of numerous routine observations in North America (discussed in detail later),

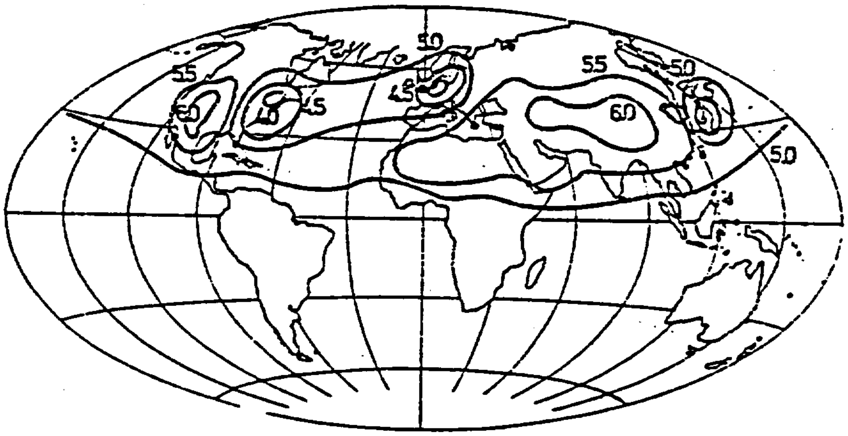


Figure 4-2 Distribution of Precipitation pH in the Northern Hemisphere (Adapted from Gravenhorst, et al., 1980) (Based on extensive measurements in North America and Europe and limited measurements elsewhere)

Europe, and scattered measurements elsewhere. In addition, the pH of precipitation observed by Miller et al. (1982) in Hawaii is reported. Table 4-1 summarizes available observations of precipitation in remote areas in both hemispheres. Galloway et al. (1982) conclude that acidities at Bermuda and Alaska were from long-range transport of sulfate aerosol. In the northern hemisphere, zones of high pH (low acidity) generally occur in areas not immediately downwind of major industrial regions (such as eastern North America and Europe). In such areas the pH of precipitation may be raised by the alkaline influence of windblown dust. Examples are found in the North American prairies and regions bordering on deserts like the Sahara. An illustration of the phenomena pointed out by Charlson and Rodhe (1982) of acidic precipitation occurring in areas remote from industrial sources having low background levels of sulfur and nitrogen oxides is the precipitation acidity at Hilo, Hawaii. The annual mean pH is 4.7. Atmospheric sulfur compounds of natural oceanic origin and from remote anthropogenic sources (lower pHs are observed in flows from the North American mainland) are the main source of acidity. Charlson and Rodhe (1982) emphasize that acidic precipitation can occur in "pristine" air masses having low ambient concentrations of acidic material as a result of precipitation scavenging processes that concentrate air pollutants into small volumes of cloud water. In other words, precipitation scavenging processes are an important factor. At another subtropical oceanic location, Amsterdam Island, in the Indian Ocean, Galloway et al. (1982) measured an annual mean pH of 4.9. It was concluded that the acidity was due to mixtures of weak organic acids and strong mineral acids (primarily sulfuric).

In the northern hemisphere (Figure 4-2), zones of highly acidic precipitation (pH 4 to 4.5) occur in areas around and downwind of major industrial areas in eastern North America and Europe that have high densities of acidic pollutant emissions. Oxides of sulfur and nitrogen are the major pollutants causing this man-made acidity. On a global basis, the oxides of sulfur are greater contributors to the annual mean acidity of precipitation than nitrogen oxides. However, close to source regions (400 to 1000 km) at certain times of year, particularly winter, the latter can be of equal or even greater importance than sulfates (see for instance Figure 4-20).

TABLE 4-1 THE pH OF PRECIPITATION IN REMOTE AREAS AROUND THE GLOBE

	Monthly average precipitation pH			Length of Record of Events
	Median	Minimum	Maximum	
OCEANIC				
Samoa (1)	5.3	4.0	6.2	100s
Mauna Loa (2)	4.3	3.3	5.6	100s
Hilo, Hawaii (2)	4.7	3.7	6.0	100s
Amsterdam Island (3)	4.9	3.8	5.4	+50
Bermuda (3)	4.8	4.0	5.6	100s
WEST COAST				
Cape Grim, Tasmania (1)	6.3	5.8	7.2	12
India (4 stns) (1)	6.3	5.8	6.6	13
Ireland (3)	4.8 - 5.6			1968 - 1974
Norway (3)	4.8 - 5.2			Oct. 1977 Sept. 1979
North America (3)	5.0			Variable
CONTINENTAL				
India (9 stns) (1)	7.5	5.8	8.9	51
Grand Jct (Colo) (1)	6.5	5.4	8.0	40
Alamosa (Colo) (1)	6.8	5.0	8.2	73
San Angelo (Texas) (1)	6.6	5.2	7.3	43
POLAR				
Canadian Arctic*	5.0			Few
Inland Antarctic*	4.6 - 5.6			Few

*Estimated from ion balance (see text)

Sources:
(1) Personal communication--Don Nelson.
(2) Miller, J. M., and A. M. Yoshinaga, 1981: The pH of Hawaiian precipitation A preliminary report GRL 8:779-782.
(3) Galloway, J. W., G. E. Likens, J. M. Miller, and W. C. Keene, 1982: The composition of precipitation in remote areas of the world. Submitted to JGR.

Some insight into the nature of the acid rain phenomena is gained by considering, on a global and regional scale, the atmospheric cycle of sulfur, one of the main precipitation acidifying agents. On the global scale, sulfur in the atmosphere originates from natural as well as man-made sources. Volcanoes, production of sea-salt sulfate by waves and biogenic sources of H_2S, carbonylsulfide, and dimethylsulfide from oceans, tidal flats, and marshes are the main natural contributors. Over the years a plethora of global sulfur budgets have been constructed (Table 4-2). Early estimates obtained biogenic emissions by balancing the budget of global sources and sinks of sulfur with this source as an unknown. In recent years, more use has been made of actual measurements to estimate biogenic emissions.

An even more difficult task is to construct a global nitrogen budget. A recent attempt by Jennifer Logan (personal communication) for NO_x only is shown in Table 4-3. The uncertainty is expressed in the wide range given for the sources and sinks.

In general, natural and man-made emissions are roughly comparable when averaged on a global scale. On a regional scale, however, the ratio of man-made to natural sources can be very different. While natural emissions tend to be distributed widely around the globe with low-emission densities, man-made emissions are concentrated in a few regions and have a high-emission density. In eastern North America, for instance, the ratio of man-made to natural sources of sulfur was estimated by Galloway and Whelpdale (1980) as 20:1. In another study, it was concluded that in the American northeast natural sources of sulfur are of minor significance compared to anthropogenic ones (Henry and Hidy, 1980).

4.1.2 The Regional Distribution of Acidity and Related Ions in Precipitation of North America.

In recent years, several networks of precipitation chemistry collectors have been established at regionally representative locations across Canada and the United States (Chapter 3). In 1980, the major ion content of precipitation was monitored by the federal government at 90 to 100 sites in North America. Maps of precipitation-weighted-mean concentrations of pH, H^+, SO_4^{2-}, NO_3^-, and NH_4^+ were assembled from data in two Canadian networks,

TABLE 4-2 A COMPARISON OF ESTIMATES OF THE GLOBAL EMISSION RATES OF SULFUR (10^6 tonnes/year) FROM NATURAL AND MAN-MADE SOURCES

Natural				
Volcanic	Sea spray	Biogenic	Man made	Reference
---	45	230	40	Jung, 1963
---	45	280	40	Eriksson, 1963
---	44	98	70	Robinson and Robbins, 1972
1	44	89	50	Kellogg <u>et</u> <u>al</u>., 1972
2	44	106	65	Friend, 1973
3	44	31	65	Bolin and Charlson, 1976
3	44	37	65	Hallberg, 1976
3	44	32	65	Granat, 1976
---	44	152	70	Garland, 1977
10	44	86	60	Oavey, 1978

TABLE 4-3 GLOBAL BUDGET FOR NO_x

Sources		10^{12} gm N yr^{-1}
Fossil Fuel Combustion		21 (14-28)
Biomass Burning		12 (4-24)
Lightning		1-10
Microbial Activity in Soils		8 (4-16)
Oxidation of Ammonia		0-10
Phytolytic or Biological Processes in the Ocean		<1
Input from the Stratosphere		∿0.5
	TOTAL	24-89
Sinks		
Precipitation		12-50
Dry Deposition		10-20
	TOTAL	22-70

CANSAP and APN, and the two American networks, NADP and MAP3S, (Figures 4-3 to 4-7). In addition, maps of the deposition of these ions (Figures 4-8 to 4-11) were drawn by multiplying precipitation-concentration fields obtained from the chemistry networks by the precipitation-amount fields obtained from the meteorological networks operated by the Canadian and American weather services (Figures 4-12a and 4-12b, respectively). This procedure recognizes the fact that concentrations of long-range-transported pollutants in precipitation vary less spatially than precipitation amount (Granat, 1978) and consequently a denser network is required for the latter than the former. In constructing maps of concentration and deposition, the criteria was applied that in order to yield a representative annual mean concentration a station must have been in operation for at least two-thirds of the year. Isopleths of concentration and deposition were drawn by hand. In drawing deposition lines use was made of deposition values calculated on a 100 x 100 km grid in the American northeast and deposition values calculated at approximately 250 class-one climate stations in Canada to position lines between stations of the precipitation chemistry networks. Consequently more form to the isolines than may be readily apparent from the data points in Figures 4-8 to 4-11 is justified.

The spatial distributions for 1980 in Figures 4-3 to 4-11 constitute the best available data for use in validating long-range transport models. They also provide insight into the cause and nature of the acid rain problem. Keeping in mind the question "what role do man-made pollutants play in acidifying precipitation," it is useful to compare observed concentration and deposition patterns with those of emissions. Consider, for instance, sulfur emissions in eastern North America (Figure 4-13a). When viewed from a regional perspective, the sulfur emission pattern coincides reasonably well with the sulfate concentration or deposition pattern (Figures 4-5 and 4-9) in eastern North America. It is convincing evidence of the existence of a link between emissions and the composition of precipitation.

In order to avoid drawing false conclusions about the magnitude and spatial extent of acid-related deposition, uncertainties associated with two features of the spatial distributions reported here for 1980 should be borne in mind. These features are the position of an isoline and the representativeness of a distribution obtained in one year of those in adjoining years. Uncertainty in the position of an isoline is related to uncertainty in a

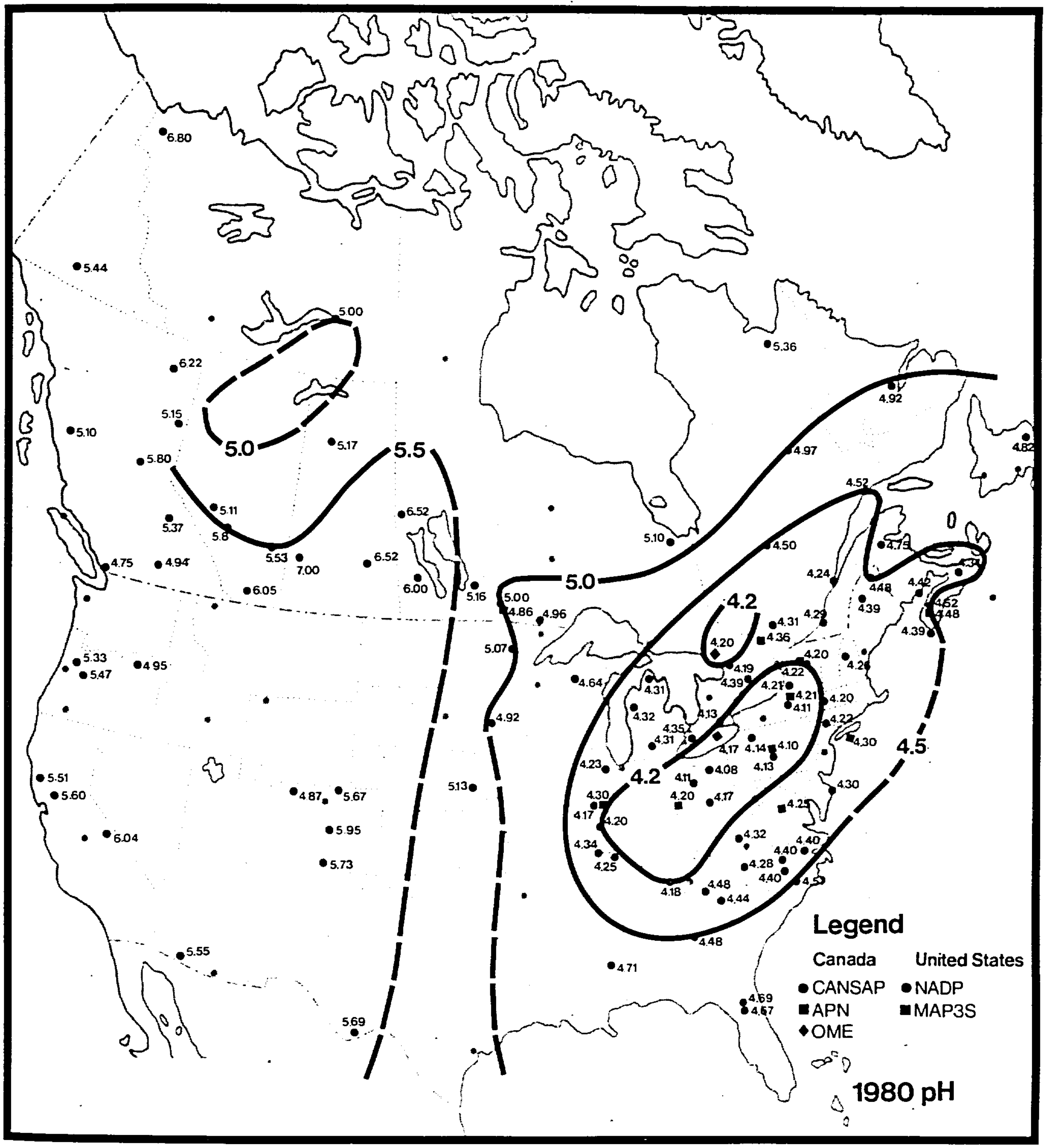


Figure 4-3 Spatial Variation of Precipitation-Amount-Weighted Mean pH in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

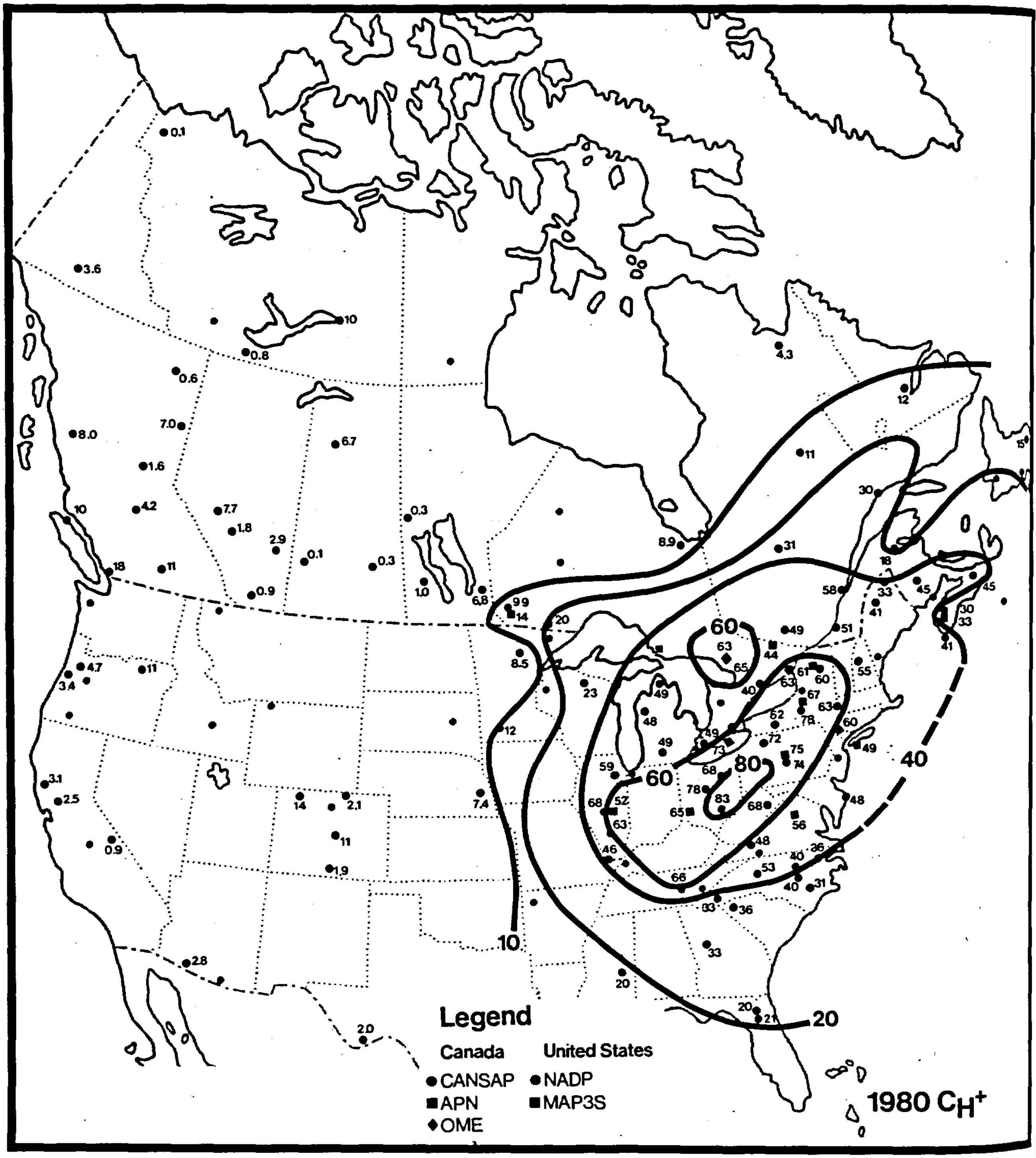


Figure 4-4 Spatial Variation of Precipitation-Amount-Weighted Mean Hydrogen Ion Concentration (micromoles per liter) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

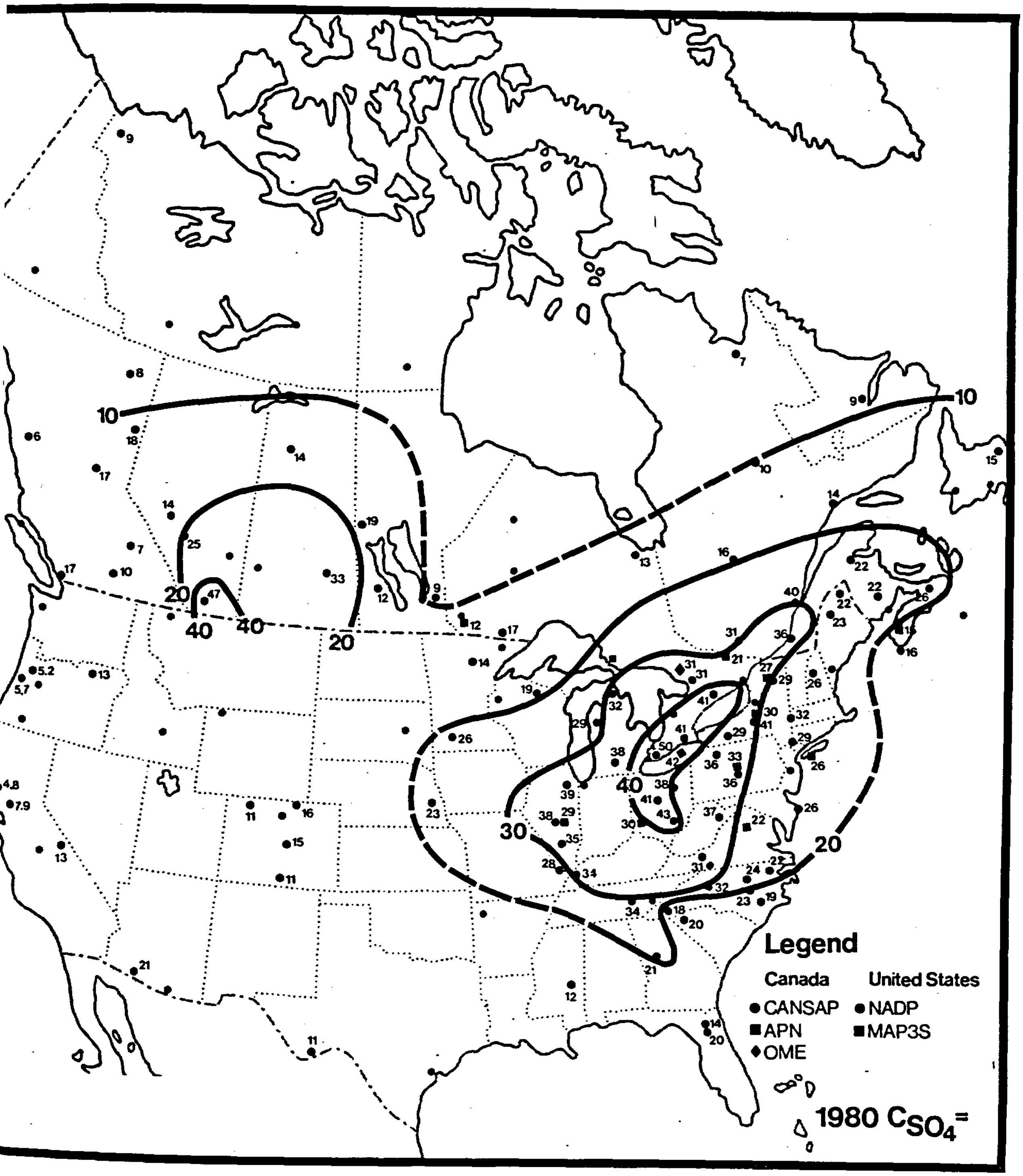


Figure 4-5 Spatial Variation of Precipitation-Amount-Weighted Mean Sulfate Ion Concentration (micromoles per liter) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

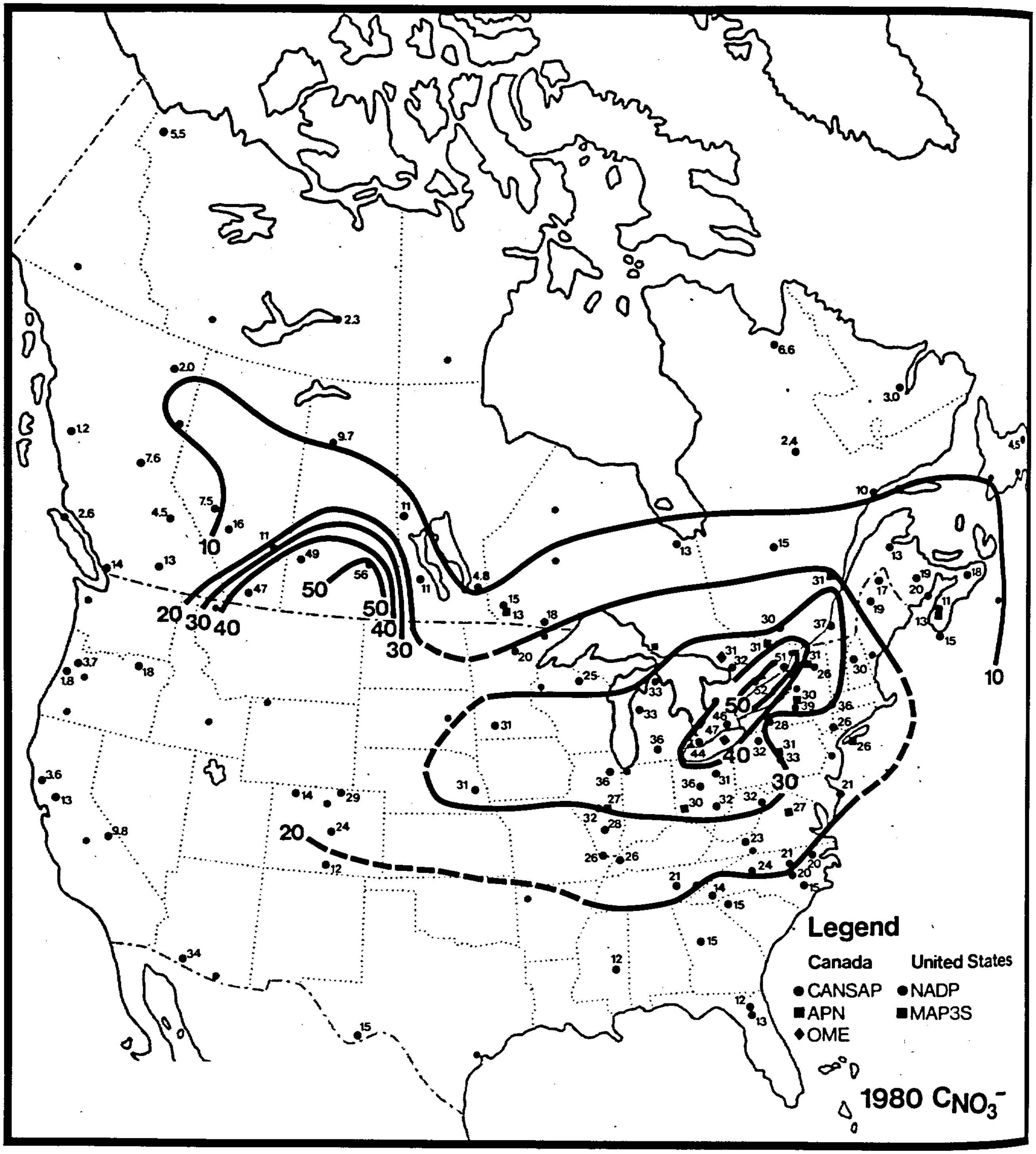


Figure 4-6 Spatial Variation of Precipitation-Amount-Weighted Mean Nitrate Ion Concentration (micromoles per liter) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

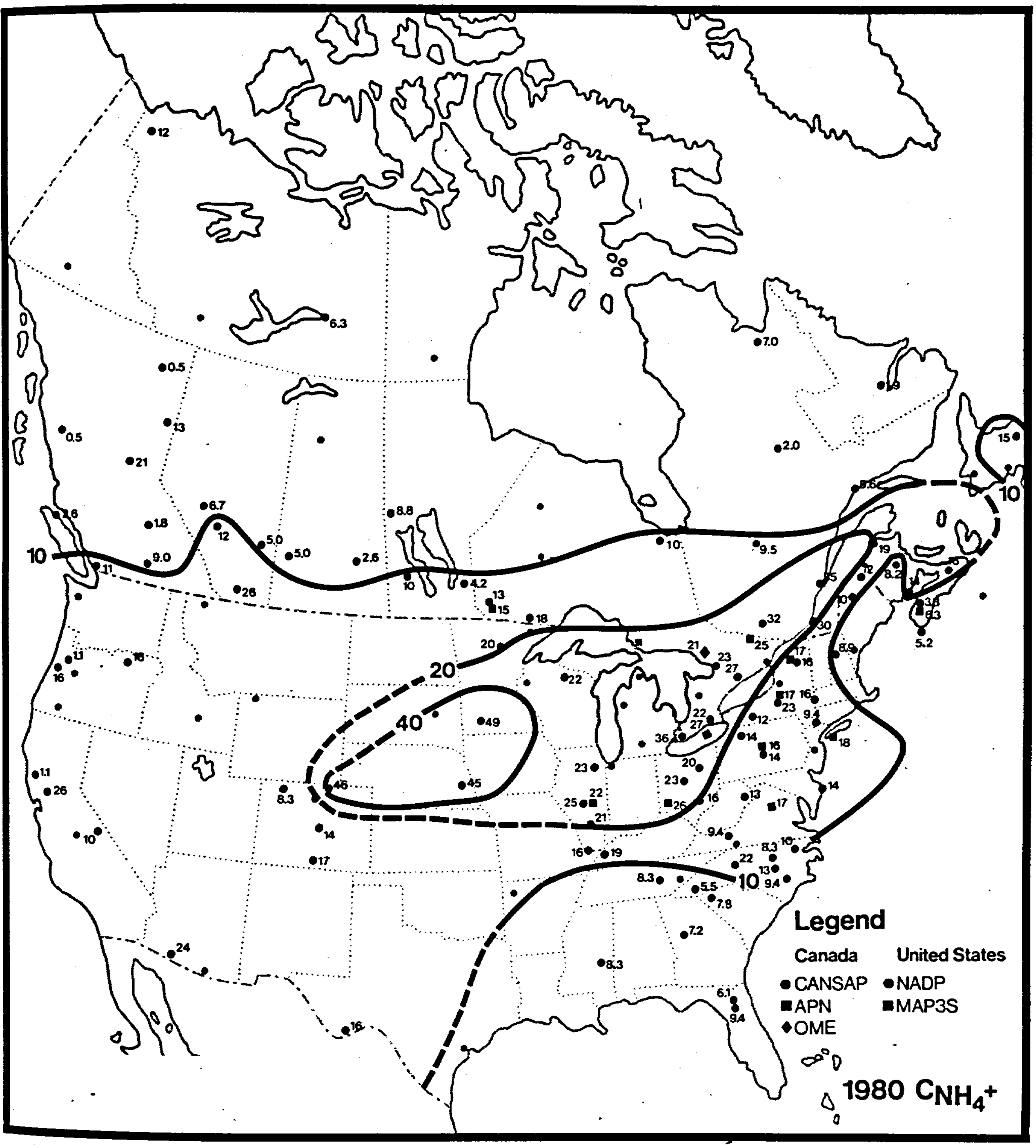


Figure 4-7 Spatial Variation of Precipitation-Amount-Weighted Mean Ammonium Ion Concentration (micromoles per liter) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

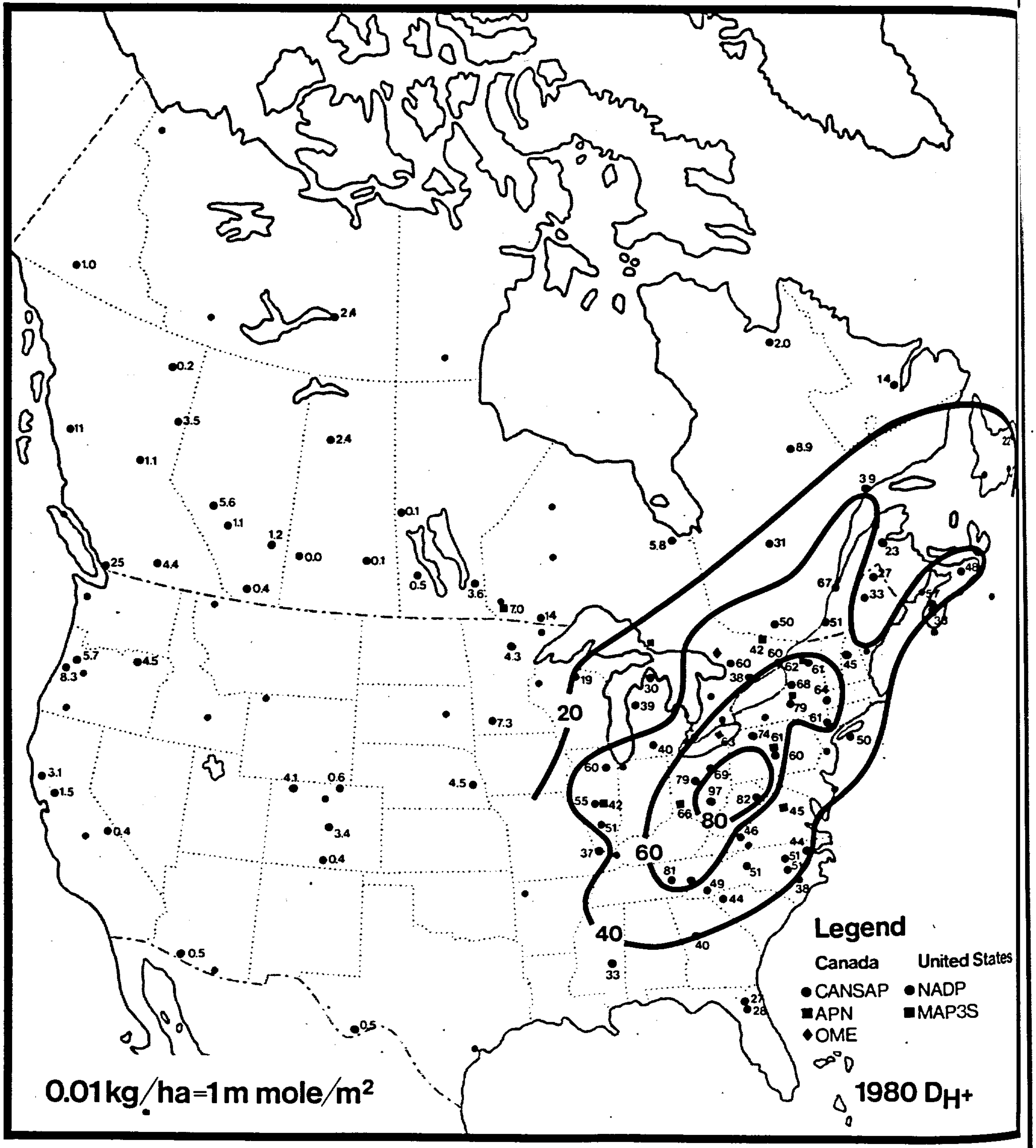


Figure 4-8 Spatial Variation of Precipitation-Amount-Weighted Mean Hydrogen Ion Deposition (millimoles per square meter per year) in North America in 1980 compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

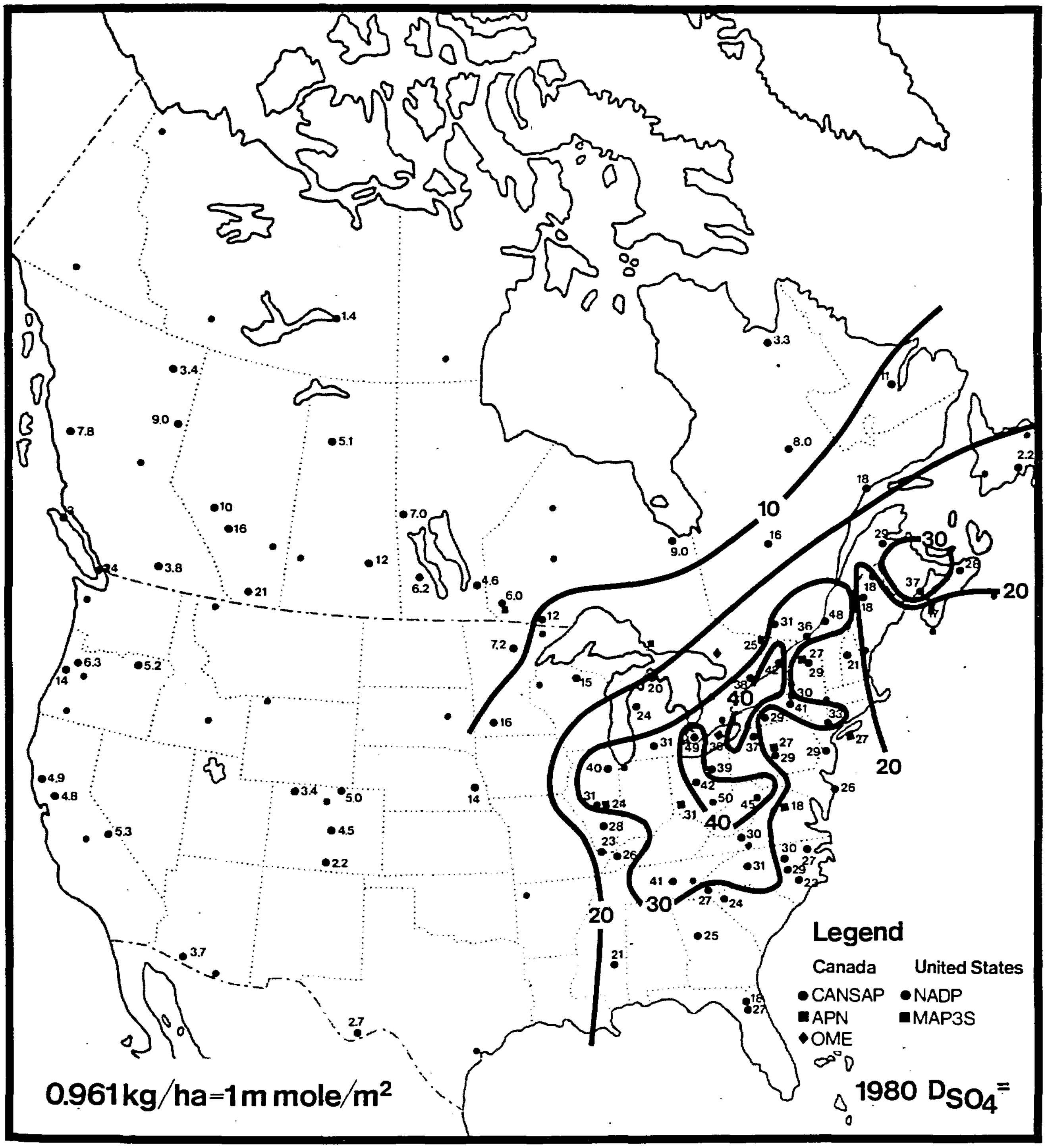


Figure 4-9 Spatial Variation of Precipitation-Amount-Weighted Mean Sulfate Ion Deposition (millimoles per square meter per year) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

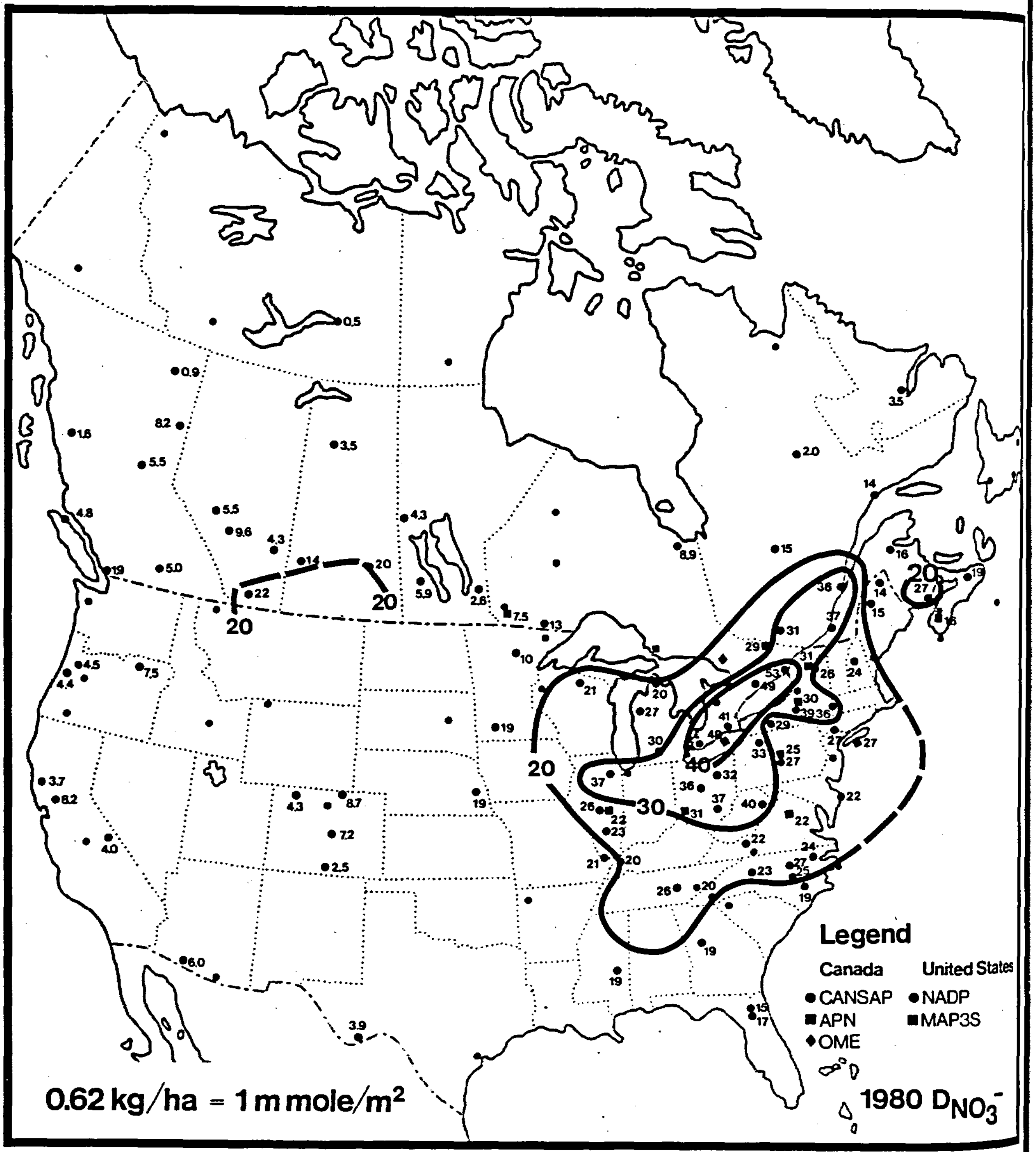


Figure 4-10 Spatial Variation of Precipitation-Amount-Weighted Mean Nitrate Ion Deposition (millimoles per square meter per year) in North America in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks

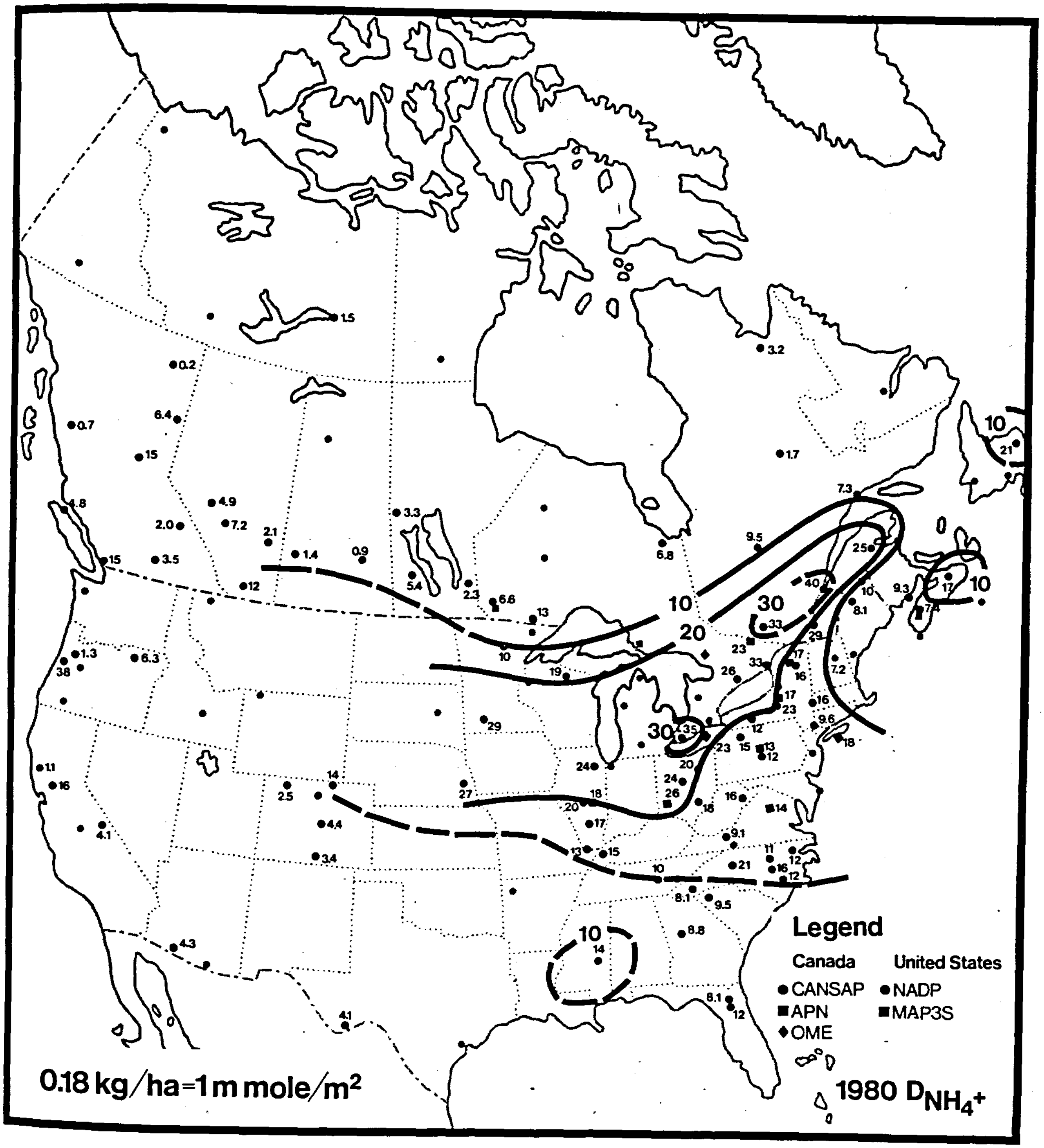
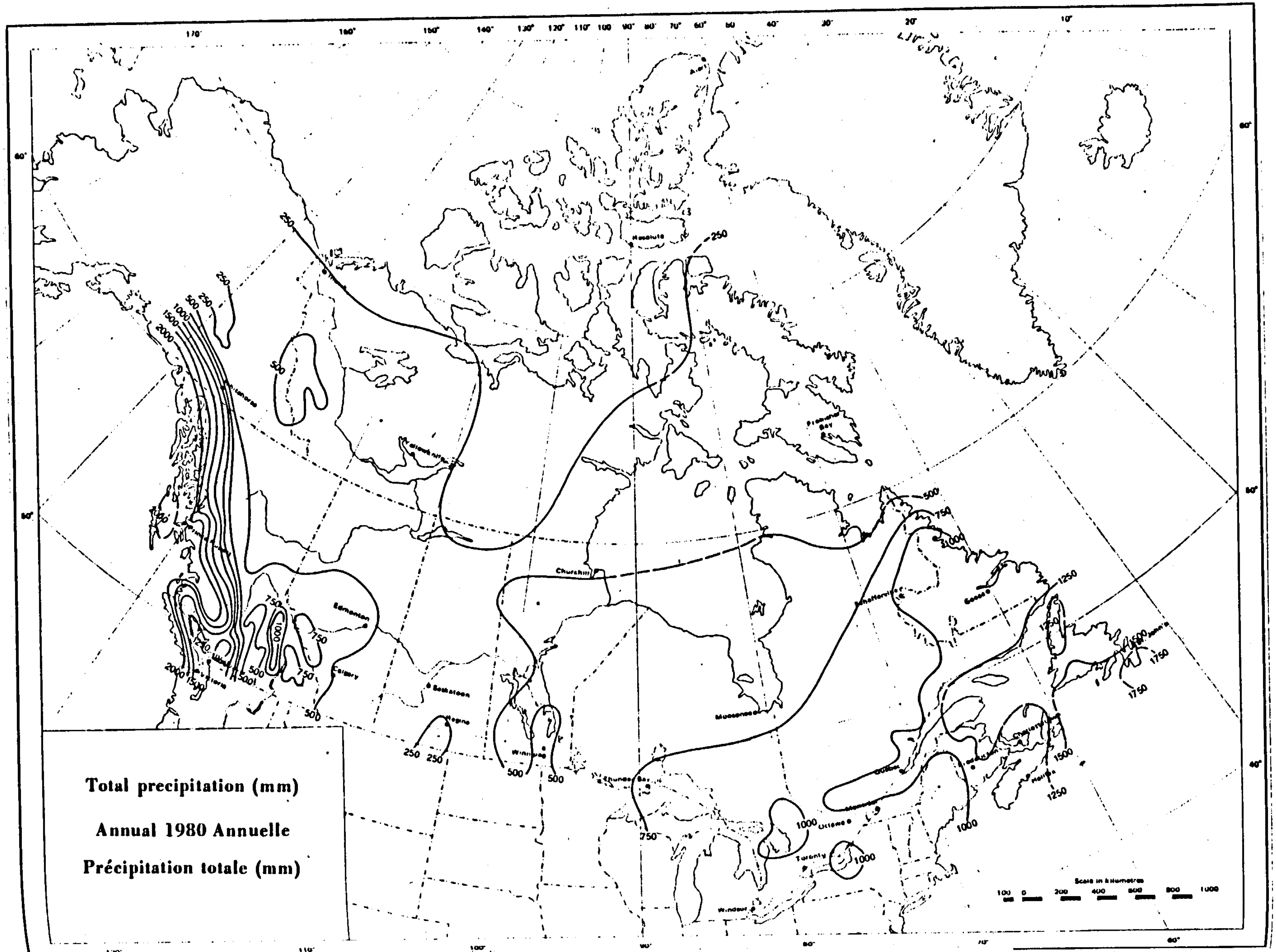


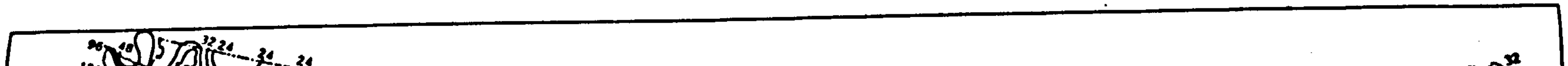
Figure 4-11 Spatial Variation of Precipitation-Amount-Weighted Mean Amonium Ion Deposition (millimoles per square meter per year) in North American in 1980 Compiled from Canadian (●CANSAP, ■APN) and American (●NADP, ■MAP3S) Networks


Total precipitation (mm)

Annual 1980 Annuelle

Précipitation totale (mm)

Figure 4-12a Spatial Variation of Canadian Annual



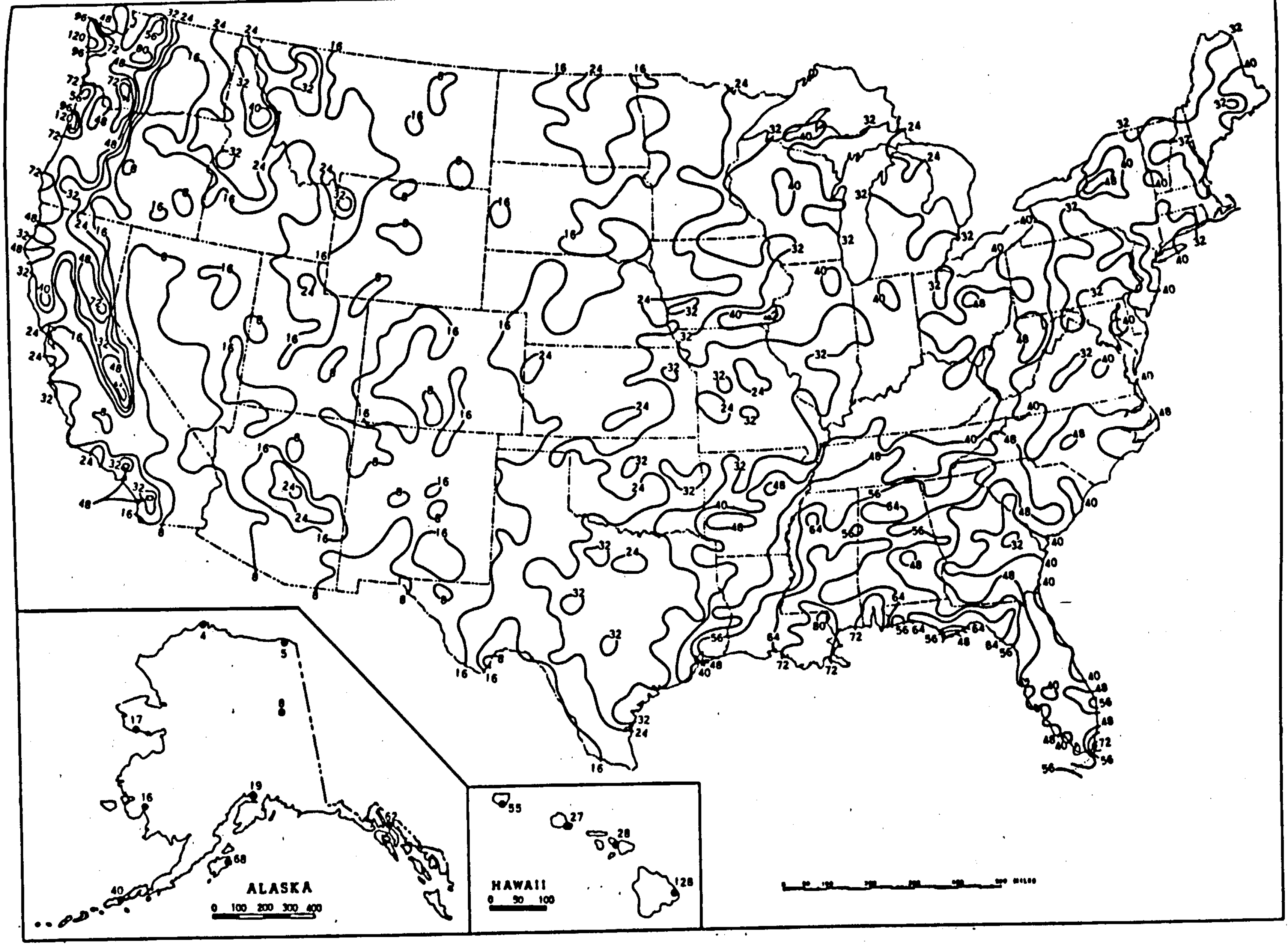


Figure 4-12b Spatial Variation of American Annual Precipitation Amount (inches) in 1980

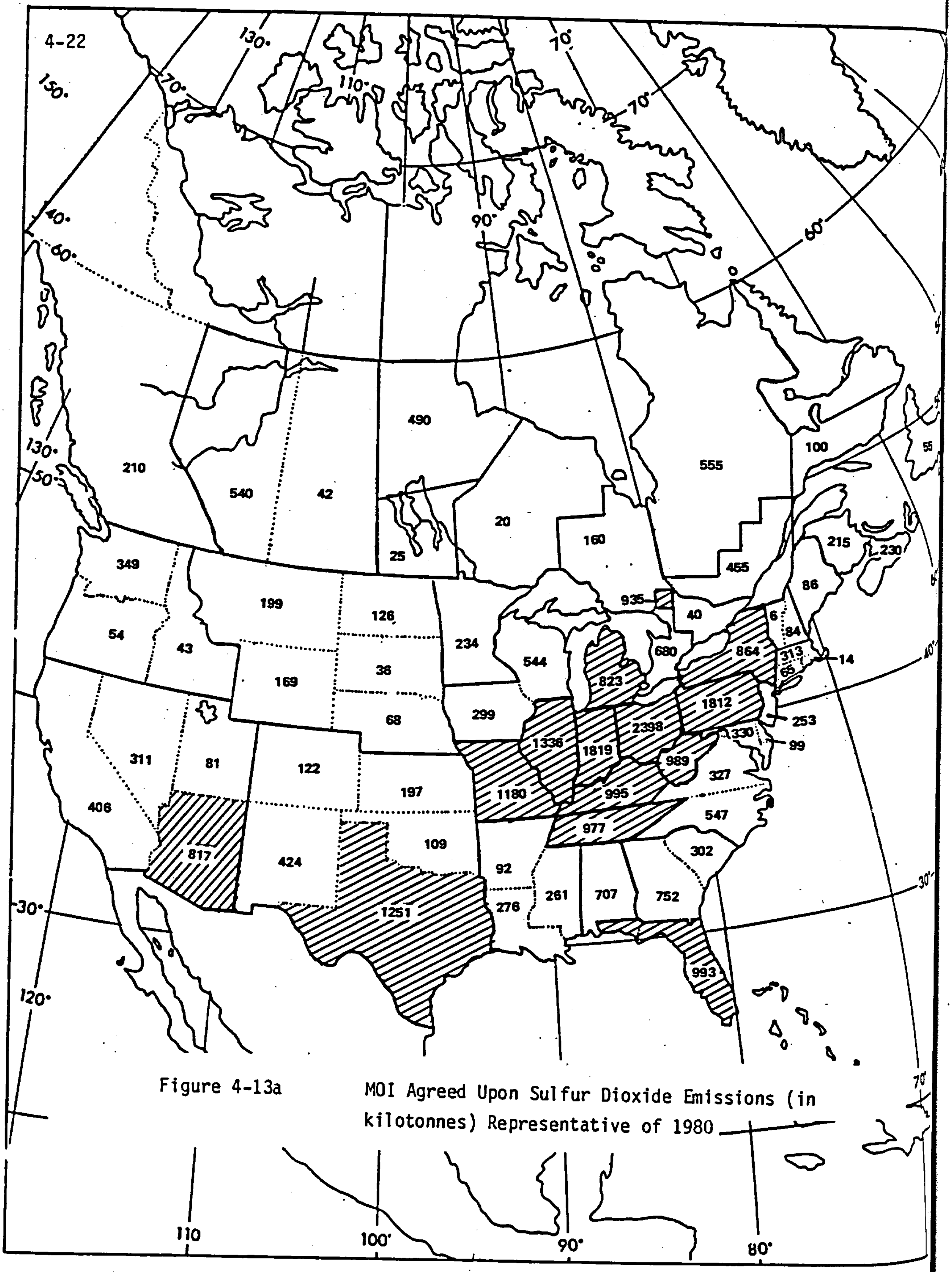


Figure 4-13a MOI Agreed Upon Sulfur Dioxide Emissions (in kilotonnes) Representative of 1980

measurement. When errors in sampling and analysis are taken into account, it is quite possible that the uncertainty in an annual mean deposition or concentration measurement is 20%. Depending on the location and density of stations such an uncertainty would translate into positional uncertainty ranging from fifty to several hundred kilometers. The representativeness of one year's distribution of that of another depends on meteorological variability and temporal changes in emissions. The influence of either factor has not been thoroughly investigated due to a lack of high quality, long term, data bases. In this regard, it sould be pointed out that the 1980 annual precipitation amounts (Figure 4-14) are significantly above normal only in the western U.S. and in parts of the Canadian Atlantic provinces, and near normal everywhere else. An annual precipitation amount measurement is generally accurate to within 10% (Peck, 1982).

4.1.3 Sulfate Ion Concentration

Background sulfate concentrations in precipitation (Figure 4-5) are 5 to 10 μmole l^{-1} in northern Canada and the Pacific coast of North America. In comparison, concentrations in eastern North America are greater than 20 μmole l^{-1} peaking at about 40 μmole l^{-1} in an area approximately 1000 by 250 km covering Ohio and southern Ontario. High concentrations in western Canada are associated with alkaline windblown dust, whereas those in eastern North America correspond to acidity (Figures 4-3 and 4-4). Sulfate concentrations reported for the United States have not been corrected for sea salt sulfate. Those in Canada have been corrected. Corrections are generally negligible (<5%) except at locations within 5 km of open ocean areas. At such sites the correction could be up to 30%.

4.1.4 Nitrate Ion Concentrations

Background nitrate concentrations (Figure 4-6) in North American precipitation are 2 to 4 μmole l^{-1}. They are low in comparison to those in areas around and downwind of major sources in eastern North America where concentrations range from 20 to 50 μmole l^{-1}. Concentrations are above 40 μmole l^{-1} in southern Ontario. The general coincidence between the maximum NO_3^- concentrations and the highest NO_x emissions in the eastern North America is also apparent (Figure 4-13b). On the heavily populated west coast of the

Figure 4-14 Spatial Variation of Precipitation Amount in 1980 as a Percent of the 30-year Normal

Figure 4-13b MOI Agreed Upon in Nitrogen Oxides Emissions (in kilotonnes) Representative of 1980

United States, concentrations are notably lower than immediately west of the Appalachians. Elevated nitrate concentrations in western Canada are associated with windblown dust as indicated by low levels of acidity, high levels of calcium (Barrie and Sirois, 1982). In contrast, elevated eastern levels of nitrate in precipitation parallel high levels of acidity (Figures 4-3 and 4-4).

4.1.5 Hydrogen Ion Concentration

Acidity can be represented in terms of the hydrogen ion concentration (μmole l^{-1}) or the negative of its logarithm pH. In the following discussion, the spatial variation of hydrogen ion concentration (Figure 4-4) is discussed but comments also apply to the pH distribution (Figure 4-3). Concentrations are highest in eastern North America, ranging from 60 to 80 μmole l^{-1} over a large area covering a roughly rectangular area 600 km wide running from western Illinois and Kentucky northeastward through New York and southern Ontario. A second region having concentrations greater than 60 μmole l^{-1} is located in central Ontario close to major emissions from smelting operations at Sudbury and Noranda. The detachment of this area from the larger area receiving H^+ above 60 μmole l^{-1} south of the Great Lakes may be a reflection of a sampling artifact rather than a real characteristic of the spatial distribution. This is because neutralization of 20 to 40% of actual precipitation acidity by contaminant alkaline substances is thought to be a real possibility at Peterborough in southern Ontario (Barrie and Sirois, 1982) and hence the 40 measured is probably a lower limit.

4.1.6 Ammonium Ion Concentrations

The spatial distribution of ammonium ion concentration (Figure 4-7) is different than those of the hydrogen, nitrate, and sulphate ions (Figures 4-4 to 6) whose patterns are roughly similar. Ammonium concentrations are a maximum (>40 μmole l^{-1}) in and downwind of the northern plains of the United States in which livestock feedlots are abundant. Intermediate levels of ammonium (20 to 40 μmole l^{-1}) occur in the Great Lakes and St. Lawrence lowlands region. Background levels in northern Canada range from 0.5 to 6 μmole l^{-1}.

Spatial distributions of the deposition of major ions, H^+, SO_4^{2-}, NO_3^-, and NH_4^+ (Figures 4-8 to 11) are on a regional scale similar in pattern to the distributions of concentration.

4.1.7 The Spatial Distribution of Acidity in the Snowpack of Acid-Sensitive Regions in Eastern Canada

In the winter of 1980-1981, a snowpack chemistry survey using helicopters was conducted in the Canadian Shield of eastern Canada (Barrie, 1982). A snow layer was sampled that had been deposited between early December and late January in freezing weather (i.e., no melts). The concentration of hydrogen ions in snowpack meltwater had a distinct spatial distribution (Figure 4-15). It was highest in eastern Ontario and southwestern Quebec (37 to 54 μmole l^{-1}) and lowest (approx. 12 μmole l^{-1}) in northeastern Quebec-Labrador. The gradient in acidity from southwest to northeast conforms to that observed in precipitation (Figures 4-3 and 4-4).

4.2 Temporal Variations

4.2.1 Precipitation

As an introduction to the topic of the temporal variability of wet deposition, it is useful to consider briefly the total experience of a pollutant particle as it moves between its source and its receptor, and to itemize those features of this experience that may contribute to the variability of precipitation chemistry with time. Some of the more important features in this regard are:

- fluctuations and trends in anthropogenic emissions,
- fluctuations and trends in natural emissions,
- dynamic variability within individual storm systems,
- variability associated with microphysical and chemical features (e.g., depletion, transformation) within individual storm systems,
- variability associated with trajectories of pollutant parcels between their sources and storm systems,
- variability associated with dry-deposition and chemical conversion processes prior to encounter with storm systems,
- variability of storm types and storm steering patterns, and
- natural variability associated with long-term climatic effects.

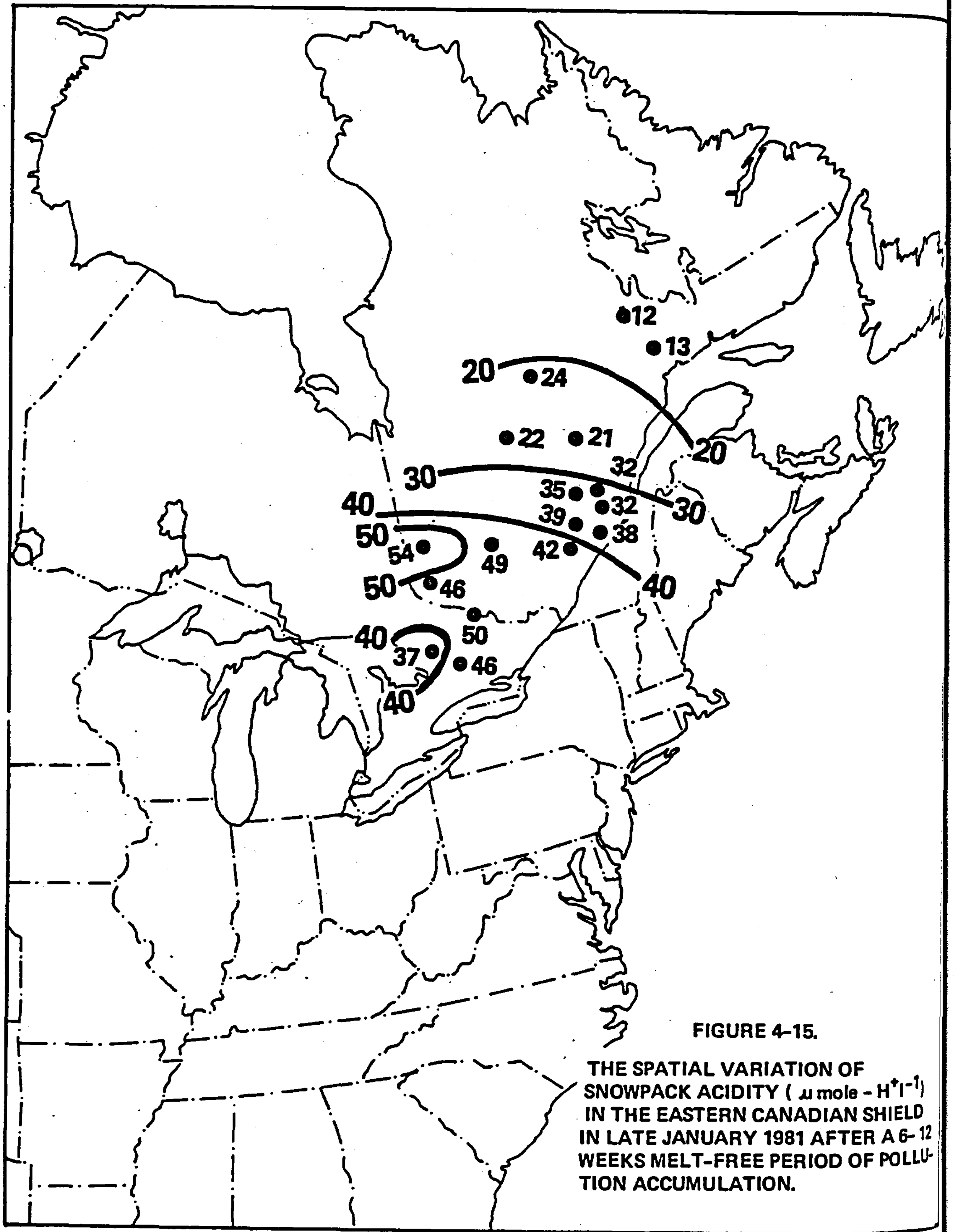


FIGURE 4-15.

THE SPATIAL VARIATION OF SNOWPACK ACIDITY (μ mole - $H^{+}l^{-1}$) IN THE EASTERN CANADIAN SHIELD IN LATE JANUARY 1981 AFTER A 6-12 WEEKS MELT-FREE PERIOD OF POLLUTION ACCUMULATION.

Several important points should be noted in conjunction with the above list. First, it should be emphasized that all of the above features pertain to "real" components of variability, and that this list does not contain components associated with measurement error. This is a particularly crucial point in the context of trend analysis, especially when one is addressing multi-network data. Typically, error components are significant in such analyses, and the resultant masking of the true trend behavior emerges as a major problem. Even within a consistent, single-network data-set, artifact variability can become a dominant feature, simply because of the variety of ways that one can select or reject data. This latter problem has led, on several occasions, to rather diverse conclusions being drawn by different investigators considering common data pools (cf. Miller, 1981).

A second important aspect of the above list pertains to the time scales of variability. Upon observing these items, it becomes obvious that the rapidity and magnitude of component fluctuations will depend to some extent on the expected lifetimes of the pollutants in question. The NO_x and SO_x compounds of primary interest in the present context have characteristic lifetimes of a few days. Corresponding ranges of wet-deposition time scales are shown, in a highly approximate manner, in Figure 4-16.

The rather gross nature of the above itemization should be noted. This is reflected in the broad ranges of characteristic time scales, and suggests that each of these categories could be decomposed to produce a finer and more highly resolved breakdown. The "storm types and steering patterns" category, for example, could be considered as a composite of short-term differences in storm tracks, superimposed on seasonal cycles and intermediate (5 to 10 year) deviations, with the possible addition of longer-term climatological trends.

A crucial feature of this itemized list is its suggestion that natural sources of variability may combine to overwhelm changes induced by man, effectively masking trends resulting from human activity. This observation should not be interpreted as suggesting that anthropogenic pollutants are not important contributors, or that associated trends are absent; it does suggest, however, that extreme care must be exercised in the

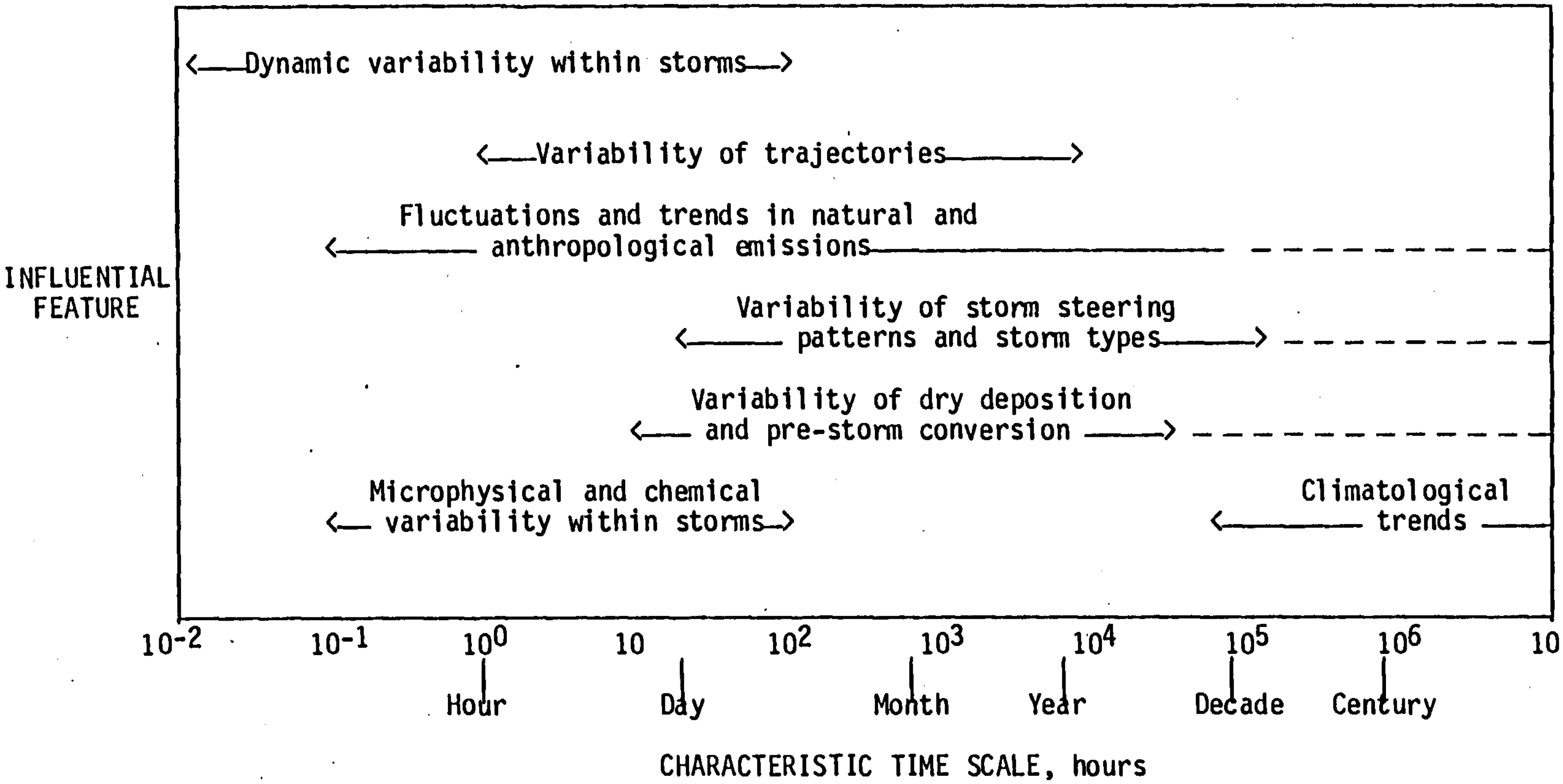


FIGURE 4-16 Schematic of Time Scales of Variability of Parameters Influencing the Chemical Composition of Precipitation

evaluation of precipitation chemistry data for the valid assessment of trend behavior. This problem was recognized at a comparatively early stage of the European Air Chemistry Network (Munn and Rodhe, 1971), and continues to be a major confounding aspect of trend analysis at the present time.

A final, highly significant aspect of the above itemization concerns the composite temporal behavior of wet deposition as a function of sample averaging time. This is a particularly important feature, both because it strongly reflects source-receptor relationships and because it directly impacts trend analysis. Moreover, this aspect is of high importance to precipitation-chemistry network design. Network collection procedures necessarily involve time-averaged samples, with the result that some information is always lost via the averaging process.

It would be expected that time-averaging would tend to suppress temporal variability, and that associated fluctuations should thus become uniformly smaller as averaging time is increased. Because of the multiple sources of variability and time scales noted in Figure 4-16, however, this is not usually the case. As one increases sampling time one does indeed tend to smooth over short-term fluctuations; however, this practice also usually introduces new sources of variability, having larger time scales. An example of the above point is provided by Figures 4-17 to 4-23, which provide a progression of precipitation-chemistry time-series data with increasing averaging time (Hales, 1982).

Figure 4-17, the most highly time-resolved figure of the series, shows the results of a sequential sampling of rain from a particular precipitation event measured at the Brookhaven National Laboratory (Raynor and Hayes, 1981). This is a relatively remote site located on upper Long Island, and while it reflects the presence of the east-coast megalopolis, it is considered to be a reasonably valid representation of regional precipitation chemistry. Key features to note from this figure are the pronounced variability of concentration during storm passage, and the obvious continua of the time-concentration curves.

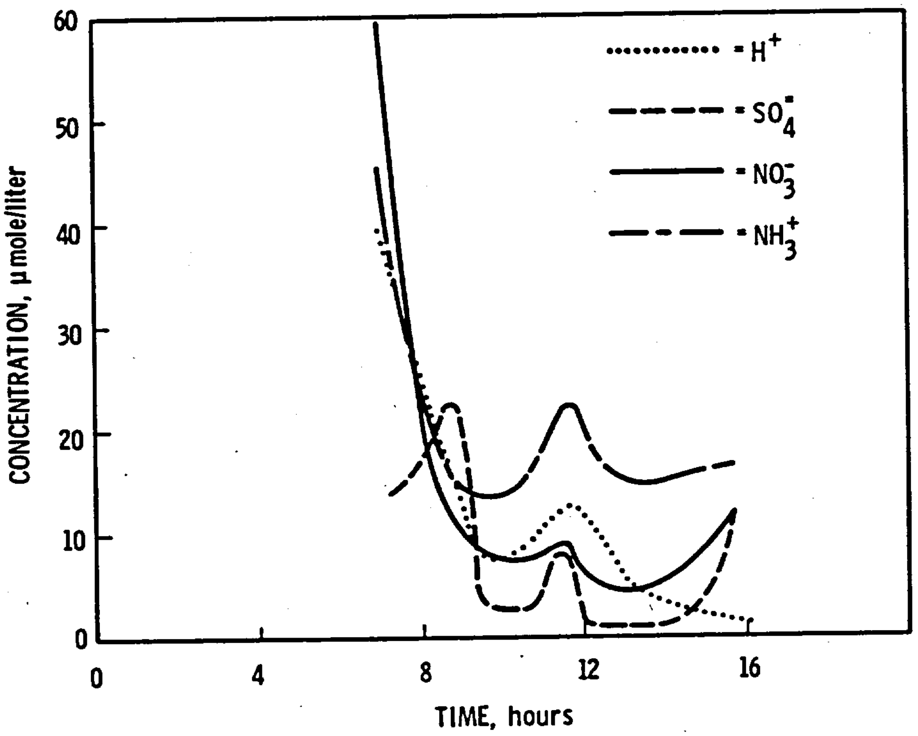


Figure 4-17 Concentrations of Selected Chemical Species in Rain During a Rain Event at the Brookhaven MAP3S Site

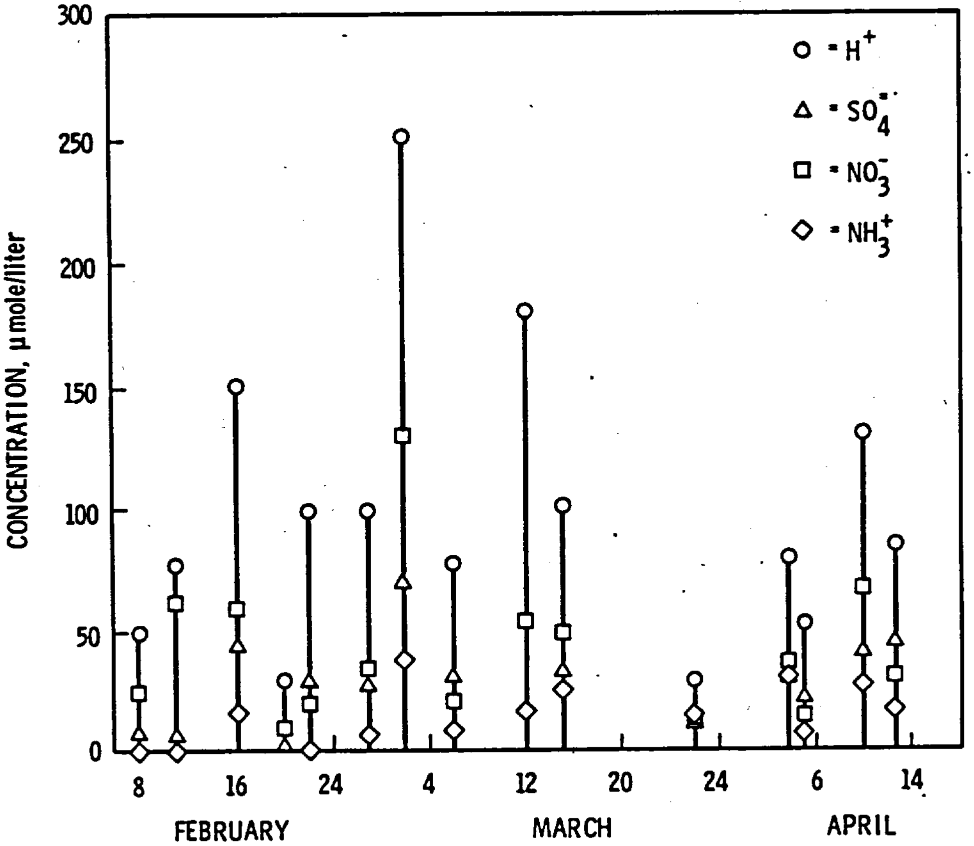


Figure 4-18 Concentrations of Selected Chemical Species in Precipitation for Several Precipitation Events Based on Event-Averaged Concentrations from the Penn State MAP3S Site

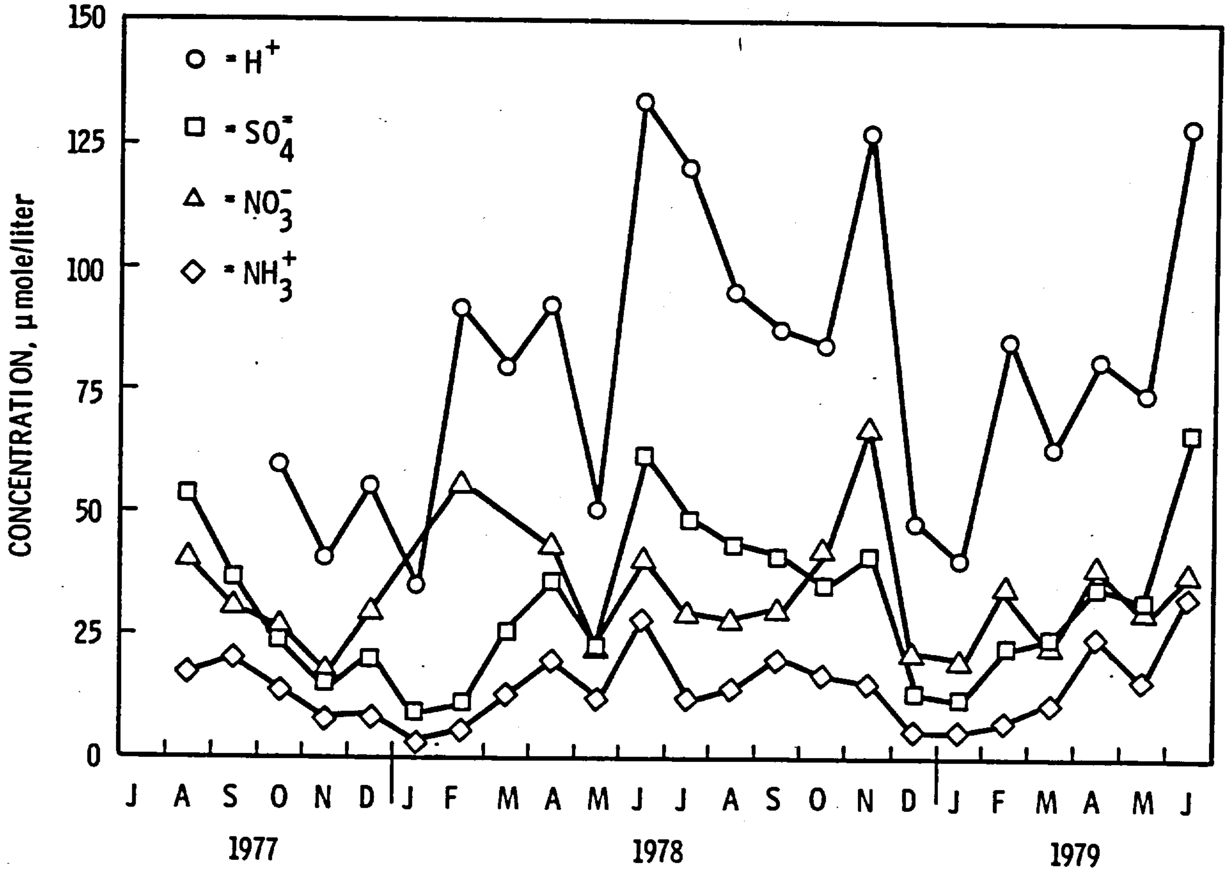


Figure 4-19 Concentrations of Selected Chemical Species in Precipitation Based on Monthly Averaged Concentrations from the Penn State MAP3S Site

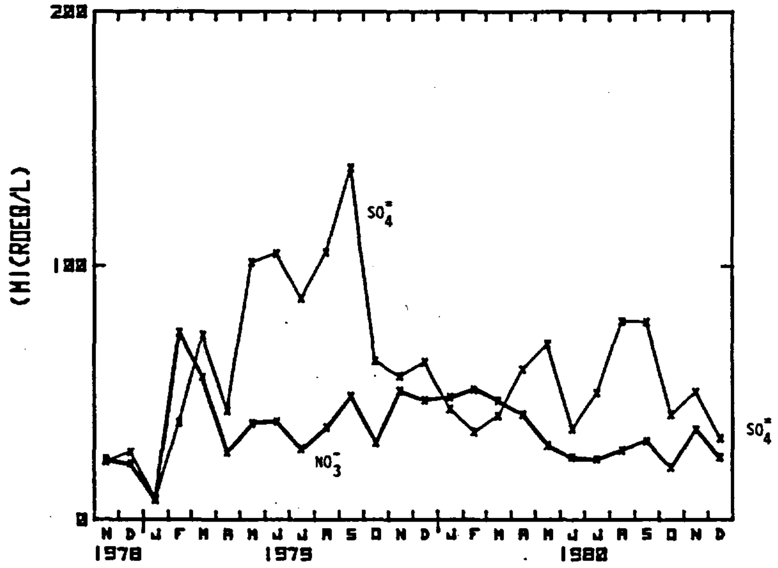


Figure 4-20a Concentrations of Sulfate and Nitrate Ions in Precipitation Based on Monthly Average Concentrations from the APN Chalk River Site

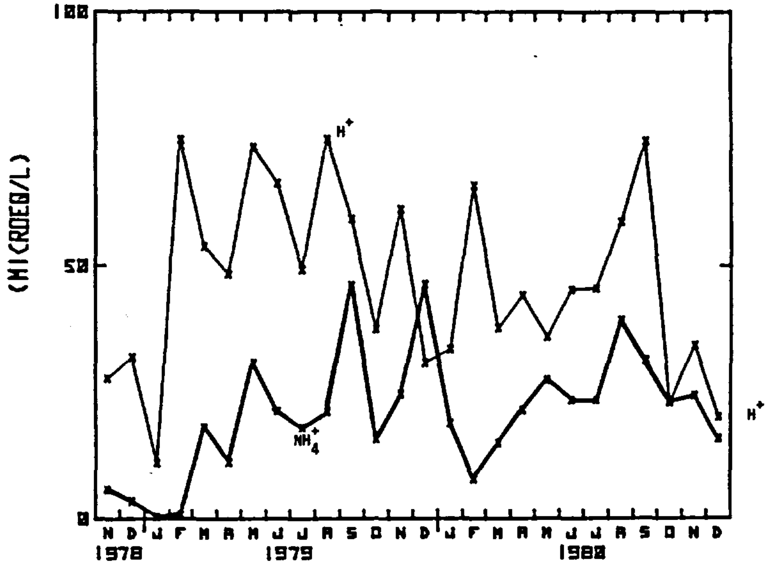


Figure 4-20b Concentrations of Hydrogen and Ammonium Ions in Precipitation Based on Monthly Average Concentrations from the APN Chalk River Site

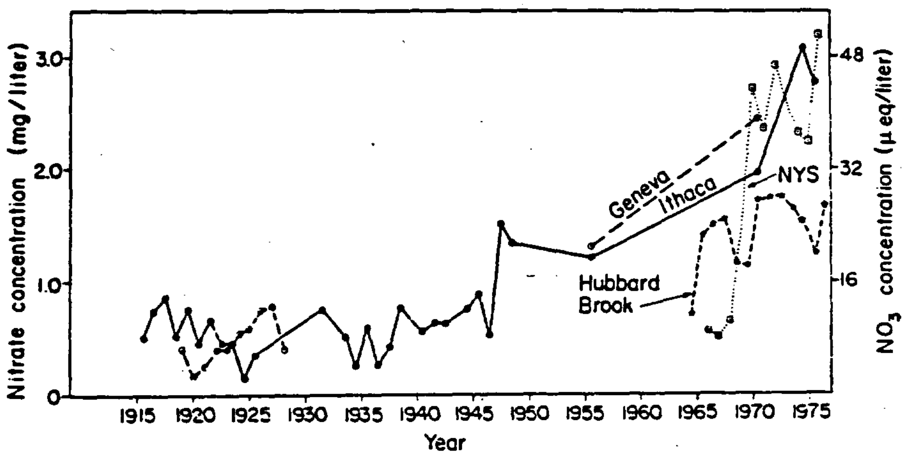


Figure 4-21 Annual Weighted Nitrate Concentrations in Precipitation at Various Locations in the Eastern United States. Data from Ithaca and Geneva, New New York from Likens (1972). Data from New York State (NYS) is the Average of 9 Stations Operated by the U.S. Geological Survey in New York and Pennsylvania

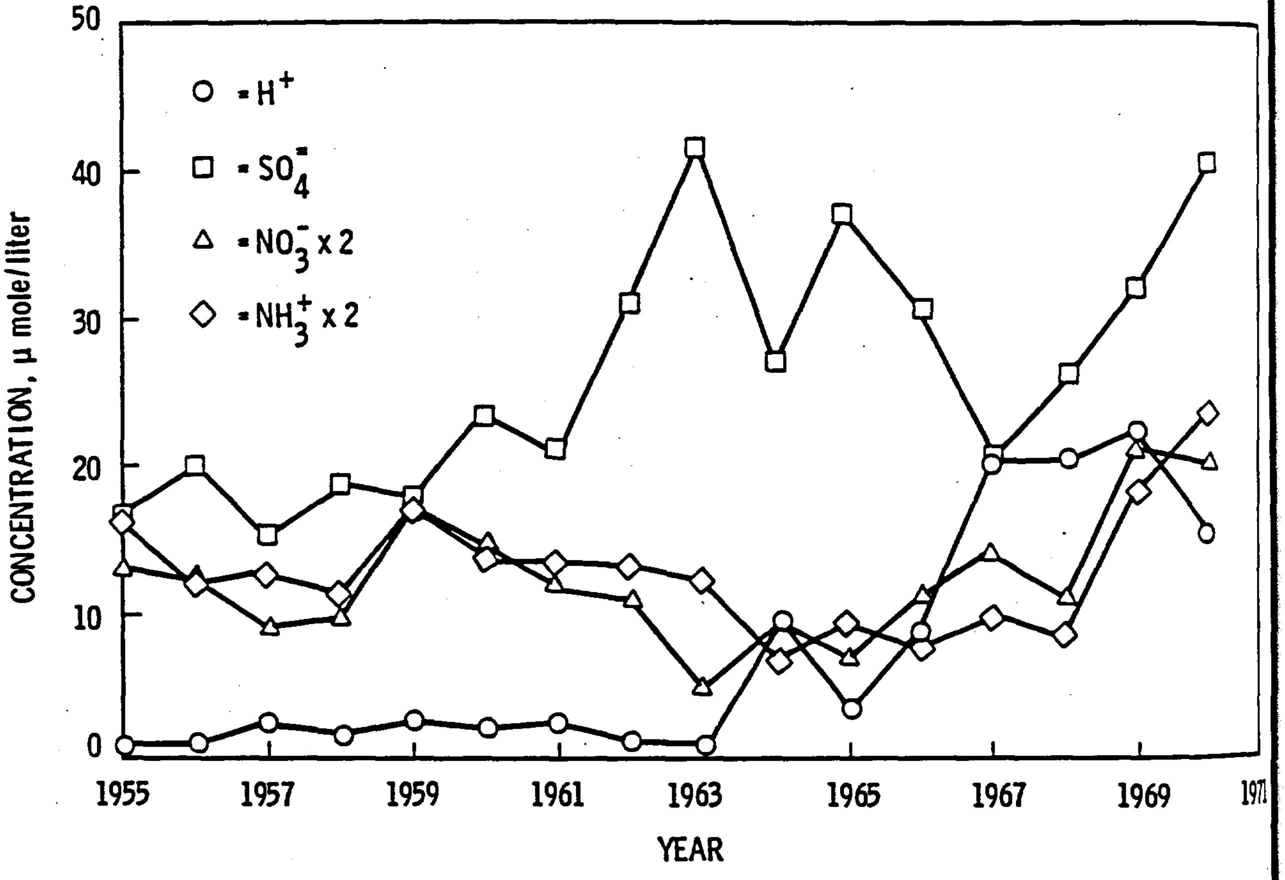


Figure 4-22 Concentrations of Selected Chemical Species in Precipitation Based on Annual Average Concentrations at the EACN Ayeplög Site in North Central Sweden (Source: Granat, 1978)

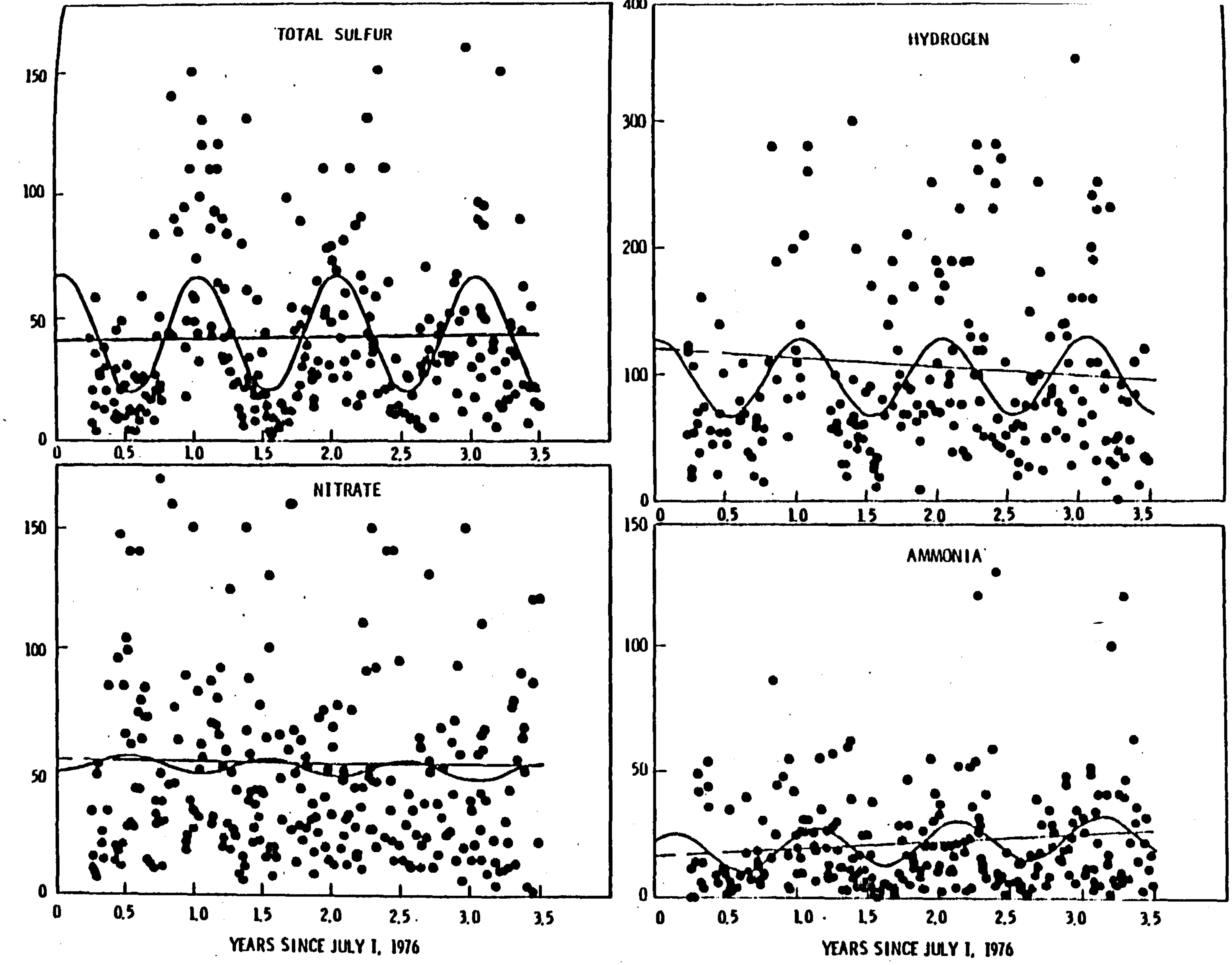


Figure 4-23 Event Concentration Measurements at the Penn State Site and Comparison of Curve Fits Using Equations (1) and (2).

Figure 4-18* is a typical result of averaging precipitation-borne pollutant concentrations over entire precipitation periods, and plotting several events in sequence. Here discrete plotting is necessary, owing to the episodic nature of precipitation. The fact that large fluctuations exist in spite of the longer averaging times should not be surprising, in view of the introduction of additional sources of variability from the sources itemized above.

Figure 4-19 pertains to an expanded data set that originated from this sampling site, but now has been averaged over one-month periods.** Similar data obtained at a Canadian APN site are shown in Figures 4-20a and 4-20b. At this point the averaging process appears to have smoothed the concentration excursions somewhat, and suggests a seasonal cycling of species such as SO_4^{2-}, H^+ and NH_4^+. However, in view of pronounced excursions typically observed from longer data sets, this apparent smoothing should be taken with some caution. This latter point can be illustrated by longer-term data sets, as shown by Figures 4-21 and 4-22, composed from data taken from a European Air Chemistry Network site over a 15-year period and data from various locations in the eastern U.S. over a 60-year period, respectively. This plot clearly indicates that caution must be used when interpreting limited data sets such as those shown in Figures 4-19 to 4-20, especially for trend analysis. A comparison of Figures 4-19 to 4-20 with North American and

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*Data from MAP3S sampling site at State Colege, Pennsylvania [MAP3S (1980)].

**Computed as $$\frac{\sum_{1}^{N} Ce\ Re}{\sum_{1}^{N} Re},$$

where Ce and Re are the concentration and rainfall amounts associated with a particular event, and N is the number of events occurring during a particular month.

European emission trends suggests that much of the observed variability is associated with natural phenomena, rather than human-induced effects.

Because of the seasonal cycling that is apparent for some ions, namely SO_4^{2-} in Figure 4-19 and 4-20, it is of some interest to examine wintertime-summertime differences in more detail. Figure 4-23 is a replot of the Penn State data set, representing the composite of event samples obtained up until January 1, 1980 (MAP3S/RAINE, 1982). The straight and cyclical lines on the four curves represent least-squares fits to the data, respectively, by the functions

$$C' = A + Bt \qquad (1)$$

and

$$C'' = \alpha + \beta t + \gamma \sin (2\Theta t + \phi) \qquad (2)$$

where A, B, α, β, γ, and ϕ are fitted parameters and t denotes time in years.

As can be noted from the curves, sulfate exhibits a distinct seasonal dependence, which is followed closely by hydrogen ion. The periodicity is highly significant in a statistical sense, despite the wide variability in the data. Moreover, the same periodicity is observed throughout the MAP3S network, although the amplitudes of the fitted curves vary from one station to the next. Ammonium ion also shows a summertime maximum. Nitrate ion, however, does not show significant periodicity. This undoubtedly reflects a fundamental difference between the behavior of SO_x and NO_x, which is probably related to the physiochemical mechanisms of the precipitation scavenging process. It can be expected that further analysis of these emerging precipitation-chemistry data bases will contribute to a much more detailed future understanding of these mechanisms.

As previously noted the multiple sources of temporal variability have a severe confounding effect on any attempt to resolve simply, on the basis of network measurements, the impact of man's activity on wet deposition. The debate of this issue is particularly intense in North America at the present time. In 1974, Cogbill and Likens published an analysis of selected historical North American data sets, in which they concluded that the northeastern U.S. has a severe "acid precipitation" problem, which is extending outward to the south and the west. More recently, Likens and Butler (1981) have reviewed the data and confirmed Cogbill and Likens' original conclusion. Figure 4-24, adapted directly from Cogbill and Likens' paper, illustrates the basis for this contention. Comparison of the 1975-76 map of H^+ ion concentration with the one for 1980 (Figure 4-4) shows little change in the area subjected to acidic precipitation in eastern North America.

Numerous additional investigators have since attempted similar interpretative efforts, with a variety of results. In a recent overview analysis, Hansen, Hidy, and Stensland (1981) conclude that the combined uncertainties caused by naturally induced temporal variability and measurement error are "sufficient to obscure any trends related to the emissions of acid precursors that may have taken place over the eastern United States." As a consequence of this continuing debate, one can conclude that it is presently unsafe to utilize existing network data to draw any reliable conclusions with regard to acidity trends in eastern North America. This situation undoubtedly will improve somewhat as more reliable data bases emerge; there is a strong suggestion, however, that more direct approaches such as spatial-pattern analysis and source-receptor interpretation methods will emerge as more useful tools for evaluating man's contribution to the atmospheric deposition problem.

4.2.2 Ambient Concentrations

In 1979, routine monitoring of the daily average concentration of sulfur dioxide, sulfates, and precipitation chemistry was carried out at rural, regionally representative sites (Figure 4-25) in eastern Canada (Barrie et al., 1980). The network is the Canadian Air and Precipitation Monitoring Network (APN). Results have recently been reported by Barrie (1982). This network and one recently initiated by the Ontario Ministry of Environment are the only ones of their kind in North America.

Monthly arithmetic mean concentrations of sulfur dioxide and particulate sulfate are given in Figure 4-26. On an annual basis, the lowest

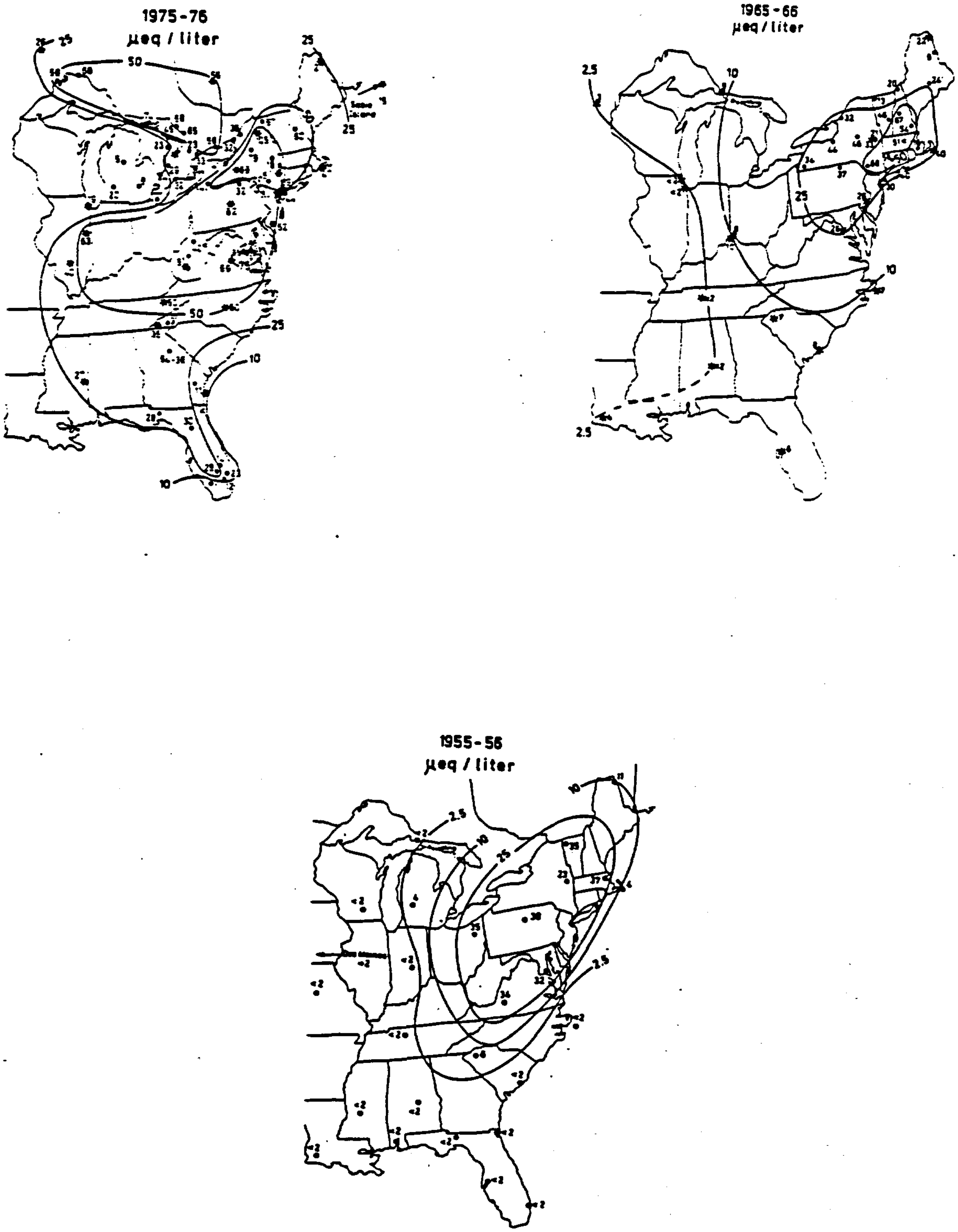

Figure 4-24 Historical Record of the Spatial Distribution of Hydrogen Ion Concentration in Precipitation According to Likens and Butler (1981)

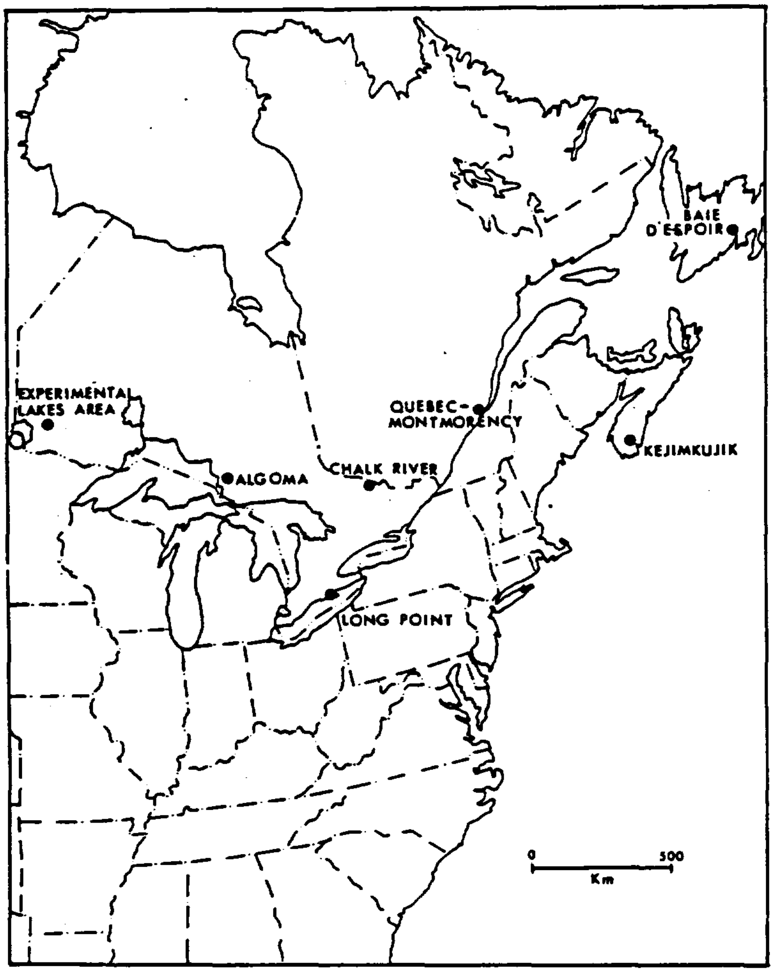

Figure 4-25 Sites on the Canadian Air and Precipitation Monitoring Network (APN) at which Daily Air and Precipitation Samples are Collected

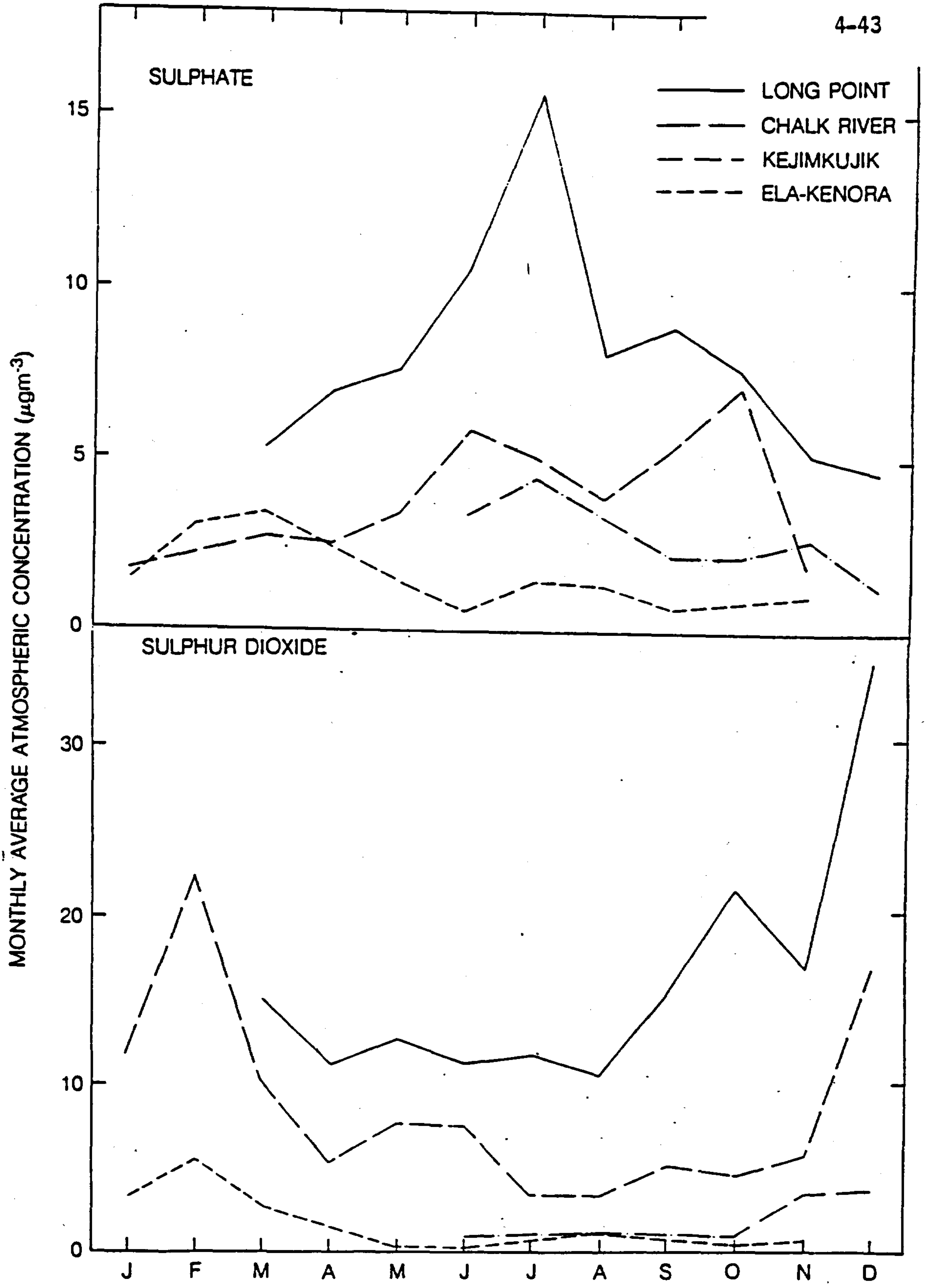

Figure 4-26 Temporal Variations of the Monthly Average Concentration of Atmospheric Sulfate and Sulfur Dioxide at APN Sites During 1979

concentrations occurred at the Experimental Lakes Area (ELA)-Kenora in northwestern Ontario (SO_2 = 1.5 $\mu g/m^3$; SO_4^{2-} = 1.6 $\mu g\ m^{-3}$). In the mid-latitudinal westerlies, ELA is upwind of major North American sulfur sources. Long Point, on the other hand, is located in an industrial section of Ontario and is surrounded by major emissions regions in Ohio, Pennsylvania, Michigan, and New York. At all sites in eastern Canada, there are seasonal variations of atmospheric sulfur dioxide levels. The concentrations are highest in the winter and lowest in the summer. On a percentage basis, the amount of variation about the annual mean concentration depends on the location. The variation is lowest within and close to source regions and highest at locations remote from source regions. The percent standard deviation about the annual average concentration is 43 at Long Point on Lake Erie, 63 at Chalk River (500 km away), 75 at Kejimkujk, and 108 at ELA, the furthest location from the major source area of emission.

Particulate sulfate concentrations are highest in summer at all APN sites except ELA-Kenora. A winter maximum in both sulfur species at Kenora owes its existence largely to meteorological factors. Higher frequency transport westward from eastern North America in winter coincides with a large winter peak of background sulfur concentrations in arctic air masses (Barrie et al., 1981) that prevail at this mid-continental location during winter.

At APN sites located in the continental pollution plume, the sulfate seasonal cycle is 180° out-of-phase with the sulfur dioxide cycle. Indications are that the summer sulfate maximum owes its existence to a summer maximum in the conversion rate of sulfur dioxide to sulfate. One manifestation of higher SO_2 to sulfate conversion in summer is that, at all stations, the ratio of SO_2 to total airborne sulfur ($SO_2 + SO_4^{2-}$) tends to be lowest in summer (e.g., see Figure 4-27 for Long Point).

On a daily basis, the concentrations of sulfur oxides are highly episodic regardless of location in eastern Canada (Figure 4-27). Polluted and non-polluted periods of 3 to 6 day duration alternate regularly. The dry deposition rates of these acidic substances, which is thought to be roughly proportional to their atmospheric concentrations, is equally episodic. A

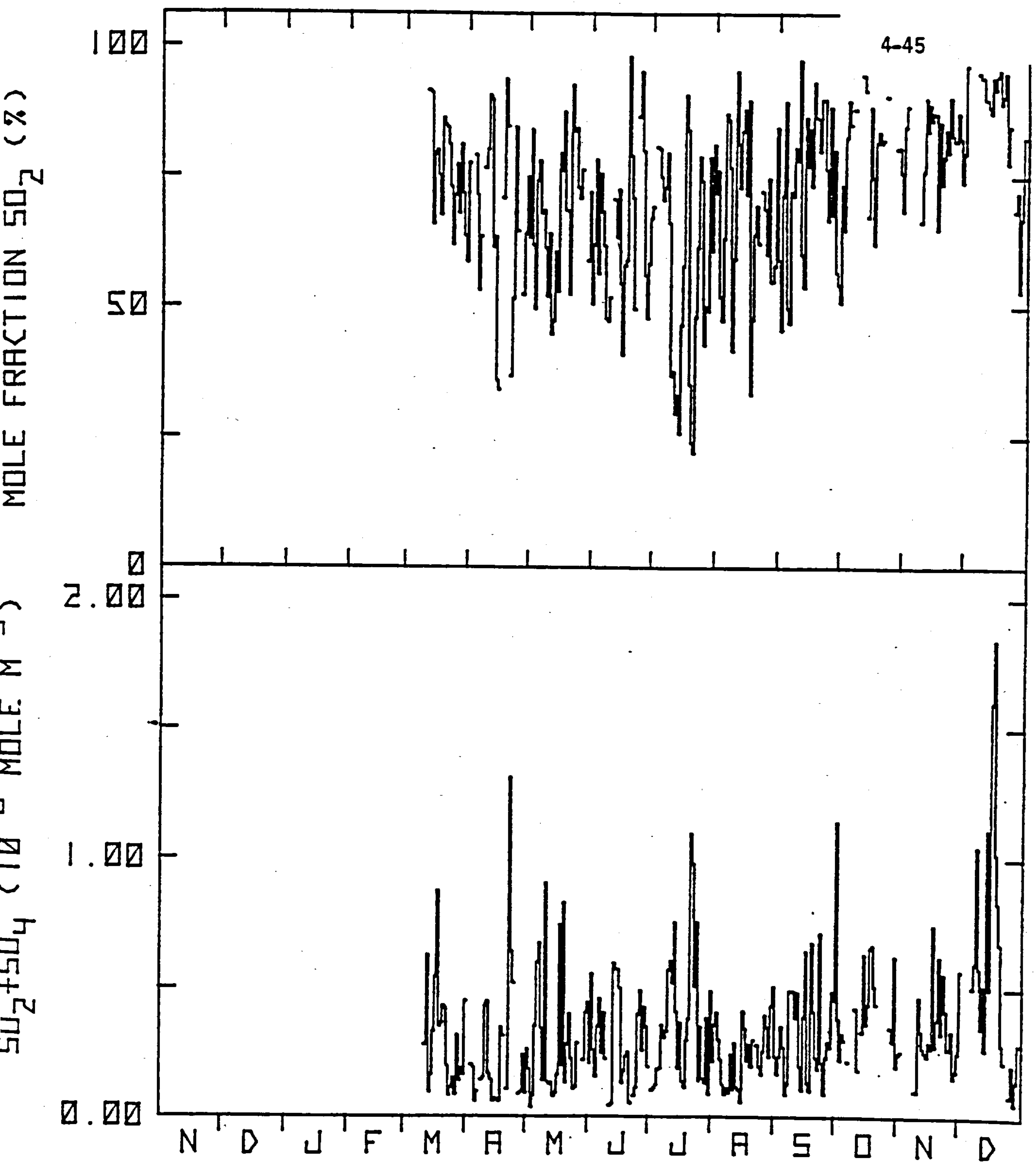

Figure 4-27 Top: The Fraction of Total Airborne Sulfur Existing as Sulfur Dioxide at Long Point on the North Shore of Lake Erie on a Daily Basis (1978-1979). Bottom: The Concentration of Total Airborne Sulfur at Long Point on a Daily Basis. (Note the prevalence of episodes of elevated sulfur levels of 3-6 days duration)

comparison of monthly wet and dry deposition rates of sulfur compounds is made later in this chapter.

4.2.2.1 The Arctic

Arctic Air

Arctic air penetrates the modeling area (i.e., North America east of the Rockies) along its northern boundary most often during the period from November to April. In mid-winter, continental arctic air can penetrate as far south as Florida on rare occasions, but, more commonly, as far south as the central eastern states.

The chemical content of continental arctic air has recently been under intense study in many northern hemisphere countries (c.f., Atmospheric Environment Arctic Issue, 1981) in connection with a deterioration of visibility referred to as "arctic haze".

It has been found that anthropogenic particulates consisting mainly of sulfates, soot and organic carbon emitted at mid-latitudes are the cause of the haze, which is most pronounced in the winter half of the year. The atmospheric concentration of these particulates as indicated by sulfate shows an annual cycle reaching a minimum value (close to zero) between June and September and a maximum value of 2 $\mu g\ m^3$ between January and March. This is illustrated in Figure 4-28 from measurements made at Mould Bay in the Canadian arctic by Barrie et al. (1981). In early 1980, weekly average sulfate concentrations ranged between 1.2 and 3.5 $\mu g\ m^{-3}$. Similar observations have been made at P. G. Barrow, Alaska (Rahn, 1981).

Particulate pollution in the arctic air mass is distributed over large areas rather homogeneously. Little difference is observed between sulfate concentrations at two sites in the Canadian Arctic, Mould Bay and Igloolik, about 600 km apart (Figure 4-28). The annual cycle of the pollutant concentration is consistent from year to year. Elevated wintertime concentrations of particulate sulfur in the air mass owe their existence to the

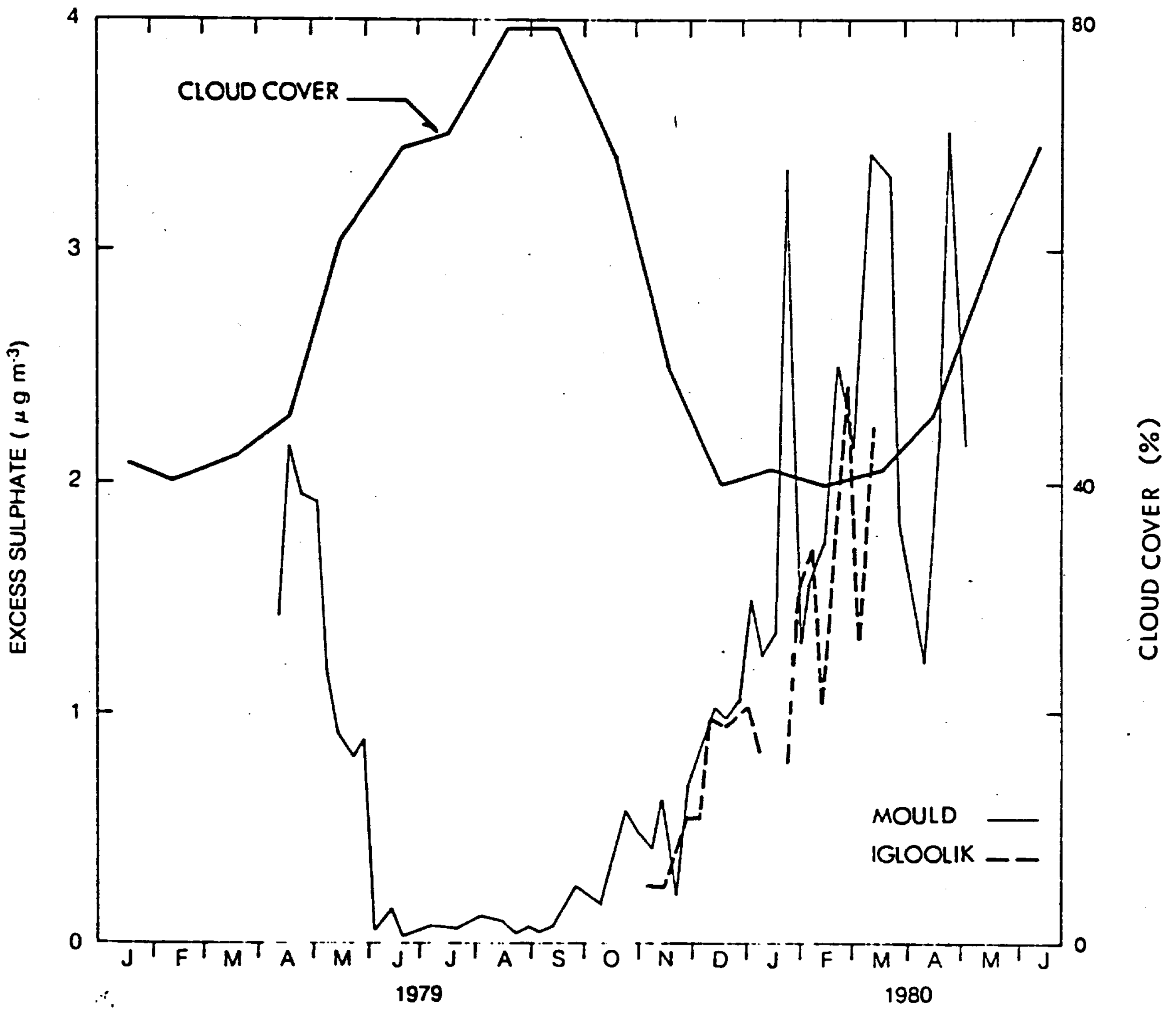

Figure 4-28 Weekly Average Excess Sulfate (non-sea salt) Concentrations in the Atmosphere at Mould Bay and Igloolek as Well as of Monthly Average Cloud Cover in the Arctic (Source: Huschke, 1969)

relative inefficiency of atmospheric pollutant scavenging processes during winter. In arctic air masses, aerosols have a lifetime of several weeks, compared to several days to a week for similar aerosols at mid-latitudes. The atmospheric residence time of SO_2 and sulfate are commonly believed to be several days and several weeks, respectively, which in the light of these recent findings can be misleading. Furthermore, the longer residence times in certain regions and seasons help to explain why hemispheric background sulfate, though less important than local or "long range transport" effects, can still be significant in producing acidic precipitation in remote areas, especially where the atmospheric concentrations of alkaline particles are small. The predominant sources of particulates in the North American Arctic are, in order of decreasing importance, Siberia, Europe, and eastern North America.

There is evidence suggesting that the background concentrations of sulfur oxides in a continental arctic air-mass that penetrates the North America modeling area undergoes an annual cycle similar to that observed in air nearer the pole. Weekly average and weekly minimum concentrations of sulfur dioxide and particulate sulfate at ELA-Kenora are shown in Figure 4-29 for the period November 1978 to December 1979. The continental arctic air-mass is usually present at this sampling location between November and April. SO_2 and sulfate background concentrations (as indicated by the weekly minimum concentration) are a maximum between January and March. They average 1 and 0.8 $\mu g\ m^{-3}$, respectively. In summer, they are below the detection limit (0.2 $\mu g\ m^{-3}\ SO_4^{2-}$; 0.5 $\mu g\ m^{-3}\ SO_2$).

The seasonal variation of precipitation pH in the polar air-mass, as estimated by Barrie <u>et al</u>. (1981) from observed particulate acidity, is shown in Figure 4-30. The pH is expected to vary annually from a CO_2 controlled value of ∿5.6 in summer to an anthropogenic sulfuric acid controlled value of ∿pH 5.0 in late winter/early spring. This cycle is confirmed by measurements of the pH of snow in a Ellesmere Island ice cap by Koerner and Fisher (1982) shown in Figure 4-31.

There is some evidence that the background pH of snow in northwestern Canada is depressed during winter. From a snowpack chemistry survey

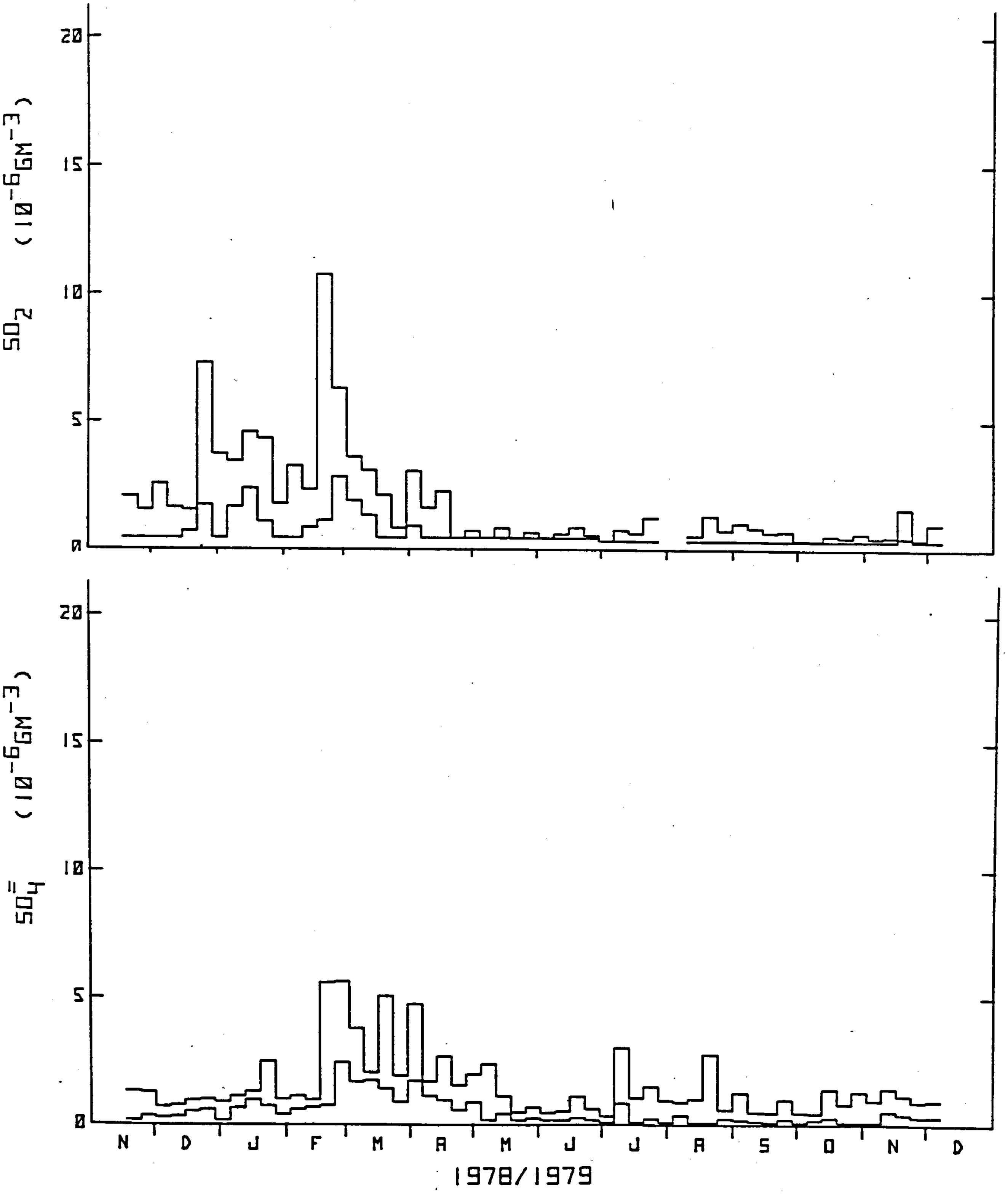

Figure 4-29 Weekly Average and Minimum SO_2 and SO_4^{2-} Concentrations at the Experimental Lakes Site (see Figure 4-26) between November 1978 and December 1979

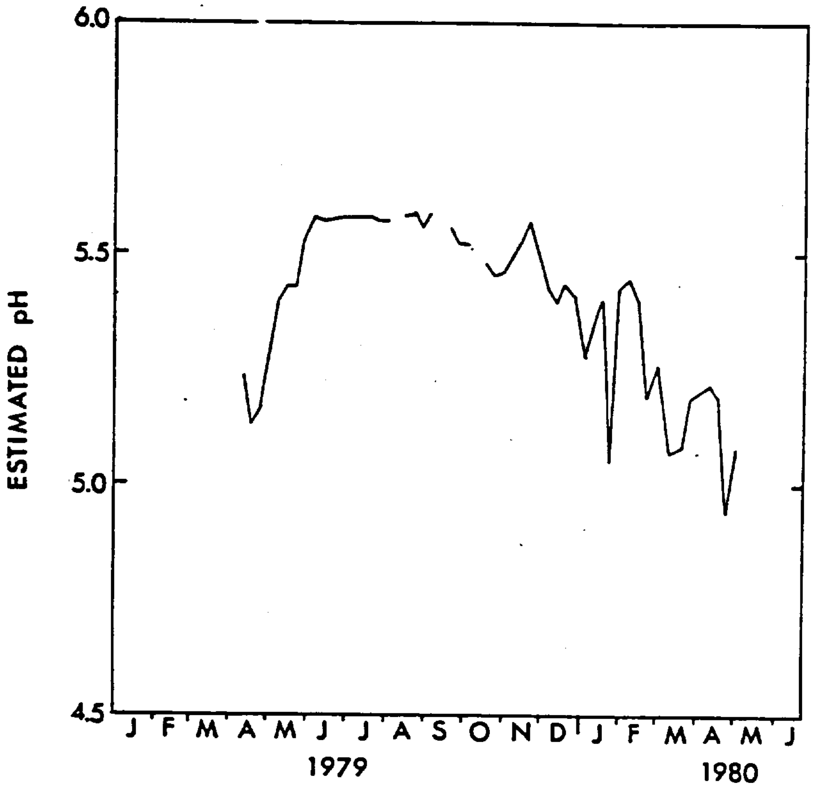

Figure 4-30 Acidity of Fresh Snowfall at Mould Bay Estimated from Measured Sulfate Concentrations, Hydrogen Ion to Sulfate Ratios in Aerosols and a Scavenging Ratio of 2 x 10^5 (by volume)

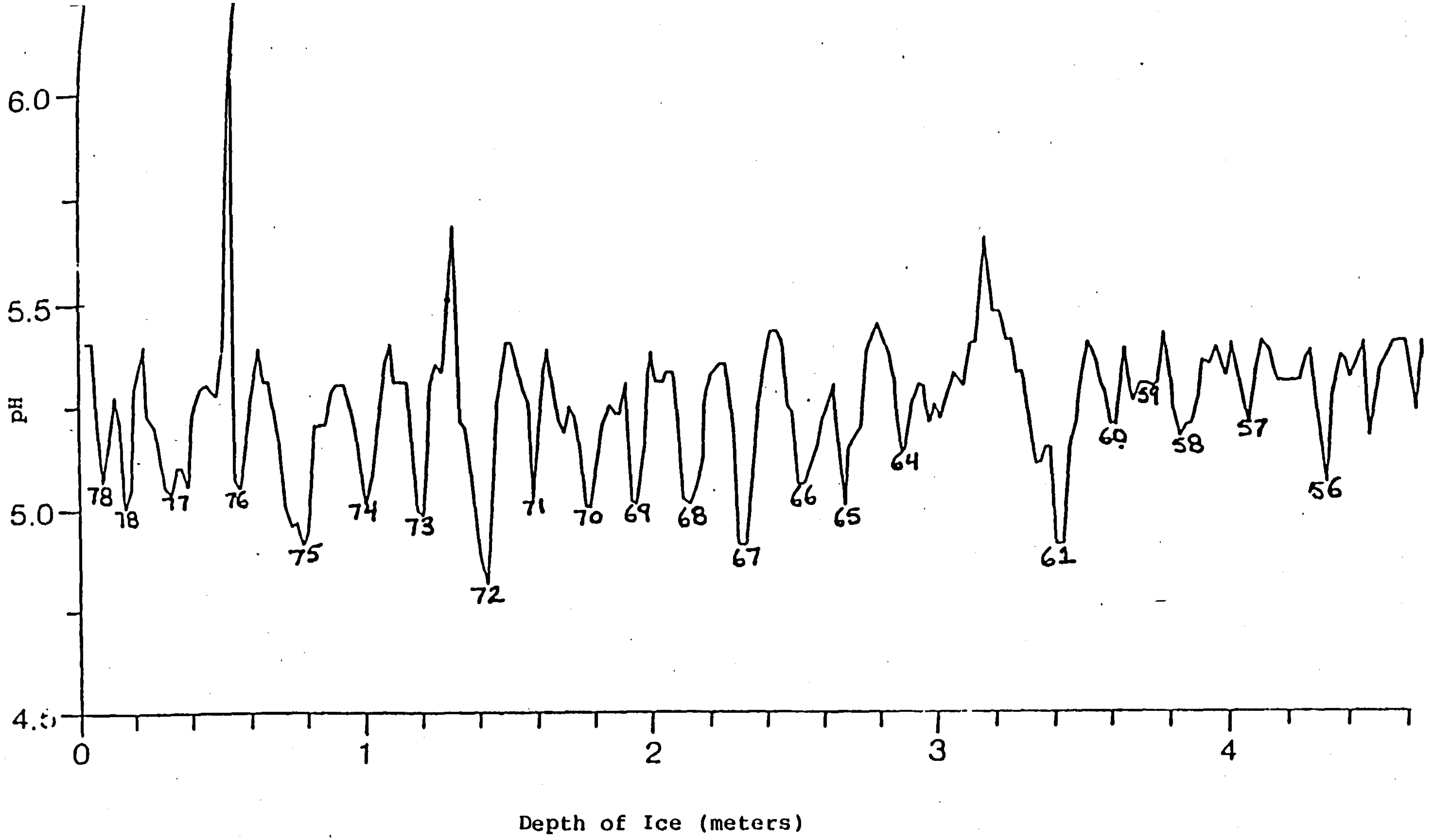

Figure 4-31 Seasonal Fluctuation in the pH of Snow in the Agassy Ice Cap Ellesmere Island for Each Year Marked (Source: Koerner and Fisher, 1981)

around an isolated thermal generating station in northwestern Alberta, Barrie (1980) found the background pH of snow that accumulated between December 1977 and January 1978 to be 4.9 to 5.0. Galloway et al. (1982) report a mean annual average precipitation pH of 5.0 in Alaska.

4.2.3 Wet Versus Dry Deposition

Monthly wet and dry deposition of sulfur oxides (Figure 4-32) were derived from APN air and precipitation data by Barrie (1982). Dry depositions were calculated from air concentrations measured by the APN network (Figure 4-26) and from estimated representative deposition velocities. The deposition velocities were estimated using monthly frequency distributions of Pasquill-Gifford stability classes and the techniques of Sheih *et al*. (1979), modified to include higher particulate sulfate surface-resistances. These values can be considered only rough estimates of the dry deposition. Wet deposition was calculated from the product of precipitation amount and volume-weighted mean ionic concentrations.

In general, dry deposition of sulfur is not negligible compared to wet. The ratio of dry to wet deposition is highest for locations such as Long Point that are close to source regions. It is also higher in winter than in summer since in winter, SO_2 concentrations near the ground are highest and precipitation amount is usually lowest.

Deposition Trends

The most convincing piece of trend data linking acidic emissions from the industrialized mid-latitudes with acidification of remote receptors is the time series of ice core acidity on Ellesmere Island in the arctic (Koerner and Fisher, 1982, Figures 4-31 and 4-33). In the last 26 years, the annual mean hydrogen ion concentration in ice has been increasing at an average rate of 0.007 μmole l^{-1} y^{-1}. Annual mean pHs were $\sim$5.3 in the late 1950s and 5.1 to 5.2 in the late 1970s. If this trend is projected back in time linearly, levels associated with the pre-industrial era (i.e., 1900 to 6000 BC) are reached by the early 1930s.

MONTHLY SULPHUR DEPOSITION (milli mole m^{-2})

F

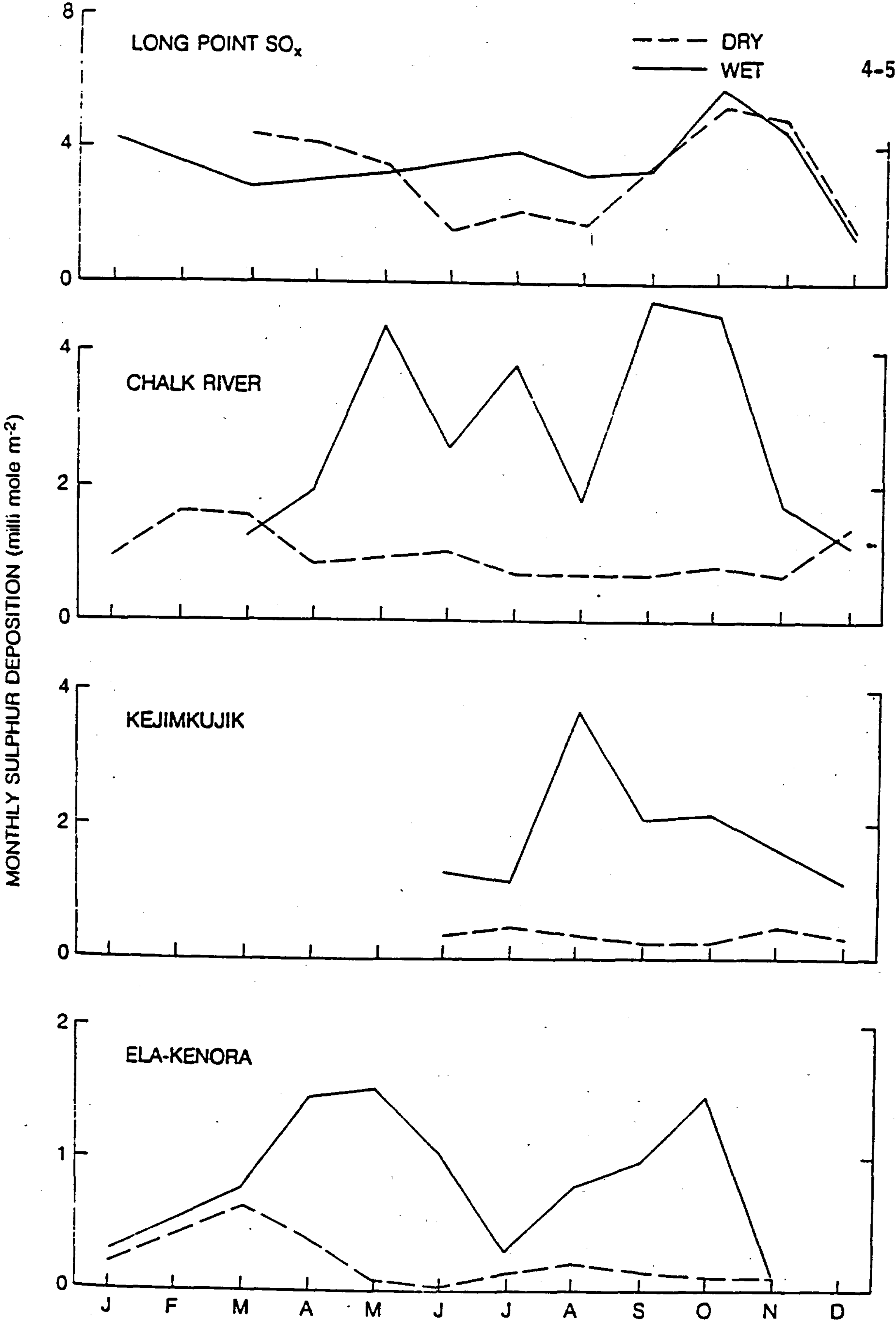

Figure 4-32 Temporal Variation of Monthly Wet and Dry Deposition of Oxides of Sulfur at APN Sites(see Figure 4-25). Dry Deposition is Calculated and Wet Deposition is Measured.

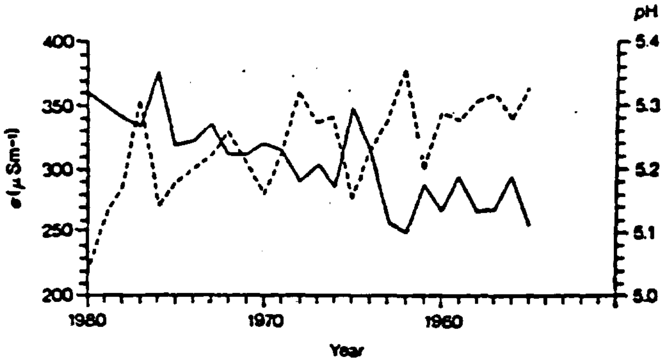

Figure 4-33 Trend in Annual Mean Acidity of Ice Cores on Ellesmere Island in the Canadian Arctic from Koerner and Fisher (1982)

4.3 Special Studies

The transport of atmospheric materials and pollutants over long distances, of the order of several hundred kilometers, requires a knowledge of not only the turbulent diffusion processes within the surface layer of the atmosphere but also of removal processes such as deposition at the ground and scavenging by precipitation. Chemical reactions in the atmosphere must also be considered since the conversion of gases to atmospheric aerosols or other gaseous chemical forms may alter the travel distance from large source areas. For example, the conversion of sulfur dioxide to sulfate aerosol leads to greatly increased transport distances for sulfur, since the rate of deposition at the ground is considerably less for sulfate.

In view of the importance of the chemical transformations, dry deposition and precipitation scavenging processes to our understanding of the long-range transport of air pollutants, a number of special field studies have been carried out to increase our knowledge of these factors. While the majority of field programs in the last decade have been concerned with the measurement of these processes on a regional or local scale, several recent studies have extended the range of measurements to the long-range transport distances. Some of these studies will be outlined in the following sections. A summary of the objectives of these studies is given in Table 4-4.

In these studies, specially instrumented research aircraft have been used to complement observations made from stationary surface monitoring locations, allowing for the horizontal and vertical characterization of regional air masses and measurement of chemical transformations that occur within the mixed layer of the atmosphere and in clouds. The results from these studies will undoubtedly allow for improved parameterization of processes important in long-range atmospheric transport.

4.3.1 Plume Studies from Point Sources

One of the most often studied chemical processes in the atmosphere has been the sulfur dioxide to sulfate aerosol conversion rate. In field studies, this oxidation process has been measured most frequently in point

TABLE 4-4 OBJECTIVES OF SPECIAL FIELD STUDIES RELATING TO LONG-RANGE TRANSPORT OF ATMOSPHERIC POLLUTANTS

Precipitation Studies

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1. Oxidation and Scavenging Characterization of April Rain (OSCAR) Study Objectives (Raynor, 1982):
    a. define the relationships between emissions of air pollutants, their deposition, and the chemical quality of precipitation;
    b. examination of selected dynamical and chemical features of selected frontal storm systems;
    c. assess the spatial and temporal variability of precipitation chemistry;
    d. provide a data base for model development;
    e. develop increased understanding of wet removal mechanisms and to identify source areas.
2. The Acid Precipitation Experiment (APEX) Study Objectives:
    a. investigate changes in atmospheric aerosol characteristics due to rainfall on an hourly time scale (Tanaka *et al*., 1980);
    b. measure concentrations of acids in air, and determine their effect on the acid composition in precipitation (Lazrus *et al*., 1980).

Regional Air Mass Characterization Studies

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1. Persistent Elevated Pollution Episodes (PEPE)/Northeastern Regional Oxidant Study (NEROS):
    a. determine the role of cloud processes in the vertical flux and transport of ozone;
    b. measure surface deposition rates;
    c. determine the dynamics of atmospheric layering;
    d. quantify long-range atmospheric diffusivities;
    e. characterize the physical and chemical aspects of transport, dispersion and transformation dynamics of urban plumes over the diurnal cycle relevant to regional scale air masses and long-range transport.

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source plumes. These investigations have usually been designed to determine the dependence of the sulfate aerosol formation rate on environmental variables such as solar radiation, temperature, relative humidity, and the entrainment of background air containing other reactive gases. The results have been interpreted in terms of a number of possible mechanisms. These include gas-phase photochemistry, liquid-phase reactions, reaction with photochemically derived oxidants or metal catalysis, and aerosol-surface reactions.

In a recent review (Wilson, 1981), data from studies involving 12 different power plant and smelter plumes have been analyzed. These data indicate that while solar radiation has a strong link with the rate and extent of conversion of sulfur dioxide, it cannot be concluded that the radiation induced or photochemical reactions are the important routes for the oxidation. Further experimental studies will require new and improved measurements of background and environmental conditions, including reactive gases, aerosols, catalytic substances and solar radiation to delineate the important oxidation mechanism for a given plume. It should be noted that almost all of these studies were carried out in dry (non-cloudy, non-precipitating) weather situations.

While the plume oxidation rates, mechanisms, and dispersion processes are important in the context of regional air mass characterization measurements, the extension of the plume chemical mechanisms to long-range atmospheric transport is probably unrealistic. The ratios and concentrations of chemically interacting species are vastly different in regional air masses, and processes other than those observed in the plume may become dominant. However, the plume processes may be important in long-range transport, since elevated plumes may remain intact for long distances under certain dry meteorological conditions.

4.3.2 Precipitation Studies

Both the dynamic and chemical processes of clouds and precipitation are important features for an understanding of the relationship between the emissions of air pollutants and the chemical composition of precipitation. While an abundance of experimental data exists on the formation of strong acids from gaseous atmospheric pollutants in solution, the direct measurement of the chemical production of these acids within cloud droplets and precipitation is limited. The nucleation of cloud droplets by acidic aerosols, neutralization by basic materials and gases in the atmosphere, and below cloud scavenging of gases and particulates are other processes for which few direct measurements have been made.

Several field programs have recently been conducted to examine these processes in more detail. The Oxidation and Scavenging Characterization of April Rain (OSCAR) study consisted of an intermediate and a special high-density network of precipitation collectors. The network was established to cover most of the northeastern United States, with two locations in southern Ontario. Supplemental data was collected by aircraft and ground-based atmospheric chemistry stations. Sequential samples from four storms during April 1981 were collected and chemically analyzed. Some of the preliminary results from one of the storms, April 22-24, indicate that in this storm a band of precipitation with a pH less than 3.75 was found to extend from Illinois into New York and New Jersey. Heavier rainfall rates were also found to lead to higher pH values in precipitation. These findings are illustrated in Figures 4-34 and 4-35 (Raynor, 1982).

A second series of field studies concerned with precipitation processes is being funded by the U.S. Environmental Protection Agency and National Science Foundation, as the Acid Precipitation Experiment (APEX). In one of these studies (Tanaka *et al.*, 1980), concurrent measurement of atmospheric aerosols and rain samples in northern Florida has shown that the atmospheric sulfur aerosol concentration, predominantly in the size range less than 1.0 µm, is not strongly affected by precipitation. Calcium, on the other hand, is found in the large particle fraction, and is apparently removed during precipitation events, hence influencing the pH of rain below cloud base.

A second APEX field study (Lazrus *et al.*, 1981), with objectives to measure concentrations of atmospheric acids and their effect on the acidic composition in precipitation, was carried out in the Ohio River Valley in November 1979. Some of the observations include: the strong acid composition

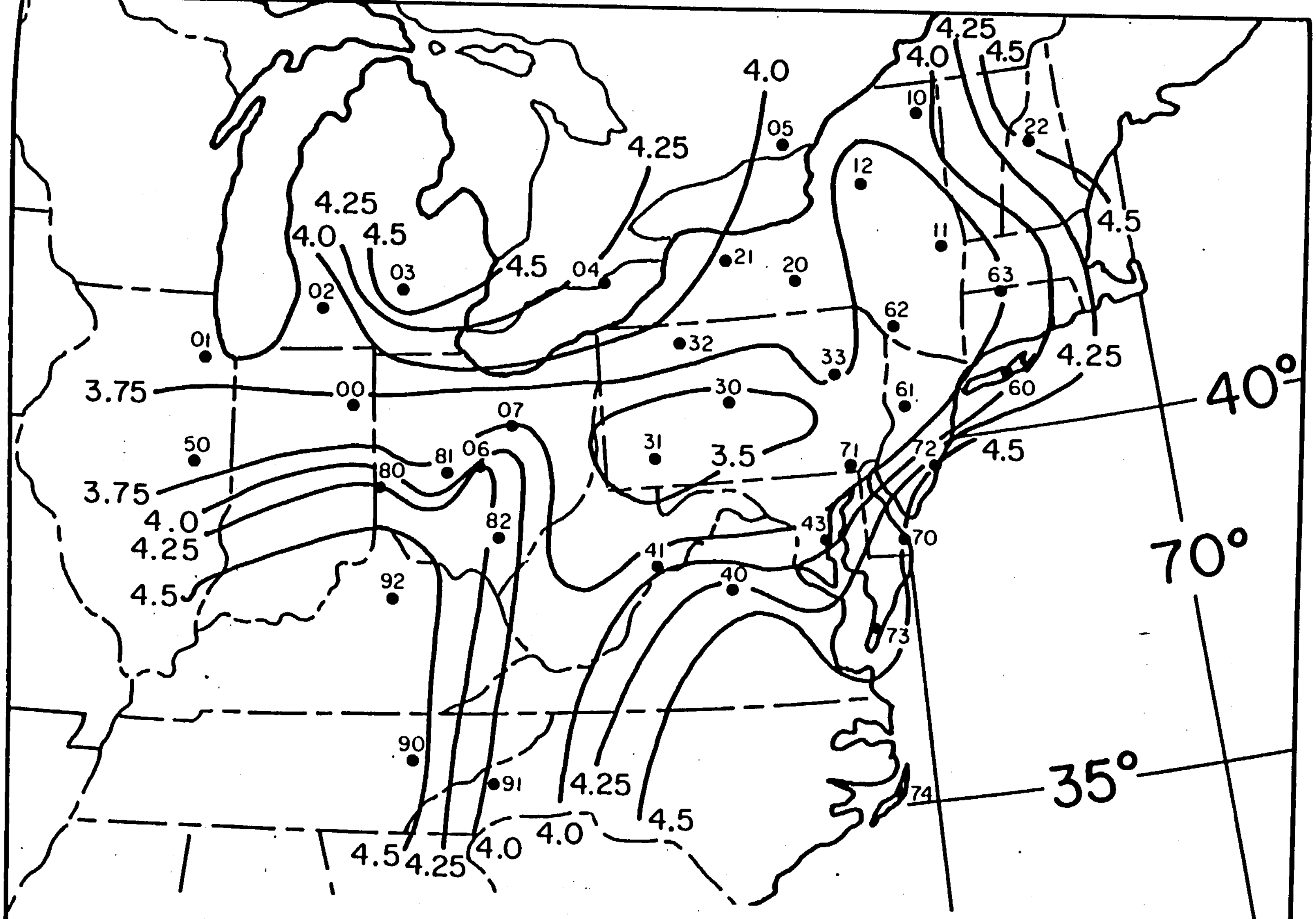


Figure 4-34 Distribution of pH of the First Sample Taken at Each Station in the Rain Event of April 22-24 (Source: Raynor, 1982)

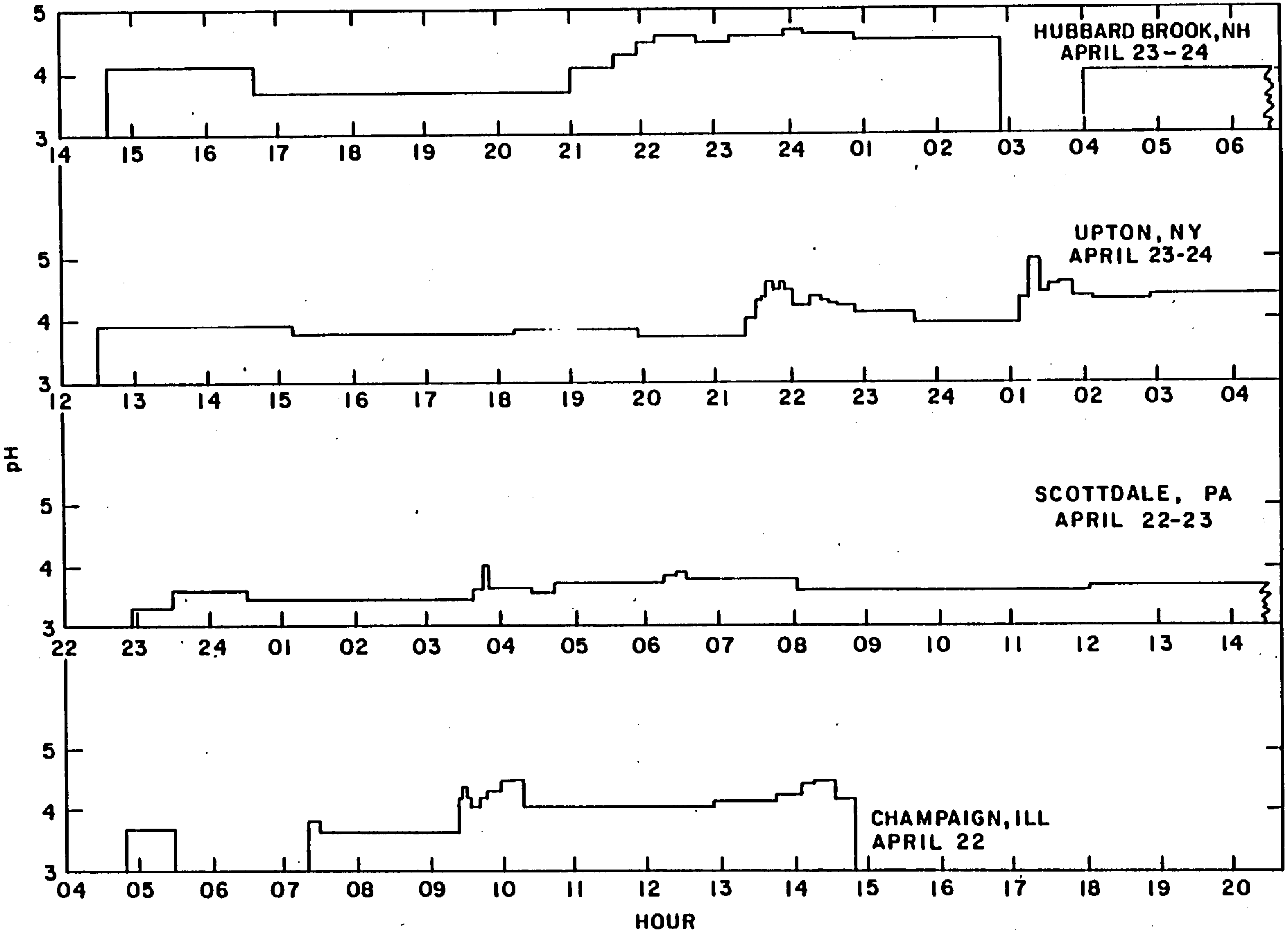


Figure 4-35 Change in pH with Time at Four Stations during the Rain Event of April 22-24. (Source: Raynor, 1982) Note: Duration of Sample is Inversely Proportional to Rainfall Rate

of dry air going into clouds cannot account for the acidity of the cloud water; below cloud removal of acidic aerosols, nitric acid or ammonia vapor is not significant; and nitric and sulfuric acid is incorporated into precipitation by formation of these acids in the cloud. Although an aircraft was used in this study to collect atmospheric and precipitation samples, the physical characteristics and dynamics of the clouds were not measured.

Further evidence for the formation of acids in clouds comes from a recently reported study (Hegg and Hobbs, 1981) concerning the formation of sulfates in clouds. The measurements suggest that while not all of the clouds measured showed sulfate production, the oxidation rates were generally far greater than those for homogenous gas-phase reaction. The data also suggests that the oxidation rate increases with pH of the cloud water and that sulfate production in solution may be a major source of sulfates in the atmosphere.

A limited program of cloud water sampling and analyses was conducted during the Cooperative Convective Precipitation Experiment (CCOPE) at Miles City, Montana, during May-July 1981. Cloud samples were collected by two aircraft (NCAR and AES) using specially designed cloud water and precipitation samplers. One of the aircraft (AES) also sampled for relevant atmospheric species (sulfates and sulfur dioxide) outside of clouds by means of filter pack techniques. Analysis of these data is currently in progress.

The use of a single aircraft has limited the interpretation of the experimental results in these studies. Considerable time is required to obtain all measurements outside of clouds before entering the cloud for measurement of cloud parameters and collection of cloud water. Any changes in atmospheric concentrations and cloud properties or dynamics could lead to the measurements of unrelated atmospheric events.

4.3.3 Regional Air Mass Characterization Studies

An important field investigation to examine chemical transformations within polluted air masses was the Persistent Elevated Pollution Episodes (PEPE) Study, which was conducted during July-August 1980. Sponsored by the U.S. Environmental Protection Agency, one part of the study was designed to examine chemical and atmospheric processes within stagnant air masses, extending over hundreds of kilometers. Through the use of tetroon tracking of the stagnant air masses, research aircraft were able to make measurements in flights from Columbus, Ohio, to as far east as New Hampshire. Vertical profiles of pollutants, including SO_2, NO_x, sulfate, nitrate, and aerosols were obtained from spiral flights while horizontal gradients were obtained from flights that occurred during the eastward tracking of the airmass. The data set is presently being completed and will be available from the Center for Air Pollution Impact and Trend Analysis of the Washington University (Vaughan et al., 1981). It is anticipated that analyses of the data base will provide critical information to the understanding of long-range atmospheric transport and acid rain issues.

During the PEPE study, concurrent measurements were made by aircraft and at fixed stationary locations in southern Ontario by the Atmospheric Environment Service and Ontario Hydro. It is anticipated that these data will be complementary to those generated in the United States and will yield important information on atmospheric chemical processes and rates in air masses flowing into southern Ontario from Ohio.

A second field program was run concurrently with PEPE study, as part of the Northeast Regional Oxidant Study (NEROS II), to provide measurements for data bases and validation of the U.S. Environmental Protection Agency's regional oxidant model. The first field measurements in this study were made in the summer of 1979 (NEROS I). While ozone was the species of interest, the atmospheric transport processes important to long-range transport will probably be applicable to other atmospheric pollutants.

Some important features that have been obtained from the ozone measurement in these studies are: elevated concentrations may be due to local sources, not necessarily reflecting general air mass concentrations; surface depletion occurs in the surface layer during the night, with continued transport aloft; elevated concentrations were found above the mixed layer and may result from venting by clouds; urban plumes may maintain some integrity for a number of hours but eventually merge and blend into a general air mass burden (Clarke and Ching, 1982).

During the Nanticoke Shoreline Diffusion Experiment, conducted by the Atmospheric Environment Service in June 1978, a series of airborne measurements were made for the regional air mass characterization in southern Ontario (Anlauf et al., 1981). The concentrations of sulfur dioxide, ozone, and sulfate measured during the study were correlated to influencing meteorological factors and calculated air trajectories. The study has shown that highly differing atmospheric concentrations of these pollutants can occur on a regional scale for air masses arriving in the study area from the south-southwest, as compared to those from the north-northwest.

4.4 Single Station Sector Analysis

Trajectory analyses have been used to investigate a variety of atmospheric gas-phase, aerosol and precipitation chemistry problems. In this type of analysis, meteorological models are used to trace out the path of an air parcel arriving at a particular site at a specified time. By way of example, in the United States, the Air Resources Laboratory model (Heffter, 1980) is often used; in Canada, the model developed by Olson et al. (1978) at the Atmospheric Environment Service is commonly referenced (see report 3-M for more details on modeling). These trajectories may be used in two ways: 1) Individual pollutant measurements or events may be associated with particular trajectories. It is then a relatively simple task to verify the degree to which these have passed over notable emission sources. 2) A more involved approach is to correlate a large number of pollutant measurements with the corresponding air parcel trajectories. Even though individual analyses may vary, generally, one divides the compass into several sectors. Then, one classifies the trajectories with the associated measured concentration and/or deposition among the chosen sectors. In this way, one may generate what one might call a "trajectory rose" (c.f., the equivalent "wind rose"); or, one may simply display it in graphic form as some authors have done.

Researchers in Scandinavia (OECD, 1977 and Joranger et al., 1980) have used trajectory analyses to fortify the reality of long-range transport of air pollutants. Their main conclusion is that sectors with associated high concentrations and/or depositions are not randomly distributed but are directed towards the main areas of sulfur emissions in Europe (i.e., to the south and southeast). In North America, several researchers (Galvin et al., 1978; Samson, 1980; Lioy et al., 1980; Anlauf et al., 1980, 1982) have used trajectories to examine meteorological events surrounding atmospheric sulfate episodes. Their findings indicate that sulfate episodes at a particular location are associated with trajectories that have passed over upstream high emission sources. The highest ambient levels were observed for southwest trajectories arriving at sites in eastern Canada and the northeastern United States. As more monitoring data has become available, various research groups have been able to produce trajectory analyses that are statistically more valid (Miller et al., 1978; Samson, 1978; Miller, 1979; Anlauf et al., 1980; Kurtz and Scheider, 1981; Parekh and Husain, 1981, 1982; Wilson et al., 1982; Jickells et al., 1982). In general, they have found that high pollutant concentrations were associated with trajectory sectors containing high emission sources, which is indicative of long-range transport of pollutants; of course, at the same time, low pollutant concentrations were associated with sectors containing minor emissions.

Using data for July of 1975 and 1976, Samson (1978) has shown that the highest particulate sulfate concentrations in New York State were associated with winds originating in the upper Ohio River valley. An analysis by Anlauf et al. (1980) of ambient pollutant concentrations near Toronto, Ontario, showed that sulfate episodes correlated well with periods of high ozone and high light-scattering coefficient (i.e., low visibility). Using 925 mb trajectories, they showed that during the summer period of 1976, the trajectories within the southwesterly quadrant were associated with the highest measured concentrations, whereas the northerly trajectories were associated with the lowest concentrations. Figure 4-36 shows the average concentrations associated with trajectories in the given sectors. A comparison with the source emissions as shown in Figure 4-13a shows that these findings point to long-range transport of air pollutants.

Recently, Parekh and Husain (1981 and 1982) completed a study on ambient trace elements and particulate sulfate concentrations as measured at several sites in New York State. The trajectories were classified among 12 sectors of 30° each. In particular, for the Whiteface Mountain site, they found that maritime tropical air masses crossing the U.S. from the Gulf of

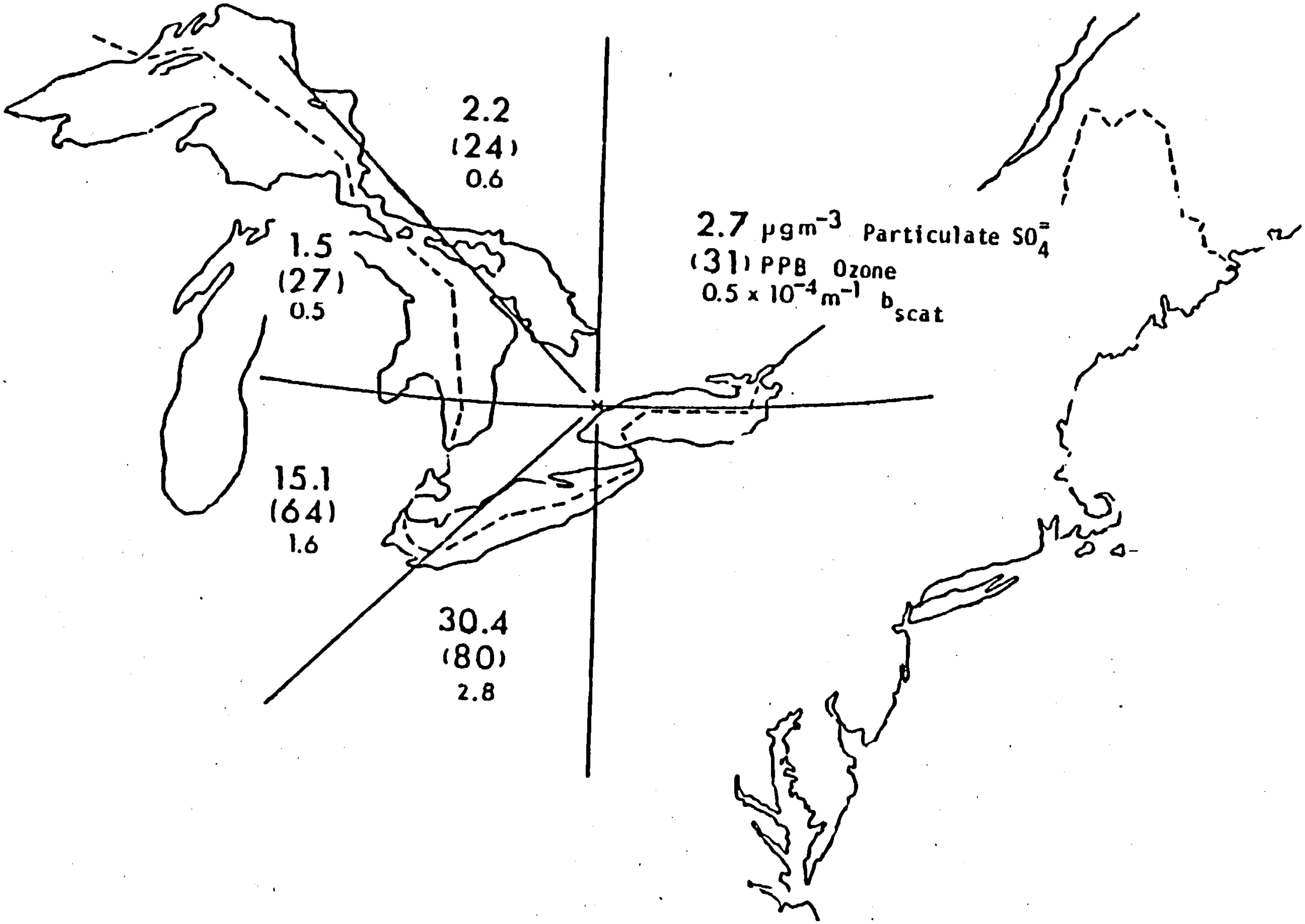


Figure 4-36 Average Concentrations of Particulate Sulfate, Ozone, and Light Scattering Coefficient for Each Sector

Mexico were the principal conveyors of high sulfate concentrations and they transported about 4 to 5 times more sulfate than the continental polar air masses from Canada.

Using data from 45 precipitation events at Ithaca, New York, from 1974 to 1976, Miller et al. (1978) computed the precipitation-weighted concentration averages for the dominant ions as a function of approach sector. The results are shown in Table 4-5. Precipitation from the southwesterly and northwesterly quadrants was found to be the most acidic and the weighted averages for SO_4^{2-} and NO_3^- were found to be almost similar for these two sectors.

Wilson et al. (1982) used a similar approach by applying a trajectory analysis to the 1978 precipitation data of Whiteface Mountain, New York and Champaign, Illinois. Data of the Multistate Atmospheric Power Production Pollution Study (MAP3S) were used for this purpose. In this study, a six-hour precipitation-weighting scheme was utilized to assign as many events as possible to a 30° approach sector for the two sites. Utilization of this technique allowed approximately 85% of the events to be correlated with a particular trajectory sector. Concentrations of the dominant ions were found to be somewhat higher for the southwest and northwest quadrants as noted by Miller et al. (1978). The concentration values were then combined with the precipitation to give a measure of the distribution of wet deposition per approach sector. The results of this analysis for Whiteface Mountain are shown in Figure 4-37. While ionic concentration is obviously an important parameter in wet deposition calculations, the amount of water appears to be critical as evidenced by the similarity in the precipitation and deposition distributions in Figure 4-37. The sector distribution for SO_4^{2-} wet deposition is essentially a mirror image of the precipitation distribution. Analyses for NO_3^-, H^+, and NH_4^+ displayed similar characteristics. Therefore, while the concentrations of the ionic constituents may be low for some directions, large amounts of precipitation from systems such as coastal storms may produce a significant input to the total wet deposition budget for a particular site. The results for the Illinois site are shown in Figure 4-38; they are similar to the Whiteface Mountain results. The ratio of

TABLE 4-5 WEIGHTED AVERAGES OF PRECIPITATION CONSTITUENTS ORDERED IN DECREASING ACIDITY

	Sector				
Ion	SW	NW	NE	SE	Units
H	129.5	115.1	46.7	24.7	μeq l^{-1}
pH	3.8	3.9	4.3	4.6	pH units
SO_4	5.02	4.75	2.23	0.90	mg l^{-1}
NO_3	2.61	2.76	1.00	0.79	mg l^{-1}
Cl	0.44	0.26	0.07	0.14	mg l^{-1}
NH_4	0.49	0.54	0.16	0.22	mg l^{-1}
Na	0.17	0.07	0.01	0.05	mg l^{-1}
Ca	0.26	0.31	0.05	0.14	mg l^{-1}
K	0.03	0.04	0.02	0.01	mg l^{-1}
Mg	0.03	0.04	0.01	0.01	mg l^{-1}
Precip	432	113	33	231	mm

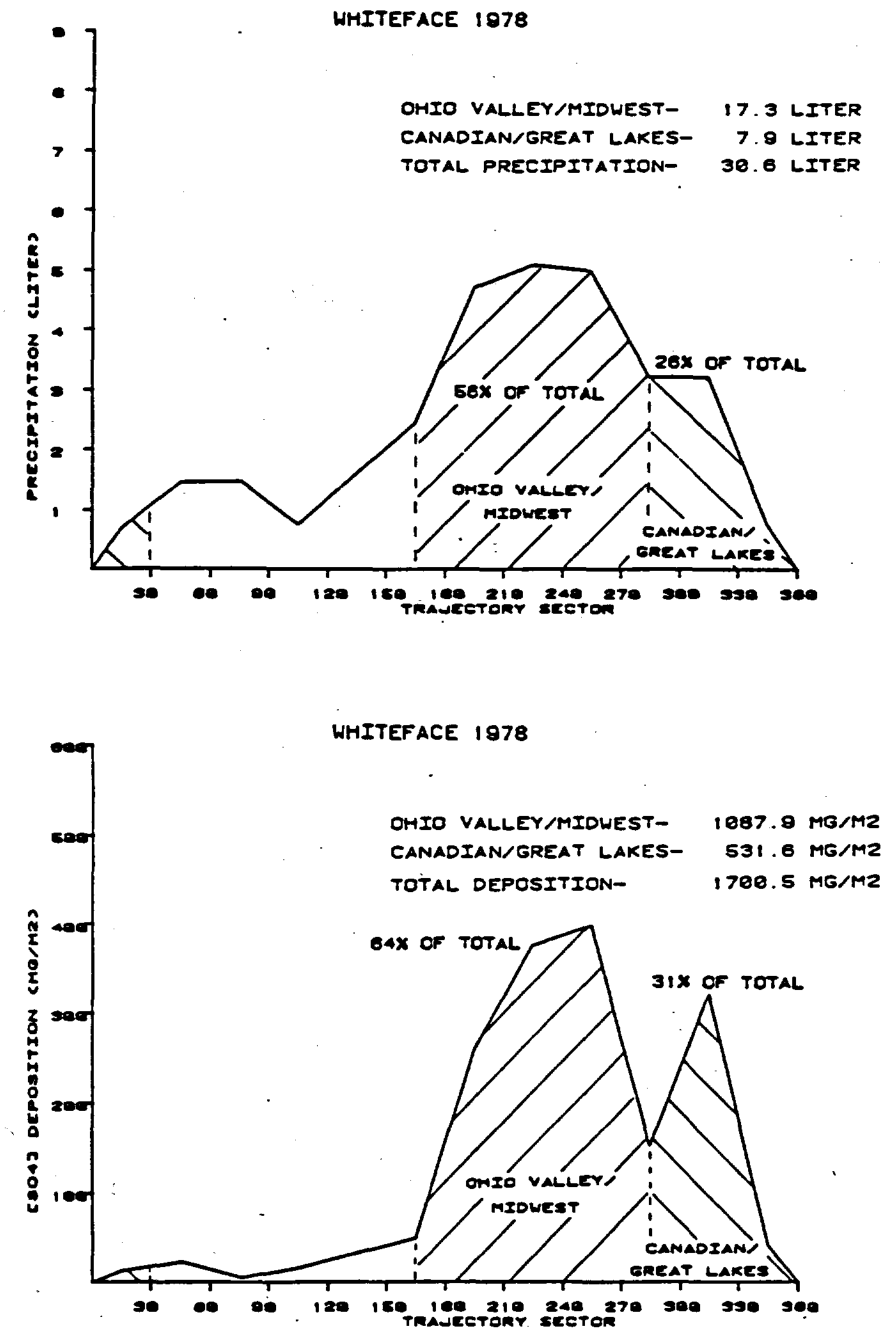


Figure 4-37 a) Precipitation Volume, and b) Sulfate Total Wet Deposition per 30° Trajectory Sector for Whiteface (1978)

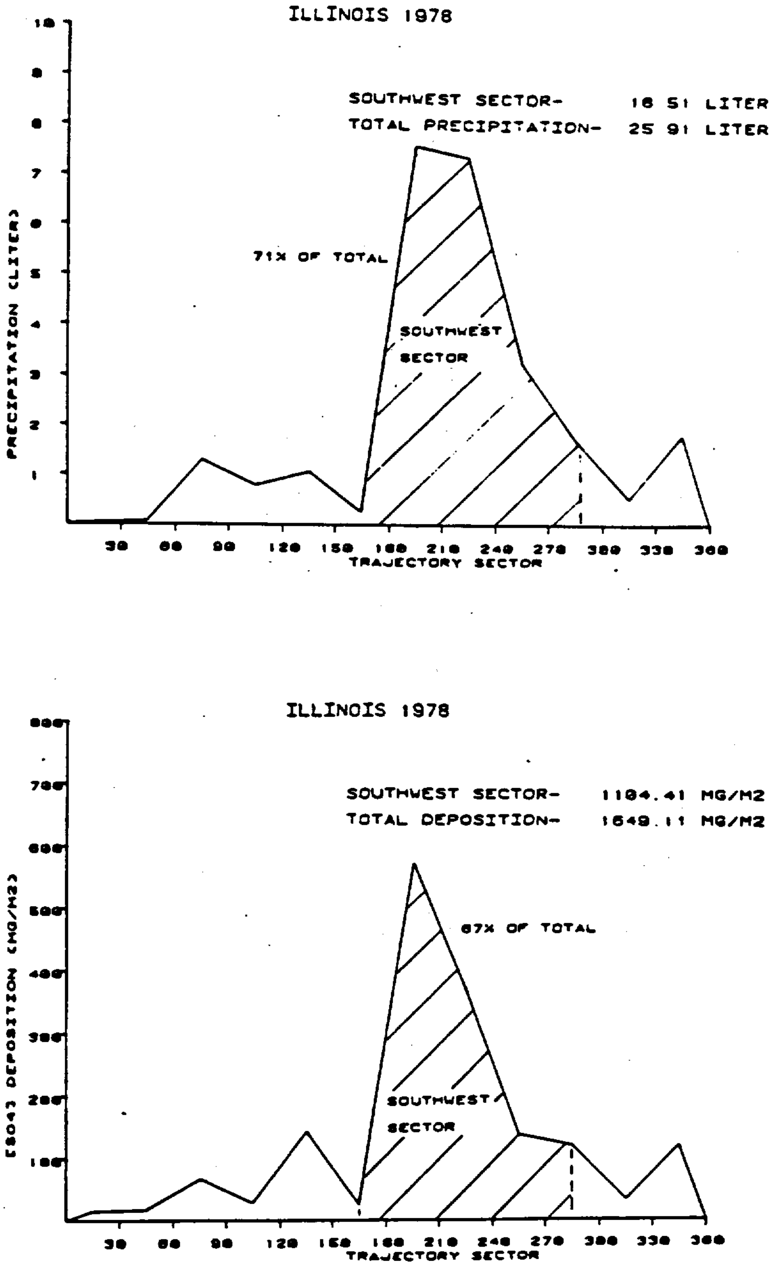


Figure 4-38 a) Precipitation Volume, and b) Sulfate Total Wet Deposition per 30° Trajectory Sector for Illinois (1978) precipitation to the wet deposition distribution for these sites is roughly the same for the dominant ions.

Kurtz and Scheider (1981) have correlated three years of precipitation measurements in the Muskoka-Haliburton region of Ontario with sea level geostrophic trajectories. They showed that for all seasons the majority of H^+, SO_4^{2-}, and NO_3^- deposition was associated with trajectories from the southerly and southwesterly octants. Events originating in these two octants contributed 75 to 80% of the H^+, 70 to 80% of the SO_4^{2-}, and 57 to 86% of the NO_3^- deposition.

A very recent trajectory analysis by Jickells _et al_. (1982) has shown that there is a strong correlation between the presence of the strong acids (in precipitation as measured in Bermuda) and the meteorological back-trajectory of Bermuda storm systems to the North American continent. This has implied long-range oceanic transport of acid rain and its precursors to the island of Bermuda from the remote continental emission sources. Figure 4-39 shows the average pH associated with the three chosen sectors; the lowest pH was associated with trajectories arriving from the North American continent.

Recent work (Barrie _et al_., 1982) at the Atmospheric Environment Service deserves some detailed consideration. In 1979, Environment Canada operated five sites in Eastern Canada as part of the Air and Precipitation Network, APN (see section 4.2.2 for a complete description). The daily pollutant concentrations (including gaseous sulfur dioxide, particulates, and precipitation) were sorted into five concentration ranges and for each range the corresponding average frequency trajectory distribution was calculated.

Figures 4-40 to 4-42 show some results of the computer analysis of the 1979 data. The frequency of occurrence of air parcels from any one sector (octant) is represented by the total length of the radial projection. The width of the projection is proportional to the concentration range (i.e., the wider the projection, the higher the concentration of the chemical species), and the length is proportional to the frequency of occurrence of measurements in the particular concentration range.

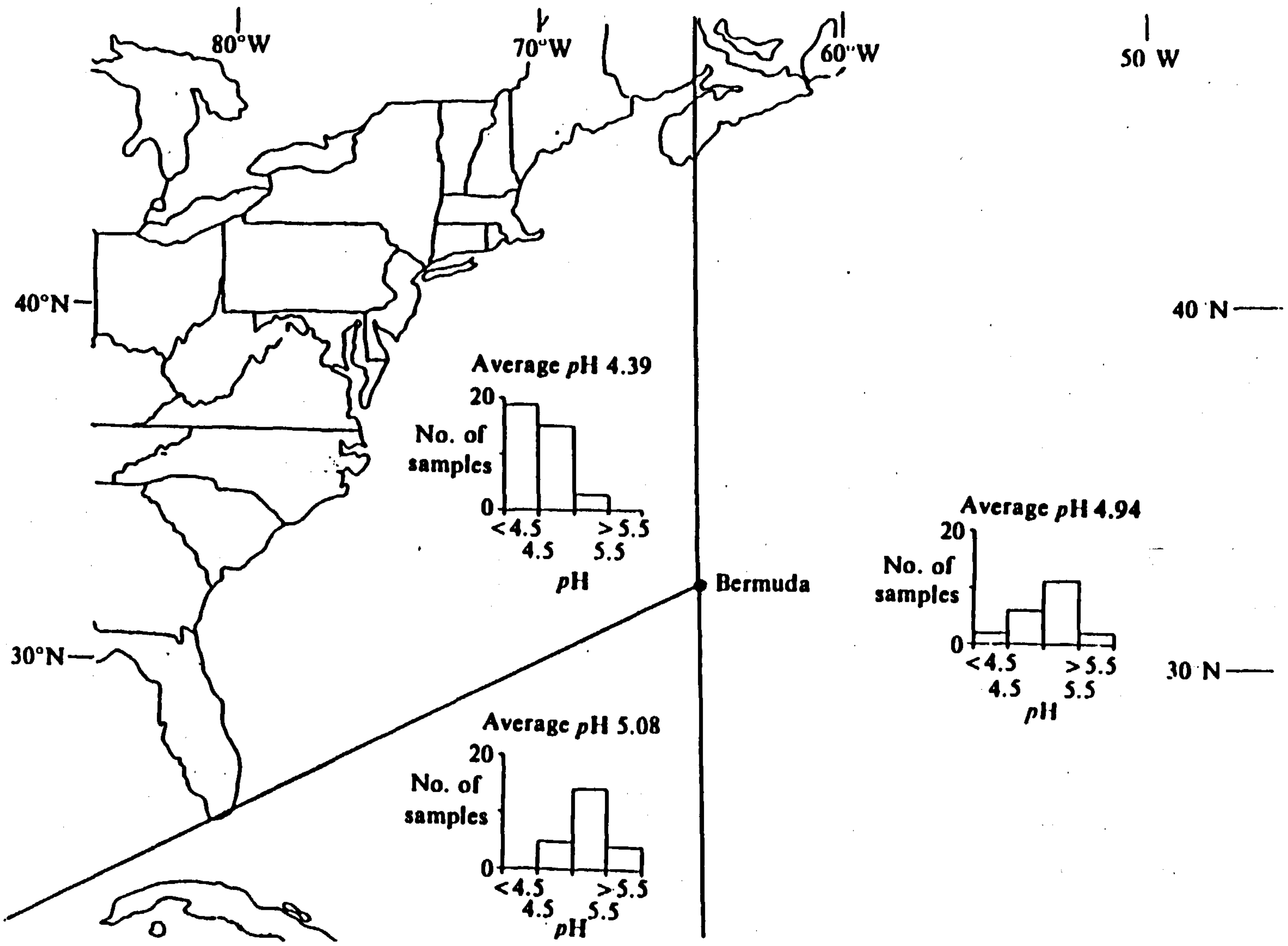


Figure 4-39 Map of the Northwest Atlantic Ocean Showing the Three Sectors Used for ARL Back Trajectories of Bermuda Rain. The Average pH of Rain Originated in each Sector is Indicated and the Distribution of pH Values of Rain Samples from that Sector are Shown in the Histograms

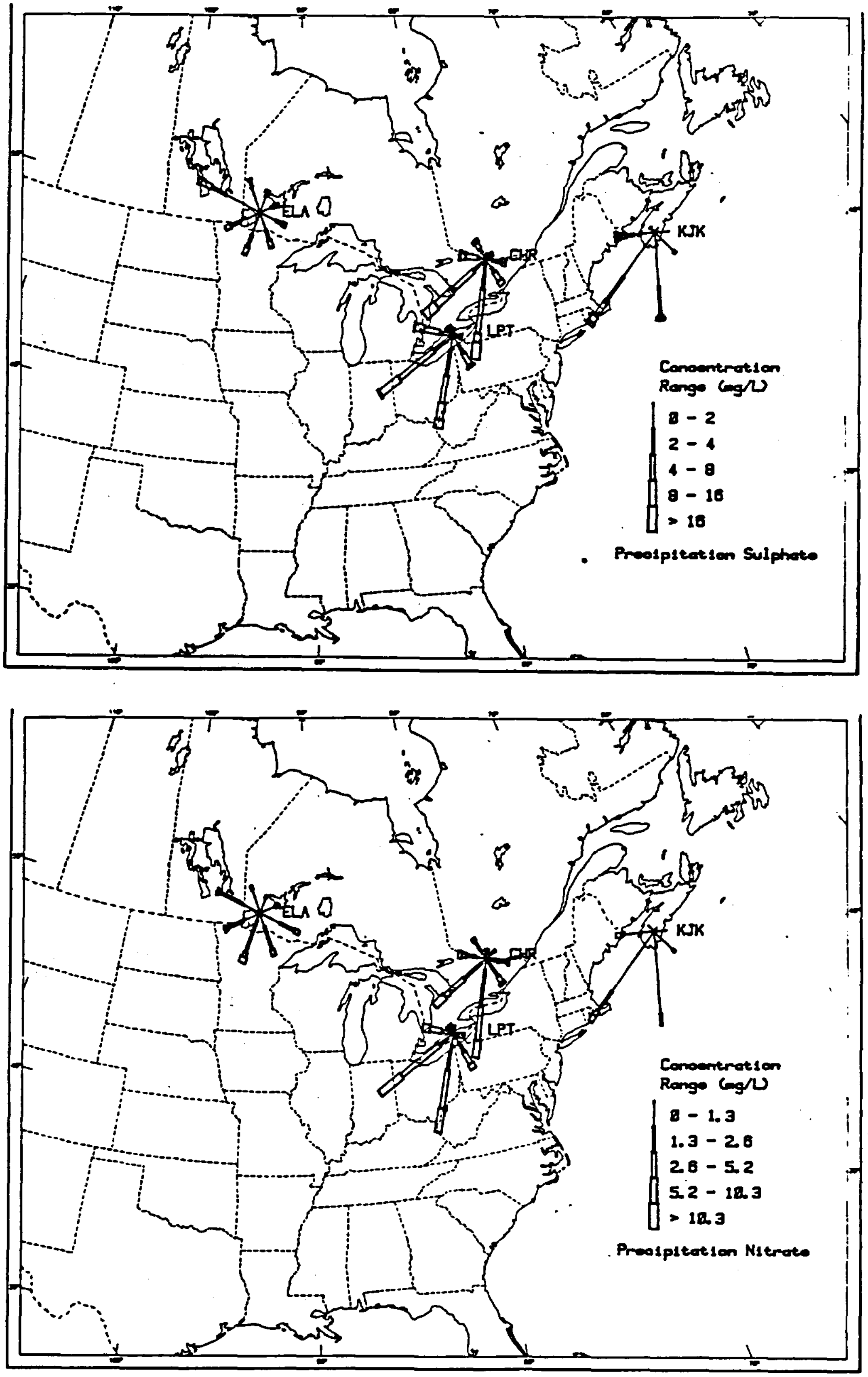


Figure 4-40 Trajectory Roses for Precipitation Sulfate (top) and Nitrate (bottom) Concentrations Measured at APN Sites

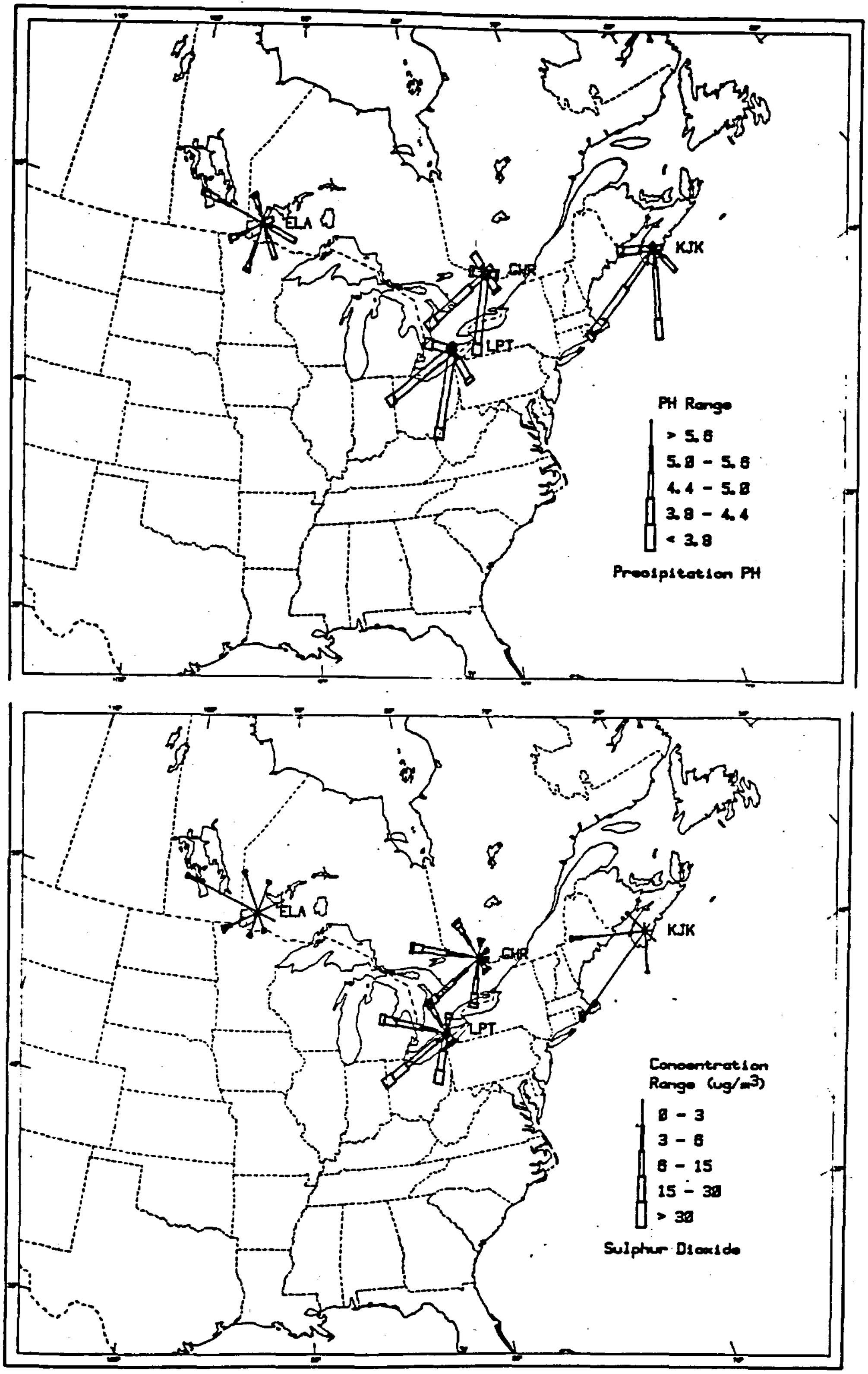


Figure 4-41 Trajectory Roses for Precipitation pH (top) and Ambient Sulfur Dioxide (bottom) Concentrations Measured at APN Sites

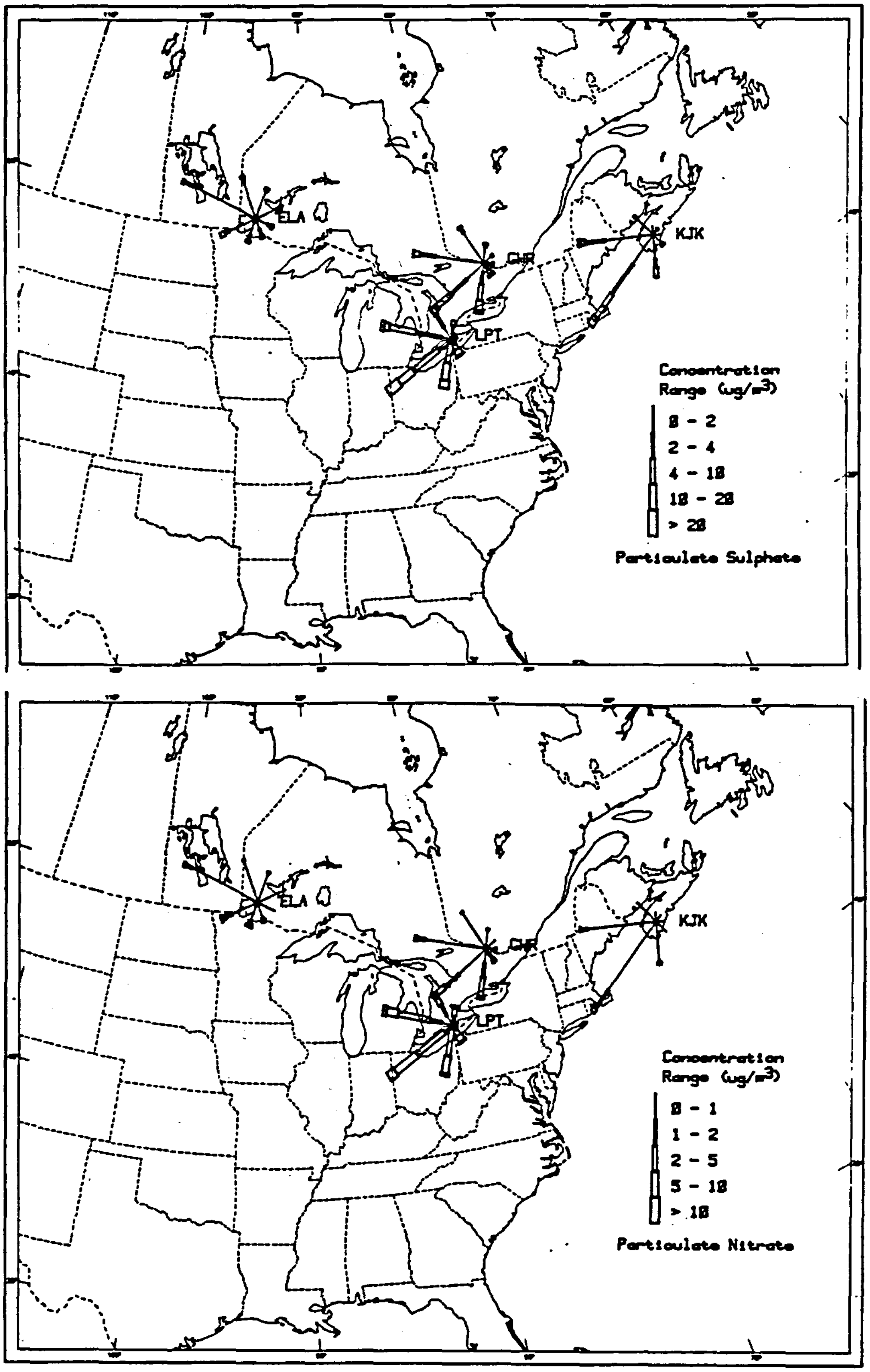


Figure 4-42 Trajectory Roses for Particulate Sulfate (top) and Nitrate (bottom) Concentrations (as Collected on Whatman 40 Filters) Measured at APN Sites

For particulates, the ELA site measured the lowest concentrations; this is not unexpected since it is in a remote location, far removed from large industrial emissions (c.f., Figure 4-26). The Long Point (LPT) and the CN Tower sites measured the largest concentrations (only Long Point is shown in Figures 4-40 to 4-42); their close proximity to large sources of sulfur and nitrogen oxides emissions would account for this. For these two sites, trajectories within the S, SW, and W octants were associated with the largest particulate sulfate and nitrate concentrations. However, at Chalk River (CHR), a more northerly site, the westerly component of high concentrations was significantly less relative to the southerly sectors; this may be explained by the lack of large area emission sources, except for Sudbury and Noranda, to the west of Chalk River. For the Kejimkujik site (KJK), the largest sulfate concentrations were associated with the SW sector, possibly due to the large emission sources on the Atlantic seaboard.

For sulfur dioxide, the findings are similar except for Chalk River where one notes that the two northwesterly components of high concentrations were as large as the two southwesterly components (unlike particulate sulfate as discussed above). In order to determine whether this was partly due to the large INCO SO_2 emission source at Sudbury, the data was split into two periods: (1) January 1 through June 6, when INCO was not operational due to a strike, and (2) June 7 through December 30, when INCO was operational. A comparison of the two periods did not show an increase in measured sulfur dioxide. Perhaps this should not be surprising since the ambient SO_2 concentrations are lower in the first part of the period (June 6 through December 30) due to less fossil fuel combustion (heating), higher mixing heights, and higher oxidation rates. These effects would tend to minimize any observable difference. A manual trajectory analysis is underway to better isolate the Sudbury and Noranda source regions.

In applying this type of trajectory analysis to precipitation events, it must be kept in mind that these events are often accompanied by frontal passages; this can reduce the accuracy of the air parcel trajectory. Nevertheless, a preliminary analysis has yielded useful information. The remote ELA site measured the least overall acidic precipitation, with the two western quadrants indicating the highest acidity (pH = 3.8 to 4.4).

Kejimkujik National Park in Nova Scotia showed the highest acidity (pH <4.4), sulfate and nitrate for the southwesterly to westerly octants. As with the case of particulates, the highest concentrations seem to originate from the eastern Atlantic seaboard. As expected, the Long Point and Chalk River sites recorded the highest overall concentrations of ionic constituents in precipitation. Most precipitation events and high concentrations were associated with trajectories within the southwesterly quadrant. In order to quantify the deposition of ionic species, a more detailed analysis would have to include the precipitation amount and concentration that is associated with each trajectory; this type of analysis is presently underway.

From the foregoing discussion, it is evident that trajectory sector analyses have provided strong evidence for the long-range transport of air pollutants in North America. Trajectory sectors associated with high concentrations point to the areas of high sulfur and nitrogen oxides emissions. The case for deposition is not so clear because the amount of precipitation is an independent variable that influences the total material deposited.

4.5 Mass Budget Studies

4.5.1 The Mass Budget Approach

The mass budget approach entails examining the fluxes of a particular constituent of interest into and out of a selected portion of the atmosphere. That is, one makes a systematic comparison of the magnitude of sources, sinks and atmospheric concentrations over appropriately large space and time scales. In the past, global budgets have involved averaging over greatly disparate source, sink, geographical, and climatic conditions, and thus have been of limited utility; ecological impacts and man's interference with the S cycle is more likely to occur on the local or regional scale.

Studies of this type may have the following purposes:

- o to identify important pathways and magnitudes of fluxes,
- o to determine time scales that characterize transformation and removal processes,

- to assess man's impact on cycles of various atmospheric constituents, and
- to provide estimates of the importance of transformation and removal processes.

The budget approach has a number of advantages: it is useful in tying together various pieces of information into a consistent picture; it enables an overall assessment to be made of time-scales involved, and of the relative importance of various pathways and processes, without laborious computations; and it can help identify the most significant uncertainties in our knowledge about the cycling of various atmospheric constituents.

There are also certain limitations to the budget approach. An inherent assumption is that steady state exists, and the concept is most useful in regions where data are available, and where both climatic and emission conditions are reasonably homogeneous. The spatial distribution of the constituent of interest inside the box or reservoir is not explicitly considered (and is assumed to be reasonably homogeneous); this is in contrast to dispersion models where spatial and temporal distributions are dealt with explicitly. Note, however, that dispersion models can be used to advantage in budget studies. A budget approach requires an appropriate choice of the size of the box or reservoir: if the box is too large, one is averaging over very different conditions; if the box is too small, the fluxes across boundaries are so large that it is difficult to make meaningful estimates of the importance of emissions, transformations, and removal processes. Rodhe (1978) recommends an optimum box size to be:

$$L = 4\, \tau_S\, \overline{V},$$

where L is the length scale, τ_S is the average atmospheric residence time of sulfur, and $\overline{V}$ is an average wind speed for the region (for sulfur in eastern North America, $L \approx 4000$ km). As in other approaches, seasonal variations in most processes and magnitudes may make annual averages misleading.

4.5.2 A Review of Recent Budget Studies

Three studies have been published in the last few years in which attempts have been made to determine regional-scale atmospheric sulfur budgets in parts of eastern North America. These are presented in Table 4-6. The first study made use of measurements and model computations to make an estimate of each budget term, but did not make an attempt to "balance" the budget. The second and third studies used only model calculations and man-made emissions within the study area.

Some of the findings of these studies follow. On the regional to continental scale, man-made sulfur emissions exceed natural ones by a factor of 10 to 20. When considering eastern North America as the budget region, one finds that the three "removal" fluxes, dry deposition, wet deposition, and outflow are of a comparable magnitude. The ratio of wet to dry deposition is greater in Canada than in the USA. This is a reflection of proximity to emission sources; i.e., dry deposition is greater in the eastern USA where emissions are larger. Approximately 30 to 40% of the sulfur emitted in eastern North America leaves the continent to the east. Finally, it is found that the magnitude of the transboundary flux of sulfur from the eastern USA to eastern Canada is comparable to eastern Canadian emissions; whereas, the Canada contribution to the USA is a factor of 3 to 5 smaller, and amounts to approximately 5% of the eastern USA emissions.

4.5.3 Recommendations

The following are suggested as ways to improve understanding of man's impact on the biogeochemical cycles in eastern North America.

- It is obviously important to reduce uncertainties in all budget terms; however, because the three main "removal" fluxes are so important, and because they have significant uncertainties associated with them, particularly the outflow to the east flux, significant research effort is required in these areas.

TABLE 4-6 RECENT SULFUR BUDGET FLUXES

Reference	Region	Time	Inflow Terms* (Tg S y^{-1}) Q_N	Q_M	I_E	I_W	I_S	I_N	Outflow Terms* (Tg S y^{-1}) D_W	D_D	O_E	O_S	O_N	O_U	Notes
Galloway and Whelpdale (1980)	Eastern North America (bounded by mainland coast on N,E,S; by 92°W on W)	ca 1974-1978	0.8	16	.06	0.5	-	-	5.5	4.5	4.3	-	-	-	Fluxes derived from measurements and model calculations
	Eastern Canada		0.3	2.1	.04	0.1	2.0	-	3.0	1.2	0.4	0.7	-	-	
	Eastern USA		0.4	14	.02	0.4	-	0.7	2.5	3.3	3.9	-	2.0	-	
Olson et al. (1981)	Eastern Canada (provinces east of Ontario-Manitoba border)	emissions 1970-1974; meteorology 1978	-	1.8	-	-	2.0	-	2.4		0.2	1.2	-	-	Model calculations Note that I_S and O_S contain 0.3 TgS from Canadian emissions, which flows south and returns
			(Tg S (2 mo)$^{-1}$)**						(Tg S (2 mo)$^{-1}$)**						
Shannon (1981)	Eastern USA	Jul-Aug 75	-	2.28	-	-	-	0.07	0.71	0.65	0.77	-	0.30	-	Model calculations
		Jul-Aug 74	-	2.28	-	-	-	0.07	0.77	0.64	0.71	-	0.40	-	
		Jan-Feb 75	-	2.60	-	-	-	0.12	0.83	0.50	1.03	-	0.49	-	
	Eastern Canada	Jul-Aug 75	-	0.36	-	-	0.30	-	0.24	0.11	0.12	0.07	-	-	
		Jul-Aug 74	-	0.36	-	-	0.40	-	0.24	0.11	0.08	0.07	-	-	
		Jan-Feb 75	-	0.36	-	-	0.49		0.28	0.12	0.17	0.12	-	-	

*Q_N	natural emissions	D_W	wet deposition
Q_M	man-made emissions	D_D	dry deposition
I_E	inflow from east	O_E	outflow to east
I_W	inflow from west	O_S	outflow to south
I_S	inflow from south	O_N	outflow to north
I_N	inflow from north	O_U	escape above mixed layer

**These numbers have been rounded-off to two significant decimals.

Notes: 1) Tg = 10^{12}g = 10^9 kg = 10^6 metric tonnes.

2) Units are in terms of S. To obtain in terms of equivalent SO_4^{2-}, multiply above numbers by 3.

- Budget computations for two quite different meteorological years would provide a measure of the variability to be expected in the individual fluxes.
- Budget computations using only natural emissions would demonstrate the role of man's emissions in this region.
- Although much more complicated, it would be of interest to undertake an NO_x budget study.

Chapter 5

OZONE

5.1 Introduction

Ozone is a pungent, faintly bluish gas that irritates the mucous membrane of the respiratory system, causing coughing, choking, and impaired lung function. It aggravates chronic respiratory diseases such as asthma and bronchitis, is corrosive, and leads to the premature aging of many materials such as rubber. Recent studies have emphasized the crop damaging potential of high ozone concentrations.

Ozone is not emitted directly by pollution sources within the troposphere but is produced as a result of the photochemical transformation of precursor chemicals; primarily nitrogen oxides and hydrocarbons. It is the prinicpal component of what is often referred to as smog.

The generation, build-up and dissipation of ozone concentrations in the atmosphere over Eastern North America have been studied by numerous researchers in recent years (e.g., Stasiuk et al., 1975; Chung, 1977; Samson and Ragland, 1977; Vukovich et al., 1977; Wolff et al., 1977; Anlauf et al., 1980). Such studies suggest that the ozone concentration at any given location is the combined result of ozone originating from a number of different sources. These sources include (see Spicer et al., 1979):

(a) natural or "background" ozone, including stratospheric intrusions;
(b) ozone generated from local anthropogenic emissions;
(c) ozone associated with long-range transport and accumulation in high-pressure weather systems; and
(d) ozone formed in urban plumes downwind of cities.

The above studies also indicate that the summer ozone life-cycle is strongly influenced by synoptic scale motion systems. Elevated ozone levels which tend to cover large regions are found typically on the rear sides of anti-cyclones or in the warm sectors of cyclones. The associated transport mechanism has been identified with synoptic-scale motion systems which advect ozone and its precursors, nitrogen oxides and hydrocarbons, over distances of several hundred kilometers. On the resulting regional blanket of ozone, "hot spots" are formed by the ozone generated in urban plumes. Hence, synoptic scale meteorological conditions related to long range transport need to be well understood in order to explain the occurrences of elevated ozone concentrations and to develop effective control strategies. In this chapter, an overview of the current ozone problem in eastern North America is presented with particular emphasis on ozone episodes associated with long range transport and accumulation in high-pressure weather systems.

5.2 Sources and Transport

5.2.1 Ozone Episodes

Ozone episodes in eastern North America are typically associated with high pressure systems which form in central Canada, move southward into the Midwest of the United States or into the Great Lakes area, and then eastward to the Atlantic Coast (Anlauf et al., 1976; Lusis et al., 1976; Wolff et al., 1977; Anlauf et al., 1980). In general, the following sequence describes the relationship between ozone episodes and synoptic weather situations (e.g., Yap and Chung, 1977) (schematically shown in Figure 5-1):

1. Ozone concentrations at the surface begin to increase when the ridge of an anticyclone passes over the region or with the passage of a warm front and the onset of regional southerly flow and warm temperatures. This is the ozone genesis stage.

2. Widespread high ozone levels (typically 80 to 150 ppb) are maintained during persistent south/southwest winds and warm temperatures, when the northwest sector of the anticyclone covers the region or in the warm sector of a cyclone, well ahead of the associated cold front. The air has previously passed over large precursor emission density areas. Ozone values in excess of 150 ppb occur on the back side of the high pressure system when the anticyclonic centre is well to the southeast of the lower Great

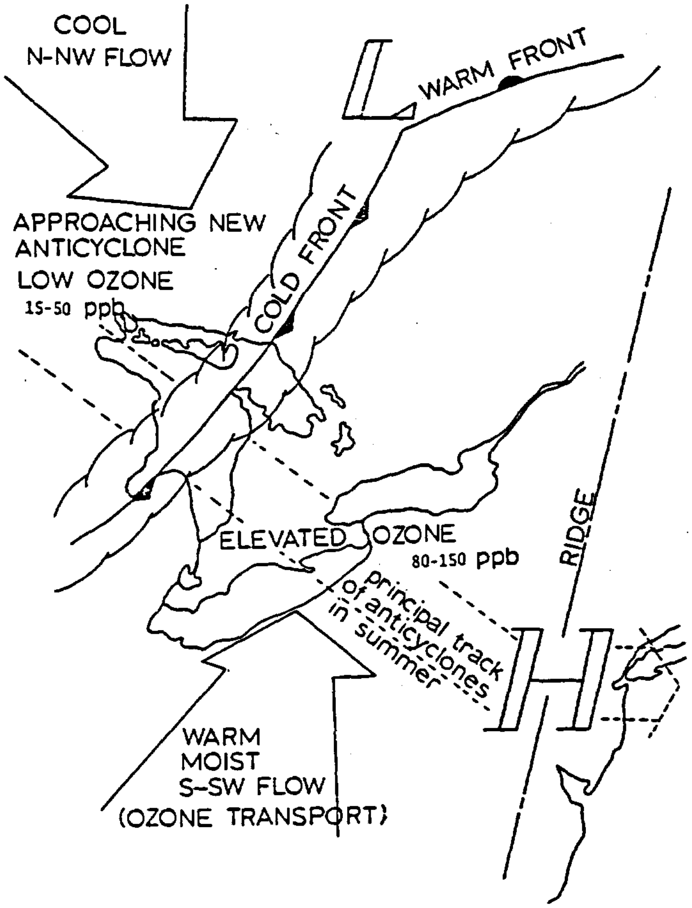


Figure 5-1 Synoptic Meterology Related to Ozone Episodes

Lakes region, often over the Mid-Atlantic Coast or just off the Coast and is quasi-stationary (slow movement eastward). This is the mature ozone stage.

3. As the anticyclone drifts eastward, and the region comes under the influence of an approaching cold front or cyclonic center itself, ozone levels are variable. This is the mixed and dissipation ozone stage.

4. Low ozone values (typically <50 ppb) occur on the arrival of new anticyclones after cold frontal passages, in the forward side of anticyclonic systems with northerly flow, near neutral stability, and reduced temperatures. This is the "background" or natural ozone stage.

Such incidences of elevated ozone episodes in the midwest and northeast United States and southen Canada are generally confined to late spring and summer months. Wolff _et al_. (1977) indicate a typical time interval of 6 to 8 days from the high pressure system's entry over the upper Midwest of the U.S. until its departure over the Atlantic (based on data from summer 1976). It should be noted that climatological statistics show that this movement is along one of the principal tracks of anticyclones in the summer (Klein, 1957). The frequency of these ozone episodes, however, varies considerably from year to year due to fluctuations in meteorological conditions. For example, an analysis of "episode days" (days on which elevated ozone levels over 80 ppb occurred simultaneously over widespread areas at more than eight monitoring sites) in southern Ontario for the five-year period of 1976 to 1980 shows a maximum of 43 days of widespread elevated levels (>80 ppb) in 1978, and a minimum of 14 such events in 1979 and 1980.

This meteorological variability is also manifested in studies of warm stagnating anticylones and associated ozone episodes (e.g., Korshover, 1975; Altshuller, 1978). Over eastern North America, warm stagnating anticyclones occur predominantly between May and October (72% of the time) and the geographical area affected includes the Midwest, mid-Atlantic and

Southeast United States. The July 1974 ozone episode (described by DeMarrais, 1979 and Vukovich, 1979), for example, affected an area of about 1 million square kilometers of eastern United States. The number of stagnation episodes during the period May to October shows considerable variation from year to year (from as little as one episode of 5 days duration to as many as 10 covering a total of 57 days can occur in any one year) (Altshuller, 1978).

In addition to the "typical ozone episodes" described above with the air mass source region in Canada, unusual patterns have also been noted. Wolff and Lioy (1978) described one such episode, which was associated with a high pressure system that formed over the southeastern United States and remained nearly stationary (the July 1977 eastern U.S. heat wave). High ozone was associated with the return (large scale southwest flow of air) around the high pressure system within an "ozone river" from Texas to southern New England. The geographical extent of this episode covered nearly two-thirds of the Eastern Quadrant of the U.S. (approximately 5 million square kilometres) and southern Canada (see Shenfeld et al., 1978), with an ozone concentration greater than 100 ppb over most of the area from the Plains states eastward. To the northeast, levels were above 200 ppb and on one occasion exceeded 300 ppb. It was estimated (Wolff and Lioy, 1978) that ozone concentrations of 90 to 130 ppb travelled about 2300 km in 48 hours.

5.2.2 Source Contribution to Ozone Burden

As indicated previously, ozone monitored at any location is the combined result of natural background levels, the meso and synoptic scale transport, and local atmospheric chemical reactions. The fraction caused by each source is generally difficult to ascertain (Lyons and Cole, 1976). An example of the approximate contributions of various sources to the total ozone burden has been provided by Spicer et al. (1979) for the Northeast Oxidant Study based on Fluorocarbon-11 (F-11) vs. O_3 extrapolations, air mass trajectory analysis, ozone distribution maps and the vertical and horizontal cross-sectional O_3 distribution. In this study, maximum background O_3 and O_3 generated from rural emissions were estimated to contribute 20 to 45 ppb hourly average (20 ppb daily average) to the ozone burden while regional O_3 associated with high-pressure systems contributed 70 to 150 ppb to hourly averages. On the other hand, the maximum O_3 generated within urban plumes was estimated to be 150 to 250 ppb hourly average. These urban ozone plumes are typically distinguishable up to 100 km downwind. Over coastal waters, such plumes have been shown to remain distinct for at least 240 km.

The recent work by Wolff _et al_. (1979) on the distribution of Beryllium-7 within high-pressure systems in the eastern United States should also be noted as it suggests that the contribution of stratospheric ozone ("background") during episodes of high ozone may be higher than previously believed (i.e., >30 to 50 ppb). That study suggests that the stratospheric ozone contribution on the back side of the high-pressure system may be higher than on the front side. Two possible mechanisms are suggested. The first involves the advection of stratospheric air near the surface behind the cold front in a clockwise circulation within the high to the back side. The second involves decoupled stratospheric "rivers" which subside and are convectively transported to surface levels on the back side of the high.

5.3 Measurement Techniques

The major considerations for making useful measurements will be considered under the three headings: (1) instrument selection, calibration, and operation; (2) network design, including the selection of representative monitoring sites and the integration of air monitoring and meterological equipment into a compatible network; and (3) a comprehensive quality assurance program involving maintenance of instrument calibration and comprehensive data evaluation. Brief consideration will be given to monitoring requirements for ozone precursor gases as part of the discussion on network design.

5.3.1 Instrumentation

Equipment for measuring ozone concentrations near the surface has evolved into three basic types; wet chemical, gas phase chemiluminesence, and ultraviolet (UV) absorption. The latter two types are preferred for both accuracy and operational considerations and are in widespread use in air quality monitoring networks. The chemiluminesence method provides for fast response and freedom from interferences by gases other than ozone. The UV absorption method is easy to use and the ozone concentration can be calculated based on the physical properties of the instrument. Instruments of each type are widely available from commercial sources.

The UV absorption technique is now widely recognized as the primary calibration standard. Laboratory instruments using the UV absorption method are maintained as standards by a number of agencies, including the U.S. National Bureau of Standards. Comparison of these standards has shown a high degree of agreement (Wendt et al., 1978). Measurements of ozone should be traceable to one of these standards. Organizations operating a network of ozone monitors should maintain an instrument of the UV absorption type as a network standard for comparison with operational instruments. This network standard should be referenced to an instrument maintained as a national (or better yet, international) standard.

Instrument response at field monitoring sites should be checked at least weekly to determine the ozone zero and span. The station ozone monitor and ozone source should be calibrated against the network primary standard at approximately six-month intervals.

5.3.2 Network Design

Although the criteria discussed here are appropriate for selection of new monitoring sites, it is probable their primary use would be in evaluation of the data from existing sites. Of importance in determining the contribution due to the long-range transport of ozone is the non-urban background station. Such stations should be in remote non-urban areas having no traffic and no industrial activity. At such a site, the contributions to the ozone concentration will be from the natural background, from ozone produced by precursor transformation over long distances, and ozone produced from pollutants and transported long distances. In practice, it is often difficult to separate these three components on the basis of surface ozone observations alone. Measurements of nitrogen oxides act as useful indicators of an anthropogenic contribution. Non-urban background stations are rare in the United States east of the Mississippi River, with the Whiteface Mountain station in northeastern New York State an example from which considerable data has been reported and analyzed. Several other sites able to make non-urban background measurements should also be implemented in the U.S. and Canada.

Since much of the long-range transport of ozone takes place in a layer well above the surface, conditions during geographically large-scale high ozone episodes may best be investigated by the use of instrumented aircraft to determine the horizontal and vertical extent of the ozone reservoir.

Information on pollutant emissions and ozone concentrations in the vicinity of population and industrial centers can best be obtained by making use of already established air pollution networks. Meteorological information is also widely available from current meteorological stations.

5.3.3 Quality Assurance

In making use of information from a number of independent measurement networks, it is important that an evaluation be made as to the type of monitoring site (urban, suburban, regional), the calibration scale to which data is referenced, and the frequency of operational and calibration checks. In many cases, these networks were established to meet requirements of air quality assurance legislation and thus have to meet certain siting and operational requirements. The large number of locations making ambient ozone observations provide a strong data base for conclusions about ozone in and around urban areas and the extent of large-scale ozone episodes. There is sufficient redundancy in the measurements to check the consistency of temporal and spatial variations within the area of an episode.

In properly apportioning the contribution to the ozone distribution between a natural background, a locally produced pollution component and a pollution component transported to the site, several regional background stations with carefully compared calibration standards should be established to measure ozone and nitrogen oxides. These stations in the U.S. and Canada would determine if any long-term trends in the ozone concentration were taking place on a broad geographic scale and would help isolate the natural component of the ozone distribution.

5.4 Summary

This survey summarizes some of the recent studies of widespread elevated ozone concentrations associated with long-range transport and accumulation in high pressure weather systems in eastern North America. Ozone episodes, and indeed the entire ozone life-cycle, are shown to be strongly influenced by synoptic meteorological conditions.

The discussion of techniques for monitoring the long-range transport of ozone has emphasized the use to be made of the extensive number of measurements already being made and the evaluation of the quality of these measurements. In addition, it is proposed that several sites using carefully inter-calibrated instrumentation be established to determine regional long-term changes in the near-surface ozone distribution.

Chapter 6

ORGANICS

6.1 Introduction

The use and distribution in the environment of man-made organic compounds has increased dramatically in the post-war period. Current estimates indicate that 40,000 to 50,000 different chemicals are routinely used in North America and several hundred new organic substances are produced every year. Many of these have chemical, biological and physical properties which are environmentally undesirable; i.e., persistence, toxicity at trace levels to mammals and other biota, teratogenic and carcinogenic effects in man. It is convenient to make a distinction between low and high molecular weight organics, since the sampling methods and environmental behavior of these two classes are different. The low molecular weight compounds, of which solvent vapors, freons, and light hydrocarbon gases are examples, will not be considered here. Rather, attention will be focussed on compounds having molecular weights of about 200 to 400 and vapor pressures in the 10^{-4} to 10^{-9} torr range. Many organic pollutants fall into this category, including polychlorinated biphenyls and polychlorinated naphthalenes (PCB and PCN), phthalate esters, pesticides, and polycyclic aromatic hydrocarbons (PAH). Detailed information on sampling methods, aerial distribution, and atmospheric removal mechanisms for these compounds have been presented in several reviews (Lewis and Lee, 1976; Bidleman et al., 1976; NAS, 1978; Galloway et al., 1979; Daisey, 1980; Eisenreich et al., 1980, 1981; Lamb et al., 1980; Simoneit and Mazurek, 1981). The intent here is not to duplicate this information but rather to briefly assess our present capabilities for collecting and analyzing trace organics in the atmosphere and the extent of our knowledge concerning their atmospheric behavior.

The atmosphere, specifically the lower troposphere, acts as an important reservoir and vehicle for distribution and transport of some of these compounds to areas hundreds and even thousands of kilometres from known sources. Measurements have identified these compounds in atmospheric particulate matter, as vapors and in precipitation in urban, rural and remote marine areas. Atmospheric pathways must therefore play an important role in the distribution of polynuclear aromatic hydrocarbons, polychlorinated biphenyl, pesticides, herbicides, and phthalate esters.

6.2 Sampling Methods

6.2.1 Trace Organics in Air as Vapors and as Particulates

High molecular weight organics are present in air as vapors and absorbed onto suspended particles, with the particle/gas (P/G) ratio depending on the vapor pressure of the organic compound and the available surface area of particulate matter in air (Junge, 1977). Most high volume sampling systems pull air through a glass fiber filter, which removes particles of 0.015 micron and larger radius with 98% efficiency (Butcher and Charleson, 1972), and then through a solid absorbent trap to retain the organic vapors. These systems sample about 300 to 600 m^3 of air in a 24-hour period, and have a distinct advantage over previously used bubblers and impingers which could sample only one-tenth this volume per day.

Several solid absorbents have been evaluated for collecting trace organic vapors, including polyurethane foam (PUF), Tenax-GC resin, Amberlite XAD-2 resin, and Florisil. The list of applications in Table 6-1 is representative, but by no means exhaustive. Most of these applications have been for chlorinated organics, with analysis by electron capture gas chromatography (EC-GC). Thus, absorbent cleanup procedures which give satisfactory blanks for electron capturing materials may not be adequate if other classes of organic compounds are to be analyzed using a less selective detection system, e.g. flame ionization. Retention of an organic vapor by a solid absorbent bed depends on the vapor pressure and the total volume of air pulled through the collector. Frontal movement of PCB vapors through PUF and XAD-2 beds has been demonstrated in laboratory and field studies (Hollod and Eisenreich, 1981; Burdick and Bidleman, 1981; Billings and Bidleman, 1982). From collection studies with PCB isomers of known volatility, a 10-g plug of PUF will effectively collect compounds less volatile than about 10^{-4} torr for air volumes of 500 m^3 or less (Simon and Bidleman, 1979; Burdick and Bidleman, 1981). This includes the PCB isomers in the most common PCB mixtures

TABLE 6-1 SOLID ADSORBENTS FOR COLLECTING TRACE ORGANIC VAPORS

Adsorbent	Applications	References
PUF	PCB, chlorinated pesticides	Billings and Bidleman, 1980, 1982; Burdick and Bidleman, 1981; Stratton *et al.*, 1978; Adams and Caro, 1980; Lewis *et al.*, 1977; Turner and Glotfelty, 1977
	Organophosphate pesticides	Lewis *et al.*, 1977; Adams and Caro, 1980
	PCN	Lewis *et al.*, 1977; Erickson *et al.*, 1978
	PAH	Thrane and Mikalsen, 1981; Krstulovic *et al.*, 1977; Dettmer and Bidleman, 1982
	Phthalate esters	Giam *et al.*, 1978, 1980
Tenax-GC	PCB, chlorinated pesticides	Billings and Bidleman, 1980, 1982
	PAH, hydrocarbons	Cautreels and Van Cauwenberghe, 1978; Broddin *et al.*, 1980; Jones *et al.*, 1977.
XAD-2	PCB, chlorinated pesticides	Billings and Bidleman, 1982; Doskey and Andren, 1979, 1981; Hollod and Eisenreich, 1981; Farwell *et al.*, 1977
	PAH	Adams *et al.*, 1977; Jones *et al.*, 1977; Strup *et al.*, 1976
Chromasorb resins	Pesticides	Thomas and Seiber, 1974; Seiber *et al.*, 1975
Florisil	Phthalates, PCB	Giam *et al.*, 1975, 1978; Atlas and Giam, 1981

(Aroclors 1016, 1242, 1254, and 1260) as well as the chlorinated pesticides DDT, DDE, chlordane, and toxaphene. Field sampling investigations have also shown the ability of PUF to collect the above vapors in a 24-hour period without breakthrough (Billings and Bidleman, 1980, 1982).

Compounds that are not well retained by PUF, for example hexachlorobenzene (HCB), are more effectively collected by Tenax-GC or XAD-2. Side-by-side field comparisons of PUF, Tenax-GC, and XAD-2 showed that concentrations of Aroclor 1016, Aroclor 1254, chlordane, and toxaphene measured with the three absorbents were in excellent agreement (Billings and Bidleman, 1980, 1982). Average relative standard deviations for organochlorine levels measured with the different absorbents ranged from 10 to 15% in most cases, with the precision limited more by the analytical method than by the sampling system. HCB concentrations measured with Tenax-GC and XAD-2 agreed well, and were several times higher than those obtained using PUF (which does not trap HCB effectively). Front and backup traps for these experiments contained 8 g PUF, 10 g Tenax-GC, or 20 g XAD-2. The breakthrough of Aroclor 1016 (mainly di- and trichlorobiphenyls) to backup traps averaged about 10% for PUF and Tenax-GC, and <5% for XAD-2.

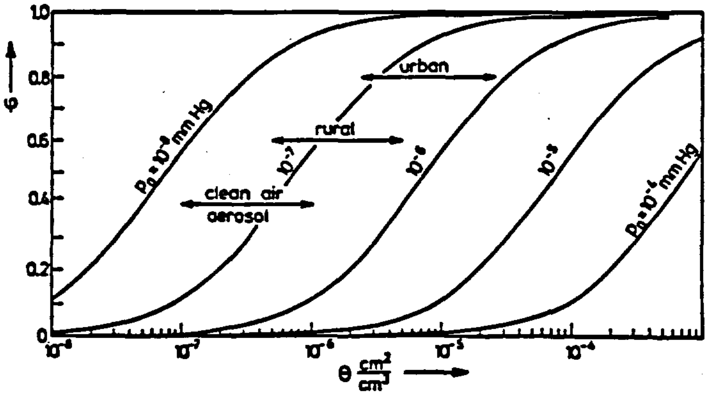
Other reports of PCB retention by XAD-2 vary. Doskey and Andren (1979) found that a 70-g XAD-2 trap retained 75 to 90% of a spike of the light PCB mixture Aroclor 1221 (mainly mono- and dichlorobiphenyls) for air volumes up to 1400 m^3, while 92 to 100% of a trichlorobiphenyl spike was retained for air volumes in the 700 to 3000 m^3 range. On the other hand, Hollod and Eisenreich (1981) observed extensive penetration of Aroclors 1242 and 1254 into a 400 to 600 g XAD-2 bed during field collections, with the PCB breakthrough volume for a 600-g resin bed approximately 340 m^3. Displacement of PCB by more strongly absorbed organics was suggested as responsible for the poor PCB retention.

Less information is available on high volume collection efficiencies for other classes of organics. Tenax-GC and XAD-2 have been evaluated for collecting PAH vapors from stack gases (Jones et al., 1977; Strup et al., 1976), however only recently have vapor-phase PAH been sought in ambient air. Cautreels and Van Cauwenberghe (1978) measured gaseous PAH, aliphatic hydrocarbons, and organic acids in urban air using a combination of high- and low-volume sampling techniques. Air was pulled through a glass fiber filter in a conventional hi-vol sampler, and the effluent stream was then split in about 16:1 ratio and the smaller volume was passed through a Tenax-GC cartridge. Thrane and Mikalson (1981) used two 12-g PUF plugs behind a 142-mm diameter glass fiber filter to trap particulate and gaseous PAH. At air volumes of 600 to 750 m^3 about 30 to 40% of the two-ring PAH (napthalene and biphenyl) broke through to the second PUF trap. Three- and four-ring PAH (phenanthrene, anthracene, pyrene) were more effectively retained, with 80 to 90% on the first PUF trap. Dettmer and Bidleman (1982) also investigated PUF for collecting PAH vapors, and found breakthrough percentages for three- and four-ring aromatics similar to those of Thrane and Mikelson. While detailed collection studies of PAH vapors from ambient air have yet to be done, the above preliminary information indicates that PUF can serve as an effective monitoring absorbent for three-ring and heavier PAH vapors in a normal 24-hour sampling period.

6.2.2 Particle-Vapor Partitioning of Trace Organics

Junge (1977) has calculated isotherms for the absorption of organic vapors to airborne particles. Figure 6-1, shows the relationship between the fraction of aerosol-absorbed organics, vapor pressure, and the available surface area of suspended particulate matter in air. How closely filter-retained/absorbent-retained ratios found with hi-vol sampling systems approximate the true P/G distribution in the atmosphere is unknown. During sampling it is possible that organics are lost from particles trapped on the filter by volatilization, or gained by absorption onto the bed of particles on the filter. Most investigators have discussed the former process as the more likely, i.e., that hi-vol sampling systems underestimate the true P/G ratio in air, but definitive experiments to settle the question have not been done.

Most reports of PCB and pesticides in air have stressed the importance of the vapor phase. Reported filter-retained percentages for PCB and pesticides have generally been under 10% (Table 6-2), although exceptions have been noted. While sampling in Denver at temperatures below 0°C and total suspended particle concentrations exceeding 100 μg m^{-3}, Billings and Bidleman



$$\text{RATIO } \varphi = \frac{\text{ADSORBED ON AEROSOL}}{\text{TOTAL CONCENTRATION}}$$

OF COMPOUNDS AS FUNCTION OF SATURATION VAPOR PRESSURE P_0 AND AEROSOL SURFACE Θ

Figure 6-1 Calculated Distributions of Organics between the Particle and Vapor Phases, ϕ = the Fraction of Aerosol-Bound Organics. From Junge, 1977

TABLE 6-2 FILTER-RETAINED/ADSORBENT-RETAINED RATIOS FOR ORGANICS

	Apparent P/G	Reference
PCB		
Columbia, SC (Aroclor 1254)	0.06	Billings and Bidleman, 1980
Denver, CO (Aroclor 1254)	1.8	Billings and Bidleman, 1982
Toronto, Ont.	0.16 - 0.75	Gilbertson, 1976
Chicago, IL (Total PCB)	0.03	Murphy and Rzeszutko, 1977
Milwaukee, WI (Total PCB)	0.16	Doskey and Andren, 1981
Madison, WI (Total PCB)	0.03	"
Lake Michigan	0.12	"
Lake Superior	0.0 - 0.05	Hollod, 1979; Eisenreich *et al.*, 1980, 1981
North Atlantic (A. 1248, 1254)	<0.05 - <0.1	Bidleman *et al.*, 1976, 1981
(Aroclor 1254)	<0.01	Harvey and Steinhauer, 1974
Gulf of Mexico (Aroclor 1254)	<0.01	Giam *et al.*, 1980
Phthalate esters		
Gulf of Mexico	0.47 - 0.75	Giam *et al.*, 1980
PAH, Other Hydrocarbons		
Urban air, Belgium		
phenanthrene, anthracene	0.03	Cautreels and Van Cauwenberghe, 1978
pyrene	0.49	"
benzofluorenes	1.2	"
benzanthracene, chrysene	3.2	"
benzopyrenes	7.5	"
n-C_{19}	0.05	"
n-C_{21}	0.26	"
n-C_{23}	1.4	"
n-C_{25}	1.7	"
n-C_{27}	1.4	"
n-C_{29}	2.4	"

TABLE 6-2 (cont.)

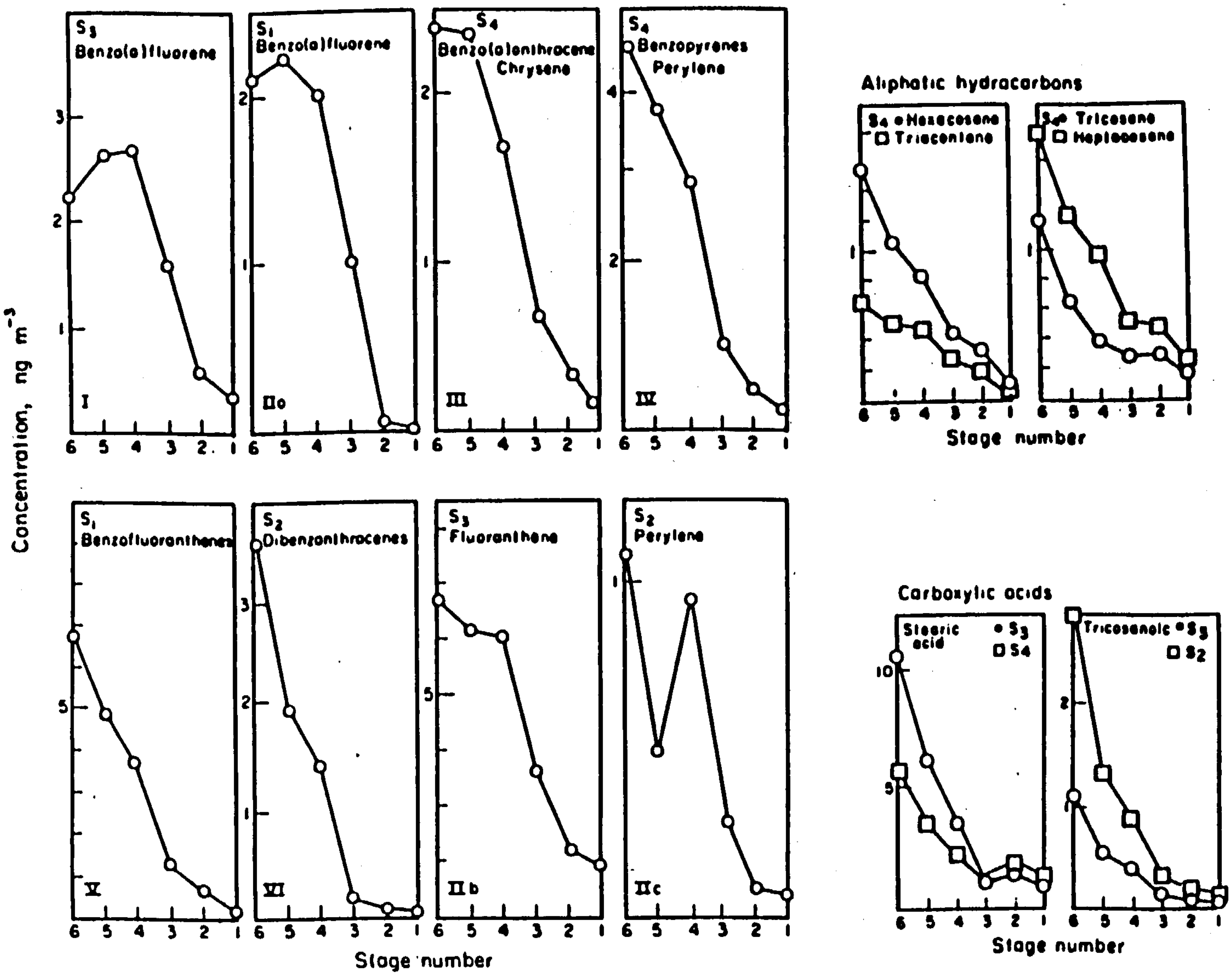
	Apparent P/G	Reference
Ghent, Belgium		
phenanthrene, anthracene		
Jan. - Feb.	0.25-0.45	Broddin *et al.*, 1980
July - Aug.	0.06-0.17	"
pyrene		
Jan. - Feb.	5.3 - 7.6	"
Aug	0.62	"
chrysene, benzanthracene		
Jan. - Feb.	13 - 22	"
July - Aug.	0.51 - 0.84	"
benzopyrenes, perylene		
Jan. - Feb.	8.3 - 17	"
July - Aug.	5.3 - 6.6	"
Lillestrom, Norway		
phenanthrene, anthracene	0.05	Thrane and Mikelson, 1981
pyrene	0.40	"
benzofluorenes	1.6	"
chrysene, triphenylene	2.8	"
benzopyrenes, perylene	8.3	"

(1982) found over half of the Aroclor 1254, DDE, and chlordane retained by the glass fiber filter. Gilbertson (1976) found 14 to 43% filter-retained PCB in Toronto. Vapor pressures for PCB and pesticides are highly temperature dependent, with the vapor pressure nearly doubling for a 5°C rise in temperature (Spencer and Cliath, 1972; Spencer et al., 1979; Westcott and Bidleman, 1981). Temperature is thus probably the single most important factor in governing P/G ratios for trace organics.

In contrast to the chlorinated organics, nearly all airborne PAH measurements have been restricted to material retained on glass fiber filters. Recent work, however, has indicated the importance of a vapor-phase contribution to the atmospheric PAH load, especially for the aromatics of four rings and lower. Cautreels and Van Cauwenberghe (1978) observed an increase in the filter-retained/absorbent retained ratio with molecular weight for PAH, aliphatic hydrocarbons, and organic acids (Table 6-2). Thrane and Mikelson (1981) found that the vapor (absorbent-retained) percentage for pyrene, benzofluorenes, and phenanthrenes was 50% or more, while 80% or more of the benzopyrenes, dibenzoanthracenes, perylene, and coronene were retained by the filter. Broddin et al. (1980) found that this distribution varied with temperature, with higher proportions of the PAH being filter-retained during the winter than in the summer (Table 6-2). Many size distributions have been measured for particulate PAH (see reviews by Lamb et al., 1980; Daisey, 1980; Simoneit and Mazurek, 1981). Highest concentrations are found on submicron particles, which may reflect a greater degree of absorption to particles with high surface/volume ratios. Size distributions for aliphatic hydrocarbons and organic acids are similar (Van Vaeck and Van Cauwenberghe, 1978, Figure 6-2).

6.2.3 Trace Organics in Rain and Dry Deposition

Most information on trace organics in rain has been obtained using continuously exposed collectors that sample precipitation plus dry deposition. The advantages of these "bulk" collectors are that they are cheap, often consisting of nothing more than a jug and a funnel. Bulk collectors require no power, an important consideration for sampling at remote sites, and they provide an integrated measure of atmospheric input per unit area. A serious drawback is that these collectors are easily contaminated by



STAGE	DIAMETER
1	>7.2
2	7.2 – 3.0
3	3.0 – 1.5
4	1.5 – 0.95
5	0.95 – 0.49
6	<0.49

Figure 6-2 Size Distribution for Particulate Organics from Van Vaeck and Van Cauwenberghe, 1978

bird droppings and insects. Moreover, they do not differentiate between input by precipitation and by dry deposition, and may not effectively mimic any natural surface.

Several recent examples of using bulk collectors to monitor PCB and pesticides in precipitation may be given. Peakall (1976) noted elevated levels of DDT in rain in upstate New York shortly following aerial DDT spraying in Washington, Oregon, and Idaho in 1974. Wells and Johnstone (1978) monitored seven stations on the eastern coastline of Great Britian for PCB, DDT residues, dieldrin, and hexachlorocyclohexane (HCH) during 1975-76. Average concentrations (ng/liter) were: total DDT = 7.9, total HCH = 10.4, dieldrin = 1.3, and PCB = 14.9. Harder et al. (1980) used stainless steel funnels emptying into glass jugs to determine aerial PCB and pesticide inputs to a South Carolina estuary. Compounds identified included PCB, chlordane, DDT, and toxaphene, with toxaphene concentrations 10 to 100 times higher than those of the other organochlorines. Toxaphene levels averaged 45 ng/liter for 60 samples collected in 1977, with some concentrations exceeding 100 ng/liter.

An interesting way to measure total aerially-derived pollutants is to analyze snow or ice cores. This bulk collection method, subject to the same contamination problems as mentioned above has been used by several workers: Peel (1975), to measure DDT in Antarctic snow, Murphy et al. (1981) to estimate aerial PCB input to lakes Michigan and Huron, Lunde et al. (1976, 1977) to measure chlorinated and non-chlorinated organics in Norway, Swain (1978) to estimate aerial PCB input to Isle Royale, Lake Superior, and Strachan et al. (1980) to survey atmospheric pesticide and PCB loadings in Southern Ontario.

Event rain sampling minimizes contamination by birds and insects, and permits rain-only values to be determined. Bidleman and Christensen (1979) and Harder et al. (1980) collected rain at a South Carolina estuary using large aluminum pans or stainless steel bowls. Concurrent measurements of PCB and pesticides in air allowed washout ratios (W = g pollutants/g rain + g pollutant/g air) to be calculated for the various organochlorines. The same collection method was used to measure DDT and HCH in rainfall on a cruise in the equatorial Arabian Sea (Bidleman and Leonard, 1982). Murphy and

Rzeszutko (1977) found 193 ± 145 ng/liter PCB in 31 event rain samples collected in Chicago, IL, and on Beaver Island, Lake Michigan in 1975-76.

The HASL automated wet/dry collector (Bogen et al., 1980; Volchok and Graveson, 1976) should be useful for sampling organics in precipitation, when used with metal or glass collection vessels. Plastics are not suitable for trace organics work because they may introduce contamination or cause losses by absorption to the plastic surface. Teflon may be on exception. Other problems are encountered in using automated precipitation collectors. Organics in the collected rain are subject to revolatilization losses and to chemical and bacterial breakdown. To circumvent these difficulties and transportation problems, some investigators are drawing the collected rain sample through a plug of polyurethane foam (Wells and Johnstone, 1978), or through a glass fiber filter-PUF combination (Murphy and Rzeszutko, 1977). In both of the above studies, the PUF plugs were coated with DC-200 silicone oil.

Dry deposition of trace organics occurs by gravitational settling and turbulent impaction of aerosol-bound materials, and absorption of vapors to the deposition surface. A variety of surfaces have been used to sample organic dry deposition. Sodergren (1972) and Bengtson and Sodergren (1974) coated a nylon mesh screen with silicone oil and exposed the nets for 2 to 3 months at a time to determine total aerial fluxes per unit area. The nets probably collected particles by filtration as well as impaction. McClure and LaGrange (1977) and Young et al. (1975, 1976) used mineral oil-coated glass plates to estimate dry deposition of DDT and PCB with over 1000 fallout samples in southern California. Heesen et al. (1979) exposed sets of these collection plates over 1- to 8-day periods and found that the collection efficiency decreased over an 8-day period; that is, residues on plates exposed for 8 days were less than the sum of residues recovered from plates exposed for 1-, 2-, or 4-day intervals over the same time period.

Murphy (1980) criticized the use of oil-coated surfaces to sample organic dry deposition, because of the possibility that the oil might scavenge vapors with an unknown efficiency as well as particles. Murphy recommended the use of a polar fluid, and has used glass fiber filters coated with diols to collect PCB dry deposition (Murphy et al., 1980). Hollod (1979) and

Eisenreich and Hollod (1981) collected PCB dry deposition on glass plates coated with glycerol. Christensen et al. (1979) evaluated three surfaces for sampling PCB, DDT, and chlordane fallout. Pans filled with water or ethylene glycol-water to simulate a natural water surface were compared to glycerol-sprayed and dry pans of the same geometry. On the average, the wet surface pans collected 1.5 to 3 times as much organochlorine dry deposition as did the dry surface pans, with no differences between the types of wet surfaces.

How well any of these surrogate surfaces approximate dry deposition to a surface of environmental interest (lake, plant foliage) is unknown. From the results of Christensen et al. (1979), one might conclude that a dry bucket of the type used in the HASL collector would underestimate dry deposition of PCB and pesticides to a water surface. Many models have been developed to predict particle and gas dry deposition to surfaces of various geometries and to water. A few recent articles on the subject are Slinn et al. (1978), Slinn and Slinn (1980), Sehmel (1980), Sievering (1981), and Doskey and Andren (1981). A workshop held at Argonne National Laboratory in November 1979 evaluated methods to measure dry deposition (Hicks et al., 1980). A conclusion of the workshop was that surrogated surfaces are not accurate enough estimators of fallout fluxes to use in monitoring networks. Instead, research was recommended on using micrometeorological parameters to calculate dry deposition fluxes from atmospheric concentrations. Other workers disagree and feel that more emphasis should be placed on field comparisons of fallout fluxes to surrogate and "real" surfaces. In any case, the inability to estimate accurately dry deposition fluxes remains a barrier to understanding the air-sea and air-land cycling of trace organics.

6.3 Analytical Methods for Trace Organics

6.3.1 Organochlorines

Electron capture gas chromatography (EC-GC) remains the most important analytical technique for chlorinated pesticides and PCB. PCB mixtures contain about 15 to 20 major components, many of which overlap gas chromatographic peaks from pesticides. Several column chromatographic techniques are available to separate PCB from the majority of the pesticides of interest however, and these methods are in use by most laboratories. A more difficult problem is the occurrence of multi-component chlorinated pesticides in samples. Gas chromatograms of chlordane, a common termiticide, contain about 15 major peaks (Sovocool et al., 1977), while technical toxaphene contains nearly 180 components (Holmstead et al., 1974). Separation of chlorinated pesticides from each other as well as from PCB can be partially accomplished by silicic acid column chromatography prior to EC-GC analysis (Bidleman et al., 1978; Zell and Ballschmitter, 1980), but extensive pre-fractionation schemes are very time-consuming. The use of glass capillary columns has greatly improved the chromatographic resolution attainable, but separation problems still exist. For example, no technique has been developed which will completely separate technical chlordane from toxaphene.

Identifications of multi-component organochlorines (PCB, toxaphene) are usually made by matching the gas chromatographic fingerprints of samples against those of standards. Sample patterns are often altered from standard fingerprints. For example, toxaphene residues in air frequently contain a higher proportion of the more volatile components (Seiber et al., 1979; Billings and Bidleman, 1980). Air samples also contain greater amounts of the lower molecular weight PCB isomers, while rain and fallout are enriched in the heavier components (Murphy and Rzeszutko, 1977; Bidleman and Christensen, 1979). In addition to identification problems, quantitation of altered fingerprints is uncertain. The electron capture detector is very sensitive for chlorinated molecules, but its response is not directly related to the number of chlorines on the molecule. Thus, gas chromatographic response factors derived from the total peak height or area of complex standard patterns may or may not give accurate results when used to calculate sample residues. One approach to this problem for PCB has been to develop response factors for individual PCB isomers in Aroclor mixtures and use these response factors to calculate PCB residues for each matching sample peak (Webb and McCall, 1973; Sawyer, 1978a,b). A second approach, again for PCB residues, has been to convert the complex mixture of PCB in the sample to a single derivative (decachlorobiphenyl) and quantify PCB in terms of the decachlorobiphenyl peak (Armour, 1973; Trotter and Young, 1975). The method was applied to PCB in air samples by Stratton et al. (1978). Unfortunately, it is sometimes difficult to obtain antimony pentachloride of sufficient purity (Trotter and Young, 1975), and some PAH may also form perchloro-derivatives (Hutzinger et al., 1973).

Many chemical derivatization techniques are available to confirm pesticide residues by gas chromatography. Perchlorination of PCB to decachlorobiphenyl has been mentioned above. Treatment of the sample with alcoholic KOH converts DDT isomers to their corresponding DDE products, and dehydrochlorinates chlordane isomers to chlorochlordenes, which have characteristic CC retention times. Toxaphene can also be reacted with alcoholic KOH to produce an altered fingerprint which can be matched against a similarly treated sample. Some references to chemical derivatization methods are given in Table 6-3.

Gas chromatography-mass spectrometry (GC-MS) has become a very important technique for confirming organic residues. If the quantities of material are too small to obtain complete mass spectra, selected monitoring of a few ions allows compounds to be confirmed at greatly increase sensitivity (Budde and Eichelberger, 1977). Halogenated aromatics and PAH generally have relatively simple spectra, but toxaphene fragments extensively under electron impact. Recently Dubay et al. (1981) have used negative ion mass spectrometry to confirm toxaphene residues in fish, with much more sensitivity than attainable by conventional electron impact mass spectrometry.

Analytical reliability for organochlorines has been checked by inter-laboratory calibration studies using a variety of sample types, including marine sediments (Pavlou and Hom, 1976), water (Aspila et al., 1977), chicken fat and milk (Sawyer, 1978b), and tissue samples (Harvey et al., 1974; Holden, 1973). Only one similar study has been done for air, and none for rain and dry deposition. Bidleman (1981) circulated extracts of high volume air samples taken in Columbia, SC, and Boston, MA, among nine laboratories experienced in pesticide and PCB analysis. Most of the laboratories used packed column GC analysis, with only two reporting the use of capillary GC. One laboratory confirmed the presence of chlordanes, PCB, DDE, HCH, dieldrin, and several PAH by GC-MS. Relative standard deviations (% RSD) for Aroclor 1254 were 18% and 44% for the Boston and Columbia samples, while percent RSDs

TABLE 6-3 CHEMICAL DERIVATIZATIONS FOR TRACE ORGANICS

Compounds	References
PCB	Armour, 1973; Trotter and Young, 1975; Stratton et al., 1978.
DDT, DDD, HCH	Sans, 1967; Young and Burke, 1972; Cochrane and Maybury, 1973.
cyclodienes: chlordane, dieldrin, heptachlor, endrin, endosulfan	Chau and Cochrane, 1969; Cochrane and Chau, 1971; Maybury and Cochrane, 1973; Chau and Lanouette, 1972; Chau and Terry, 1972; Musial et al., 1976; Chau et al., 1974.
HCB	Baker, 1973
toxaphene	Harder et al., 1980; Gomes, 1977; Crist et al., 1980
organophosphate pesticides	Coburn and Chau, 1974; Singh and LaPointe, 1974.
phthalate esters	Giam et al., 1976

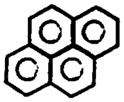
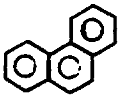
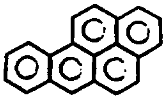
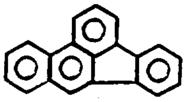
for Aroclor 1016/1242 were 47% and 43% for these two cities. Precisions for pesticides were generally poorer than those for PCB. RSDs ranged from 35 to 75% for most pesticides, and as high as 116% for toxaphene. A great need exists for more of these intercomparison studies for air, rain, and fallout, as well as for interlaboratory comparisons of sampling techniques.

6.4 Important Atmospheric Organics

6.4.1 Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons are produced by common combustion sources such as coal, wood or oil burning and are also found in the exhaust from diesel engines. Fused chains containing five or six carbon atoms with delocalized electrons characterize the molecular structure of PAHs and enhance their environmental stability. In general, PAHs have high melting points, low vapor pressure and low water solubility. Specific data for some typical PAHs are summarized in Table 6-4 (Lao et al., 1973; Eisenreich et al., 1980; National Research Council, 1979).

TABLE 6-4 SPECIFIC DATA FOR SOME TYPICAL PAHs

Compound	Molecular weight	Boiling Point °C	Vapor Pressure mm Hg 25°C	Structure	Potential Carcinogenic effects
Pyrene	192	>360	0.09		Not carcinogenic
Phenanthrene	178	340	0.04		Not carcinogenic
Benzo(a)pyrene	228	>360	6.6×1^{-7}		Potent carcinogenic
Benzo(b)fluoranthene	252	393	Approx. 10^{-7}		Potent carcinogenic

PAHs, monitored in urban areas, are found to be strongly associated with particulate matter (Pierce and Kutz, 1975; Lao et al., 1973; Cautreels and Cauwenberge, 1978). However, the vapor pressures of some PAHs are greater than 10^{-6} Torr and evidence indicates that 10 to 50% of these PAHs exist in the vapor form at summer temperatures. Present sampling techniques are unable to differentiate between the true amounts of PAHs associated with particulate matter or in the vapor form. Particulate PAH content is experimentally defined as the fraction found on a filter medium whereas the vapor form is the fraction passing through the filter. The latter fraction can be trapped by passing the air through a chromatographic support (Kornis et al., 1980; Peters and Seifert, 1979; Pierce and Kutz, 1975; Lao et al., 1973; Barton et al., 1979). Ample evidence exists for the toxic and carcinogenic properties of PAHs.

Analytical Technique for PAHs

PAH are commonly analyzed by either gas chromatography or high performance liquid chromatography (HPLC). A thorough review of analytical methods for PAH has appeared (Bartle et al., 1981), so the subject will be touched only briefly here. Excellent resolution of PAH mixtures is obtained on glass capillary columns coated with non-polar or slightly polar station phase, such as SE-52 or SE-54. Separation on these columns is controlled by vapor pressure alone. Selectivity for PAH may be achieved on a nematic liquid crystal phase such as NN'-bis(p-alkoxybenzylidene)-α,α'-bi-p-toluidine, which allows resolution if isomeric PAH such as anthracene and phenathrene, and benzo(a)pyrene and benzo(e)pyrene. If a flame ionization detector is used, identifications are based strictly on retention time since this detector is non-selective. PAH can also be detected by electron capture, although few applications of this detector for airborne PAH work have been reported. Perhaps the interference by chlorinated hydrocarbons in air is too great. Electron impact mass spectra of PAH are simple, consisting of intense molecular ions with a few lower ions resulting from hydrogen losses. Quantitative GC-MS analysis of PAH using selected ion detection has been developed, which eliminates the need to pre-fractionate the sample extract (Cautreels and Van Cauwenberghe, 1977, 1978; Broddin et al., 1980). A drawback of GC-MS is that in most cases differentiation of PAH isomers cannot be achieved.

Separations of PAH by HPLC are not as efficient as obtained by using capillary GC, however, HPLC has several advantages. A choice of stationary phases and solvent systems makes it possible to separate PAH that are difficult to separate by GC. Reversed-phase columns such as chemically bonded C_{18} are most popular. These are capable of separating PAH isomers and methyl-substituted PAH, when used with a gradient elution system. Polar amine phases have also been used. These columns separate PAH by ring number, with methyl substitution having little effect on retention time. Both UV and fluorescence detection are used for HPLC analysis of PAH. The UV detector is universal for PAH, while fluorescence is more sensitive and selective. Wavelength choices for selective fluorescence detection of PAH have been discussed by several workers, and the subject is reviewed in Bartle _et_ _al_. (1981).

Several workers have investigated different solvent systems to extract PAH from particles on glass fiber filters. Acetone, benzene, and cyclohexane all recover PAH efficiently from filters. Soxhlet extraction or ultrasonic vibration is used as an extraction technique; the ultrasonic method has been adopted by NIOSH (1977). Extraction of PAH is difficult from carbon black and fly ash, even by the ultrasonic method. A number of schemes have been worked out to separate PAH from other organics prior to the final analysis step, including absorption chromatography on silica gel or Florisil, size exclusion chromatography, and solvent-solvent partitioning. References to several of these methods, as well as extraction techniques, are given in Bartle _et_ _al_., (1981).

A great aid to developing reliable analytical procedure for a trace constituent is to have available a certified standard. The National Bureau of Standards has developed two urban particulate matter standards (standard reference material 1648), collected in St. Louis, MO, and Washington, DC, which are certified for trace metal content. Very recently, the Washington dust sample has also been certified for PAH. The use of this reference material by all laboratories analyzing air samples for PAH should increase the overall quality of PAH analyses. Unfortunately, similar reference materials for organochlorines are not yet available.

Measurements

The low vapor pressures of most PAHs suggest that these compounds should be found principally in the atmospheric aerosol. Factors that influence the vapor to particulate ratio for PAHs in air include the total aerosol surface area available, the aerosol carbon content and the temperature. Extensive measurements have shown that PAH concentrations are highest in urban air, i.e., close to the major sources. Rural sources are relatively unimportant. The increased burning of fossil fuels and the lower average mixing heights for the atmosphere in winter ensures that the highest ground level concentrations occur in winter months (23). Volatility losses are also minimized by low temperatures, contributing to higher apparent concentrations in the winter (Peters and Seifert, 1979; Funke *et al.*, 1981; Katz *et al.*, 1978; Pierce and Kutz; 1975; Lao *et al.*, 1973; Bidleman and Olney, 1975). This is especially true for the lower molecular weight PAHs with the highest vapor pressures. Results obtained from urban and suburban areas of four Ontario cities, Toronto, Hamilton, Sarnia and Sudbury, during late winter and spring of 1977 indicate typical levels (Katz *et al.*, 1978; Pierce and Kutz, 1975) of:

0.11 to 3.5 ng m^{-3} for B(a)P,
0.02 to 3.8 ng m^{-3} for B(e)P,
0.17 to 7.8 ng m^{-3} for B(b)F,
0.06 to 5.1 ng m^{-3} for B(k)F,
0.01 to 0.40 ng m^{-3} for Pereylene,
0.01 to 0.37 ng m^{-3} for Dibenzo(def, m, n, o)chrysene,
0.78 to 10.5 ng m^{-3} for Benzo(ghi)perylene,
0.61 to 2.76 ng m^{-3} for Naptho(1,2,3,4,def)chrysene,
0.01 to 0.43 ng m^{-3} for Benzo(ast)pentaphene, and
0.05 to 1.13 ng m^{-3} for Dibenzo(b,def)chrysene.

Other measurements of B(a)P concentrations of:

0.15 to 1.3 ng m^{-3} for N.Y.C.,
5.7 ng m^{-3} for the U.S. urban average,
1.6 ng m^{-3} for Antwerp,
5.2 ng m^{-3} for Ghent, and
1.5 ng m^{-3} for Milan,

show that the Canadian values are typical of urban areas.

Due to control measures and pollution abatement programs, a downward trend in atmospheric PAH concentrations has been observed in the past 10 years in the U.S., from 6 to 7 ng m^{-3} for B(a)P in the late 1950s to 2 ng m^{-3} in the early 1970s (Eisenreich et al., 1980).

PAHs have not been measured as extensively in rural and remote areas. The range of concentrations are 0.02 to 6 ng m^{-3} and 0.04 to 5 ng m^{-3} for phenanthrene and anthracene in rural areas, somewhat lower than the range of values for urban air.

Since many PAHs have vapor pressures lower than 10^{-6} Torr, it is not unexpected that greater than 80% are usually associated with atmospheric particulate matter. Measurements have consistently found particulate PAHs to be associated with atmospheric aerosols in the smallest size ranges (Cautreels and Cauwenberge, 1978).

Deposition of monodisperse particles from atmosphere by gravitational settling or turbulent impaction has been investigated in detail (Slinn et al., 1978; Sehmel, 1980). Particle deposition velocity is a complicated function of particle size and micrometeorological parameters; deposition velocities for hydrophobic particles are minimal in the 0.1 to 0.5 μm diameter range, and are higher for larger and smaller particles. The situation is even more complex for hydrophilic particles, which have been pastulated to grow as they encounter high relative humidities near the air/water interface (Slinn and Slinn, 1980, Figure 6-3).

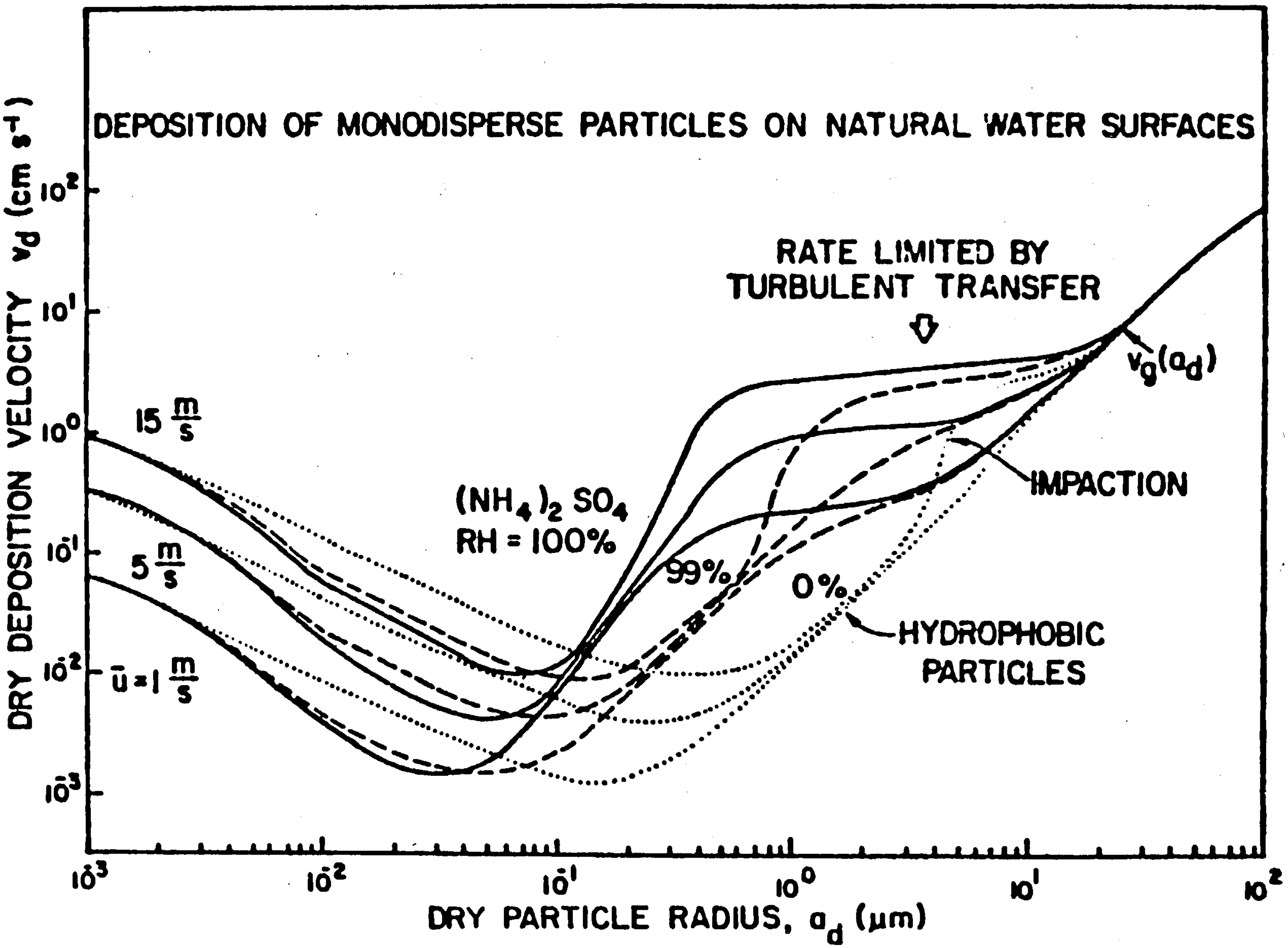


Figure 6-3 Predicted Dry Deposition Velocities for Hydrophobic and Hydrophilic particles to a Water Surface. From Slinn and Slinn [illegible]

Deposition velocities can be measured under field conditions by dividing the flux to a selected receptor surface by the ground-level atmospheric concentration. A compilation of these V_d values for gases, trace metals, and radionuclides to a large number of surface types is given by Sehmel (1980). Conspicuously absent in Seheml's listing are V_d values for organic pollutants. Only a handful of V_d's for trace organics have been measured, and all are for organochlorines. These are listed in Table 6-5. Because the aerial concentration used to calculate V_d's include both the particulate and vapor-phase materials, one might expect V_d's for trace organics to vary with the P/G ratio in ambient air. Bidleman and Christensen (1979) found that this was indeed the case. Estimates for the dry deposition velocity of particles, of less than 1.0 micron diameter range from 0.05 to 1.0 cm sec^{-1}. Revolatization from water (Henry's Law constants are in the 10^{-4} to 10^{-5} atm. m^3 $mole^{-1}$ range) or re-entrainment processes should be unimportant. Conclusive measurements of the fluxes for the 70 different PAH compounds (Lao et al., 1973) observed in atmospheric particulate matter have not been made; however, consideration must also be given to photochemical and other reactions leading to formation of new related compounds which may be far more toxic. In this class of compounds are nitro substituted and chlorinated PAHs.

Considering the magnitude of urban area emissions of these compounds and the anticipated increase in coal use in the next 10 to 30 years, the existing downward trend for PAH concentrations may be reversed in the future and these compounds may represent a problem of increasing magnitude in the atmosphere.

6.4.2 Polychlorinated Biphenyl

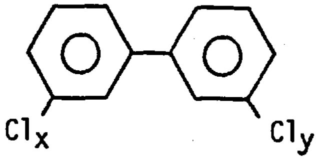
Polychlorinated biphenyls consist of two bonded benzene rings with varying deprees of chlorine substitution. A possible 209 isomers and congeners comprise the compounds called PCBs and commercially labelled Arochlors. Principally produced for use as dielectric fluids in transformers and capacitors and other products requiring thermal stability, PCBs are widely distributed in the environment. Although production was discontinued in North America during the 1970s, large quantities are still in commercial use. An estimated 8.2×10^7 kg enter the environment annually (National Research

TABLE 6-5 DRY DEPOSITION VELOCITIES FOR TRACE ORGANICS

Compound	Location	V_d, cm sec^{-1} Range	Mean	Surface	Reference
Aroclor 1254	LaJolla, CA	0.3 - 3.0	1.2	mineral-coated glass plates	McClure, 1976
	Columbia, SC	0.01 - 2.6	0.43	water-filled or glycerol-sprayed pans	Bidleman and Christensen 1979
	North Inlet estuary, SC	<0.01 - 0.48	0.15	"	"
Aroclor 1016	Columbia, SC	<0.002 - 0.16	0.03	"	"
Total PCB	Minneapolis, MN		0.14	glycerol-coated plates	Eisenreich and Hollod, 1981
p,p'-DDT	Columbia, SC	<0.2 - 10.9	1.3	water-filled or glycerol-sprayed pans	Bidleman and Christensen, 1979
	North Inlet estuary, SC	<0.04 - 1.4	0.28	"	"
Chlordane	Columbia, SC	<0.01 - 0.26	0.068	"	"
	North Inlet estuary, SC	<0.003 - 0.24	0.04	"	"
Toxaphene	Columbia, SC	<0.01 - 0.19	0.12	"	"
	North Inlet estuary, SC	<0.05 - 0.73	0.24	"	"

Council, 1979). Table 6-6 lists important physical and chemical properties of Arochlors still in use (MacKay et al., 1981; Eisenreich et al., 1980).

TABLE 6-6 IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES OF ARACHLORS

Mixture	Chlorine content	Vapor Pressure μm Hg 25°	General structure	Mean No. of chlorines
Arochlor 1242	42%	4×10^{-4}		X + Y = 3
Arochlor 1248	48%	4.9×10^{-4}	"	X + Y = 4
Arochlor 1254	54%	7.7×10^{-5}	"	X + Y = 5
Arochlor 1260	60%	4×10^{-5}	"	X + Y = 6.3

Because of relatively high vapor pressures most PCBs exist in gaseous form at summer temperatures (MacKay et al., 1981; Eisenreich et al., 1980). A large volume of evidence exists on the toxic and carcinogenic effects of those compounds (National Research Council, 1979).

Measurements

Many measurements of PCBs in air have shown that most are present in the vapor form during periods of moderate to high temperatures, i.e., greater than 10°C (McClure, 1976; Doskey and Andren, 1981a, 1981b; Eisenreich et al., 1980; National Research Council, 1979). Measurements from winter studies conducted at less than 0°C indicate that as much as 65% and 9% for Arochlors 1254 and 1016, respectively, are filter retained or associated with particulate matter in urban air (Bidleman et al., 1981). Typical ranges of concentrations observed for PCBs are 0.5 to 30 ng m^{-3} for urban areas, 0.1 to

2 ng m^{-3} for rural areas and 0.05 to 2 ns m^{-3} for background regions (Eisenreich et al., 1980). One to 50 ng l^{-1} have been observed in rain sampled at sites spread across Canada. PCBs have also been identified in the air of the North Atlantic 1200 km east of the U.S. coast (Bidleman and Olney, 1975), in the Gulf of Mexico at concentrations of 0.13 to 0.79 ng m^{-3} and at Pigeon Key* off the Florida coast at 0.04 to 1.1 ng m^{-3}. In spite of the controls placed on production of PCBs in North America during the 1970s, it may be some time before a downward trend is detectable in air concentrations.

The presence of PCBs in the marine areas described above clearly demonstrates that the atmosphere plays a major role in the transport and dispersal of these compounds. Data from studies in Lake Superior (Eisenreich et al., 1980) and the North Atlantic (Bidleman and Olney, 1975) also indicates that the atmosphere may be the major source of PCBs for remote areas.

The deposition velocity for the high molecular weight PCB mixture Aroclor 1254 was greater than that for the lighter Aroclor 1016, and p,p'-DDT was deposited more quickly than the more volatile chlordane isomers. Christensen and Bidleman (1979) found that V_d's for organochlorines in urban air increased rapidly with wind speed, probably as a result of increased turbulent impaction to the collection surface. McClure (1976) also observed higher V_d's for PCB with increasing wind speed. The estimated deposition velocities are as low as 0.01 and as high as 0.2 cm sec^{-1} (Bidleman and Christensen, 1979; Bidleman and Olney, 1975; Doskey and Andren, 1981b; Eisenreich et al., 1980).

Given the very large variation in V_d values and other parameters even for the same compound deposited to the same surface (Table 6-5), predictions of fallout fluxes from aerial concentrations and V_d values are apt to be accurate to not better than an order of magnitude. Eisenreich et al. (1981) estimated a PCB fallout flux of 7.8×10^4 kg yr^{-1} to Lake Superior, assuming $V_d = 0.3$ cm sec^{-1} and an aerial concentration of 1.0 ng m^{-3}. Much more work could be done to determine V_d values as a function of wind speed in

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*Giam and Atlas-Searex Report, Jan. 1979.

the field, the P/G ratio, and the charcteristics of the collection surface, and the statement by Slinn et al. (1978) seems most appropriate: "Particle dry deposition and resuspension are probably our most glaringly deficient aspects of our knowledge of pollutant transfer to the ocean ...".

The wide ranges in the estimates reflect the uncertainties in obtaining even the most fundamental data for these compounds. Additional uncertainties exist because a true knowledge of the soluble to particulate PCB ratio in the water column as well as the gaseous to particulate PCB ratio in air are not unambiguously known (Doskey and Andren, 1981a, 1981b; MacKay et al., 1981; Eisenreich et al., 1980; MacKay et al., 1979). Because of limitations with sampling techniques these ratios are experimentally defined as for PAHs. The observed, i.e., measured, partitioning both in the air and water columns may be sufficiently different from the true partitioning that the current discussion on the atmospheric role remains a theoretical exercise. In addition, PCBs are complex mixtures. At present, parameters used in assessing PCB behavior in the atmosphere are based on those mixtures and not on the individual properties of each of the isomers. Each isomer or congener has its own Henry's Law constant, solubility, volatility, washout ratio and dry deposition velocity. Present sampling and analytical methods are unable to distinguish and provide data on each component of the mixture. These limitations as well as the inability to easily detect PCBs at concentrations significant in the atmosphere do not permit an unambiguous answer to the role of the atmosphere as a source or sink for PCBs.

Many investigators have documented the presence of pesticides and PCB in rain and snow. Far fewer attempts have been made to correlate concentrations in rain with ground-level atmospheric concentrations. Washout ratios (W = g pollutant/g rain g pollutant/g air) for trace organics are collected in Table 6-7 along with estimates of W for vapor-phase organics. From the discrepancy between field W values and those calculated for vapors, it is clear that p,p'-DDT, Aroclor 1242/1016, and Aroclor 1254 are washed out on particles, not by vapor dissolution in raindrops.

Washout ratios appear to be higher for the less volatile organics, which are preferentially adsorbed to airborne particles: for example, W for

TABLE 6-7 WASHOUT RATIOS FOR TRACE ORGANICS

Location and Reference	Aroclor 1016/1242	Aroclor 1254	p,p'-DDT	HCH	Chlordane	Toxaphene	Phthalates
Chicago-Lake Michigan (Murphy and Rzeszutko, 1977)	14	103					
North Inlet estuary, SC (Bidleman and Christensen, 1979)		94	87		8	246	
Continental shelf, U.S. (Harder *et al*., 1980)						33	
Enewetak Atoll, North Pacific (Atlas and Giam, 1981)	<1			38			34
Equatorial Arabian Sea (Bidleman and Leonard, 1982)			68	23-41			
Vapor-phase W*	0.04	0.01	0.3	50		90	

*Calculated from water solubilities and vapor pressures.

Aroclor 1254 is higher than W for Aroclor 1242, and W for p,p'-DDT exceeds that of the more volatile chlordane (Table 6-7). The P/G ratio thus influences rainfall removal in the same manner as for dry fallout. Predictions of P/G ratios as well as vapor-phase washout rely on an accurate knowledge of pollutant physical properties, particularly vapor pressure and water solubility. Such properties are poorly defined for a number of compounds of interest, especially complex mixtures like PCB and toxaphene.

Washout ratios have been used to estimate annual rainfall fluxes of pollutants to water bodies, in the same way that fallout fluxes are estimated from V_d's. Doskey and Andren (1981) estimated a 2500 kg yr^{-1} rain input of PCB to Lake Michigan, based on a W for particulate PCB of 130 and the assumption that 13% of the PCB was particulate (based on actual measurements over Lake Michigan). In comparison, Murphy and Rzeszutko (1977) found that 5000 kg yr^{-1} PCB entered the lake during 1975-76, based on actual measurements of PCB in rainfall in Chicago and on Beaver Island. Other estimates of rainfall input of organochlorines have been based on direct measurements of these pollutants in precipitation. Wells and Johnstone (1978) monitored rainfall at seven stations along the eastern coastline of Great Britain from 1975-76, and calculated annual inputs of 0.3 to 2.1 metric tons PCB and chlorinated pesticides to the North Sea. Exchange of vapors across an air/water interface is usually discussed in terms of the two-film diffusion model, popularized by Liss and Slater (1974). Vapor transfer across an air/water interface is controlled by diffusive fluxes in air and water films at the interface. The exchange rate is limited by the resistance to mass transfer in the air and water films, with the ratio of the gas-to-liquid resistance (R_{GL}) given by:

$$R_{GL} = RTK_L/HK_G$$

Here K_G and K_L are the gas- and liquid-phase exchange constants, R is the gas constant, T is the absolute temperature, and H is Henry's Law constant* (which may be calculated from the water solubility and vapor pressure of the

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*Calculated by dividing the solute vapor pressure at saturation at 25°C by the solute's solubility in water at 25°C.

organic compond). MacKay et al. (1979) calculated R_{GL} as a function of H, K_G, and K_L. For values of $H > 5 \times 10^{-3}$ atm-m^3 mole^{-1} the resistance to vapor transfer is almost entirely in the liquid phase. For $H < 5 \times 10^{-6}$ atm-m^3 mole^{-1}, gas-phase resistance dominates. The resistance to mass transfer in both phases is important in controlling the exchange rate for intermediate values of H. Accurate values of H are thus essential for predicting the exchange rate of pollutant vapors across an air/water interface. Values of H for commercial PCB mixtures may be derived from solubility and vapor pressure data compiled by MacKay and Wolkoff (1973). Both water solubilites and vapor pressures for individual solid PCB isomers are lower than corresponding values for the liquid commercial mixtures, but Henry's Law constants for the isomers agree surprisingly well with values for the PCB mixtures. Values of H for PCB, i.e., in the range 1×10^{-4} to 7×10^{-4} atm-m^3 mole^{-1}; and 10 to 80% of the resistance to PCB vapor transfer occurs in the air film, depending on the values chosen for K_G and K_L (Westcott et al., 1981). H values for other organics are given in Table 6-8.

TABLE 6-8 VOLATILIZATION PARAMETERS FOR TRACE ORGANICS*

Chemical	Solubility, moles m^{-3}	Vapor pressure, atm	H, atm-m^{-3} mole^{-1}
Aroclor 1242	9×10^{-4}	5.3×10^{-7}	5.6×10^{-4}
Aroclor 1254	3.7×10^{-5}	1×10^{-7}	2.7×10^{-3}
DDT	3.4×10^{-6}	1.3×10^{-10}	3.8×10^{-5}
HCH (lindane)	2.5×10^{-2}	1.2×10^{-8}	4.8×10^{-7}
dieldrin	6.6×10^{-4}	1.3×10^{-10}	2×10^{-7}
phenanthrene	7×10^{-3}	2.8×10^{-7}	3.9×10^{-5}
pentachlorophenol	5.3×10^{-2}	1.8×10^{-7}	3.4×10^{-6}

*Based on literature solubility and vapor pressure data. Adapted from Eisenreich et al. (1981).

Direct experimental verification of the two-film model is hampered by the fact that organic pollutants exist in air and water in both the particulate and dissolved states. For example, Doskey and Andren (1981) collected values of H or "effective" air/water partition coefficients of various investigators which ranged from 10^{-2} to 10^{-7} atm m^3 $mole^{-1}$. The lowest values were not true Henry's Law constants, but effective constants for systems containing water-borne particles. Prediction of exchange rates for trace organics are extremely sensitive for the value chosen for H, for example, depending on whether the flux of PCB is under gas- or liquid-phase control, Lake Michigan is either a source (by volatilization) or sink (by gas deposition) for airborne PCB (Doskey and Andren, 1981).

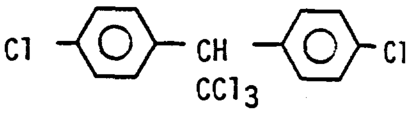
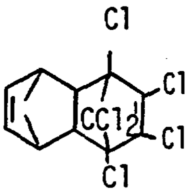
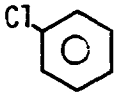
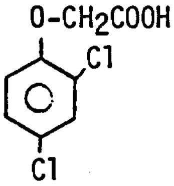
6.4.3 Pesticides and Herbicides

Pesticides and herbicides are a chemically diverse group of compounds used in agriculture, forestry and other activities requiring pest and weed control, ensuring their widespread distribution. The persistence of these compounds is demonstrated by the continued presence of DDT in environmental samples from Canada and the U.S. long after its use was terminated. Some of the more important and/or persistent pesticides and herbicides used in North America both in the past and the present are shown in Table 6-9 (Eisenreich *et al*., 1980; Ramel, 1977). At times environmental problems arising from the use of these compounds have been attributed to impurities resulting from side reactions or contaminants during manufacture rather than to the pesticide molecules. The best known example of this problem is the dioxin contaminant found in 2,4D and 2,4,5T formulations. The emulsifier used to spray fertilizer, a product widely used in control of spruce budworm, is suspected of causing health problems for people residing in the spray regime.

Measurements

The measured ranges of concentrations of some pesticides are given here to indicate typical values obtained. This is not meant to present a thorough documentation of the extensive data available. Dieldrin concentrations are approximately 0.5 to 10 ng m^{-3} in urban areas, 0.01 to

TABLE 6-9 SOME IMPORTANT PERSISTANT PESTICIDES AND HERBICIDES USED IN NORTH AMERICA

Compound	Molecular weight	Vapor Pressure µm Hg 25°C	Structure
p,p DDT	354.5	1×10^{-7}	
Toxaphene	413.6 (AVE)	9×10^{-6}	
Aldrin	365	6×10^{-6}	
Chlorobenzene	113	11.9	
2,4 Dichlorophenoxy Acetic Acid	221	(1.0 at 160°C)*	

*Herbicide Handbook of the Weed Society of America.

0.1 ng m^{-3} in rural areas and 0.5 to 1.3 ng l^{-1} has been measured in precipitation at sites spread across Canada (Eisenreich et al., 1980). Total DDT (i.e., the sum of DDT and DDE) banned in the early 1970s is still found at measurable concentrations, 0.01 to 1 ng m^{-3} in urban areas, 0.01 to 0.05 ng m^{-3} in rural areas and 0.8 to 5.6 ng l^{-1} in precipitation (Eisenreich et al., 1980). Toxaphene, a volatile pesticide, used widely in cotton growing areas, has been observed at concentrations of 0.02 to 10 ng m^{-3}, 0.02 to 2 ng m^{-3} and < 0.1 to 1.9 ng m^{-3} in urban, rural and remote marine areas near Bermuda, respectively (Bidleman and Olney, 1975). Data for PCBs and total DDT from the Gulf of Mexico (Giam et al., 1980) show that concentrations in marine regions are lower than continental regions; however, the ratio of these two volatile components does not appear to change from continental to marine regions. These compounds appear to be transported and dispersed (i.e., diluted) by the atmosphere and the atmosphere is considered to be the ultimate reservoir for volatile organic-chlorine pesticides and herbicides. Loss mechanisms to land surfaces and open water do not appear to be very important. Estimated and measured Henry's Law constants for these compounds are 3.8×10^{-3} atm. m^3 $mole^{-1}$, 8.2×10^{-5} atm. m^3 $mole^{-1}$ and 4.2×10^{-7} atm. m^3 $mole^{-1}$ for chlorobenzene, p,p DDT and Dieldrin, respectively (Eisenreich et al., 1980; Bidleman et al., 1981). Studies in Lake Zurich in Switzerland on 1,4 Dichlorobenzene further support the postulate that the atmosphere acts as a major reservoir for these types of compounds. 1,4 DCB is a volatile organochlorine molecule (i.e., a good model compound for PCBs and many pesticides and herbicides). It was found that volatilization was the most important elimination mechanism for 1,4 DCB from Lake Zurich and that the atmosphere was the major sink for volatile chlorinated hydrocarbons occurring in surface waters (Schwarzenbach et al., 1979). Similar soil-based studies reveal that volatilization is a major loss mechanism from soils for volatile pesticides and herbicides. Washout ratios of many of these compounds are in the 10^4 range and deposition velocities for dry deposition processes are estimated to be as low as or lower than <0.2 cm sec^{-1} indicating that the atmospheric residence time should be relatively large and therefore, transport of these compounds over long distances is an important dilution mechanism.

Historically, the findings of pesticides in rainwater in England and the U.S. during the mid 1960s provided the first evidence of long-range aerial transport for these chemicals. However, toxaphene and HCH may be rained out as vapors, as these organochlorines have relatively high water solubilites and low vapor pressures. Harder et al. (1980) found that 1.2 kg toxaphene was rained out into a 26 km^2 estuary on the South Carolina coast during the summer of 1977.

The use of pesticides and herbicides is now more carefully controlled than when they were first introduced. However, the total use in agriculture and forestry is expected to increase in the future. Since the atmosphere is believed to be a major reservoir or sink the transport to distant regions is a virtual certainty. The concentrations of pesticides and herbicides in the atmosphere in remote regions and possible effects at low levels are yet to be investigated. Improvements are required in sampling to determine particulate versus soluble or volatile fractions in water and air as well as in the ability to detect these compounds at ambient atmospheric concentration levels in remote regions.

6.4.4 Phthalate Esters

Almost 450 kilo-tonnes per year of phthalate esters are produced annually in North America for use primarily in the plastic's industry. Samples from the environment invariably contain phthalates; however, it is not clear whether these truly reflect environmental levels or are the result of sampling or laboratory contamination. The volatility and potential health problems and widespread use of these compounds requires that some attention be directed to understanding the paths of entry, distribution, and removal of these compounds in the environment.

Di-ethyl hexyl phthalate (DEHP) and Di-n-butyl phthalate (DBP) two typical phthalate compounds have been found in the air over the Gulf of Mexico at concentrations ranging from 0.72 to 1.8 ng m^{-3} and 0.16 to 3.7 ng m^{-3}, respectively (Giam et al., 1980; Eisenreich et al., 1980). Reliable estimates for phthalates in rain are not available. These concentrations are one to two orders of magnitude lower than in continental air and similar to values reported for the North Atlantic. Significant amounts of both compounds were found associated with particulate matter as well as in the vapor phase.

Measurements at Pigeon Key, Florida, have found values of 1.5 to 31.2 ng m^{-3} for DEHP and 2.5 to 87.2 ng m^{-3} for DBP*. About 40% of the phthalates were found to be associated with the smaller size fractions of the atmospheric aerosol as measured by an Anderson impactor. Because of contamination problems much of the data concerning phthalates is suspect.

It is not yet clear whether the atmosphere plays as important a role in transport and dispersion of phthalates as in the case of the organochlorine compounds. Deposition rates may be higher and the water solubilites of the compounds at 3.2 and 1.2 mg l^{-1} for DBP and DEHP (Giam et al., 1980),

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*Searex newsletter, Jan. 1979.

respectively, are much higher than for many organochlorine compounds. In addition, vapor pressures of 1.4×10^{-5} and 6.2×10^{-8} mm Hg at 25°C (Giam et al., 1980) for DBP and DEHP are lower. For these reasons the atmospheric lifetimes of these compounds may be significantly shorter than for many of the organochlorine compounds.

6.5 Conclusions

The atmosphere provides important pathways for the movement and dispersal of organics into other areas of the environment. It may also be the ultimate reservoir for some of the more toxic man-made organic compounds such as PCBs, pesticides and herbicides. Precise data is lacking, however, on fundamental parameters required to understand the behavior of those compounds in the atmosphere. Improvements are required in sampling methodologies to obtain realistic estimates for partitioning between particulate matter and the gaseous form in the atmosphere and to obtain a detection sensitivity meaningful at atmospheric concentration levels. Nearly all aspects of the deposition of trace organics from the atmosphere are in need of further study. Field measurements of V_d's and W's for a suite of organic pollutants are needed so that correlations between these parameters and physical properties can be better established. Collection methods for rain and (especially) dry deposition could be improved. Finally, a great need exists to better define the water solubilities and vapor pressures for trace organics. Improvements are also required in analytical methods for PCBs and phthalate esters to ensure that data is sufficiently detailed and that problems with contamination and quantification are eliminated. In addition, if the atmosphere is a significant reservoir for many organics, then the potential photochemical reactions that could change these compounds into more hazardous materials or lead to easier removal of these chemicals requires urgent attention. Such studies are as yet in infancy.

Chapter 7

HEAVY METALS

7.1 Introduction

Heavy metals are gaining increased recognition as a significant potential hazard in the environment through their ability to cause a broad spectrum of deleterious human health and ecological effects (Fulkerson et al., 1974; Bowen, 1979; CEC and WHO, 1981). Of this imprecisely defined category of elements, members frequently measured in environmental samples are listed in Table 7-1.

TABLE 7-1 HEAVY METALS* COMMONLY MEASURED IN ENVIRONMENTAL SAMPLES

Antimony	(Sb)	Copper	(Cu)	Manganese	(Mn)	Tin	(Sn)
Cadmium	(Cd)	Iron	(Fe)	Mercury	(Hg)	Vanadium	(V)
Chromium	(Cr)	Lead	(Pb)	Nickel	(Ni)	Zinc	(Zn)

*This list does not include the important trace elements arsenic and selenium (which are often referred to as heavy metals) as they are actually metalloids with physical and chemical properties intermediate between those of metals and non-metals.

Many of the heavy metals in this table are not environmental contaminants of concern as they rarely satisfy the criteria commonly used to assess a potential chemical hazard to man and the environment. These criteria are: toxicity (or other adverse biological effects), susceptibility to bioaccumulation, widespread commercial use, and likelihood of entry into the environment in harmful quantities (Wood, 1974; NAS, 1975; Harris, 1976; Science Council of Canada, 1977; OECD, 1981).

At present, identification of the most harmful heavy metals in the environment is an extremely difficult task due to the number of factors requiring consideration and a paucity of suitable and/or reliable data. A multitude of so-called priority lists, ranking schemes, and hazard indices have been proposed for toxic or hazardous substances, including heavy metals (Wood, 1974, Harriss and Hohenemser, 1978, Walsh *et al.*, 1978; Keith and Telliard, 1979; APCD, 1980, U.S. EPA, 1980). To our knowledge, however, there still exists no completely objective procedure for setting priorities or ranking heavy metals (or any other group of chemicals) in terms of their harmfulness in the natural environment.

Heavy metals are introduced into the atmosphere by various natural and anthropogenic sources (Lee and Duffield, 1979; Nriagu, 1979). Natural sources include volcanoes, wind-blown dust, forest fires, vegetation, and the oceans. Man contributes to the atmospheric burden of heavy metals through combustion of fossil fuels, mining, smelting and refining of metals, incineration of liquid and solid wastes, and various modes of transportation. In Canada, national emission inventories have been produced for the major anthropogenic sources of mercury, copper, nickel, antimony, lead, manganese, vanadium, cadmium, cobalt, and tin (Vena, 1981). On the basis of 1969-1971 production estimates, and assuming no changes in process or control technology, Flinn and Reimers (1974) projected significant increases in emissions from stationary sources in the U.S. through to the year 1983 for all heavy metals for which data were available. Nriagu (1979) has assembled evidence to show that sharp increases in the man-induced release of Cd, Cu, Pb, Ni and Zn have occurred since the beginning of the 20th century. The ratios of the 1971-80 to the 1901-10 emissions of these heavy metals are said to be consistent with the historical changes in rates of metal deposition observed in polar ice cores in the northern hemisphere (Boutron, 1979).

On the basis of emission rates, atmospheric concentrations, and known temporal trends in deposition, Galloway *et al.* (1980) expect the trace elements antimony, cadmium, copper, lead, selenium, silver and zinc to show the greatest concentration increases in atmospheric deposition due to human activity.

7.2 Some Considerations Pertinent to the Atmospheric Transport of Heavy Metals

The long-range transport (here defined as >100 km from the source) of heavy metals in the atmosphere is primarily dependent upon:

1. the physical state of the metal (solid, liquid or gas),
2. the chemical form (specie of the metal),
3. the size distribution of the aerosol, and
4. the prevailing meteorology.

Heavy metals (with the exception of volatile elements such as Hg) are generally emitted from anthropogenic sources in association with particulate matter. Particles in the sub-micron range show enhanced metal concentrations (Davidson et al., 1974), have long atmospheric residence times, contain most of the elemental mass of the aerosol (Linton et al., 1976), and can enter the human respiratory tract (Hatch and Gross, 1964).

In attempting to establish source-receptor relationships at great distances, it has been helpful to define the enrichment of heavy metals in a sample relative to the normal crustal abundance (Gordon et al., 1974). These so-called "enrichment factors" are useful in identifying abnormal or excessive elemental enrichments of atmospheric aerosols and can provide clues for the identification of emission sources (Parekh and Husain, 1981). Assessing anthropogenic contribution to the atmospheric enrichment of heavy metals requires care and needs to take into consideration natural (e.g., volcanic) and biogenic contributions. Modeling of atmospheric transport of pollutants is another method frequently used to establish the contribution of sources to distant receptors.

For several elements the anthropogenic emissions are sufficiently well known, both in quantity and spatial distribution, to indicate that the material is transported over long distances. Downwind measurements made during episodic pollution events (i.e., pollution with traceable origin) form the bulk of the evidence for atmospheric heavy metal transport from industrial sources (Lantzy and Mackenzie, 1979; Parekh and Husain, 1981; Navarre _et_ _al_., 1981).

A substantial amount of information exists on the heavy metal content of atmospheric aerosols from natural as well as anthropogenic sources. However, much less information is available directly linking emissions from anthropogenic sources with their deposition at distant sites. Studies are continuing to provide more direct measurements of long-range transport of airborne pollutants, including heavy metals. Identification of single-source plumes is now possible even at long distances from their point of origin. As a result of such plume measurements, evidence is emerging regarding regional transport and dry deposition for various metallic elements (Small _et_ _al_., 1981). Nevertheless, considerable difficulties associated with this type of measurement exist, since sampling times become excessively long at distances >50 km from the source.

The long-range transport of sulfur-bearing aerosols has now been well established (Galvin _et_ _al_., 1978). If heavy metal concentrations of atmospheric aerosols can be correlated with either particulate sulfate or total sulfur concentrations, detection of the occurrence of air pollution episodes as well as identification of those heavy metals which originate primarily with stationary combustion sources would be possible (Navarre _et_ _al_., 1981).

The following section deals with monitoring techniques used to obtain information on ambient air concentrations as well as wet-only and dry-only deposition fluxes (rates) for heavy metals emitted into the atmosphere. The remainder of this chapter will identify and provide a review of some of the data (with a geographical emphasis on North America) obtained through the application of the monitoring techniques described. The treatment of this subject matter is not intended to be comprehensive in scope or exhaustive in depth; rather, it provides a key or a guide to some of the pertinent scientific literature on these topics.

7.3 Monitoring Techniques

For the purpose of this chapter, monitoring techniques for heavy metals released into the atmosphere are divided into two broad categories. These are: monitoring of ambient air concentrations and monitoring of atmospheric deposition. In turn, deposition measurements for airborne heavy metals may be divided into two classes--wet and dry deposition measurements. The former refers to atmospheric deposition aided by precipitation and the latter to all other removal processes of the airborne pollutants at or near the surface of the earth. Even though the importance of both wet and dry deposition mechanisms has been recognized, monitoring techniques are more advanced for wet deposition than for dry deposition. For a more detailed treatment of monitoring practices and techniques applied to airborne particulate matter, readers are referred to sections 2.1 and 2.2 of this report. However, some sampling problems specific to heavy metals will be highlighted here.

7.3.1 Techniques for Monitoring Atmospheric Concentrations

With the exception of mercury and possibly cadmium, the heavy metals mentioned in Table 7-1 occur in the atmosphere primarily in association with suspended particulate matter rather than in the gas phase. In the past, collection of non-volatile heavy metals associated with atmospheric aerosols has usually been performed according to standardized procedures involving high-volume sampling (Jutze and Foster, 1967). Special considerations and techniques are, however, necessary in monitoring heavy metals (e.g., mercury) capable of existing in the atmosphere in volatile forms (Matheson, 1977; Schroeder, 1981). In recent years, low-volume sampling methods have been used extensively for these special situations.

Application of the high-volume sampling technique to the determination of ambient air concentrations of heavy metals has been described and characterized in considerable detail (Clements _et_ _al_., 1972). The inherent limitations of standard "hi-vol" procedures in providing meaningful data for heavy metals, with respect to assessment of their environmental behavior and human health effects, are now widely recognized. Development and deployment of dichotomous samplers, cascade impactors, and high-volume samplers with size-selective inlets has remedied some of these deficiencies and are providing much needed information on the size distribution of suspended particulate matter in the atmosphere.

7.3.2 Techniques for Estimating Dry Deposition Flux

Dry deposition of particles (and hence heavy metals associated with such particles) is a complex phenomenon which is a function of particle size, surface properties and atmospheric conditions (Hicks *et al*., 1980). Direct dry deposition flux monitoring employing surrogate surfaces, e.g., a Harwell collector (Cawse, 1972) or an open vessel, are felt to be inadequate in simulating the natural surface (Hicks *et al*., 1980). Another approach to obtaining the dry component of the deposition flux is to measure the total deposition on a natural surface (e.g., snow) and then subtract out the wet-only deposition. Alternatively, one can measure airborne concentrations as a function of particle size and use deposition velocities, obtained through intensive studies, to estimate dry deposition flux.

In theory, dry deposition fluxes of small, non-sedimenting particles may also be determined using micro-meteorological techniques such as flux-gradient and eddy-correlation methods. In practice, however, these methods are expensive and difficult to implement for particle deposition measurements. They require fast-response, selective chemical sensors capable of following small concentration changes.

For routine monitoring, a less rigorous method of estimating heavy metal dry deposition flux (F) is through a knowledge of the ambient air concentration (C) and the deposition velocity (V_d) since by definition $F = CxV_d$. The ambient air concentration can be obtained by filtration methods such as high-volume or low-volume sampling using an appropriate filter medium. For the more volatile species, chemically impregnated filters or impingers with a suitable chemical solution should be used. The deposition velocity may be inferred from particle sizing experiments. Limited information is available on deposition velocities of different metals (McMahon and Denison, 1979) but much more experimental work is needed before accurate estimates of dry deposition flux for heavy metals can be made by this method.

7.3.3 Techniques for Estimating Wet Deposition Flux

Certain problems with respect to precipitation sampling still exist. These pertain to adsorption of heavy metals on collector surfaces (Struempler, 1973; Batley and Gardner, 1978; Subramanian et al., 1978) or preservation and fixation of certain volatile metals such as mercury (Barton et al., 1981) in precipitation samples. The adsorption properties depend on the particular metal, type of collector surface and the metal concentration in precipitation. For heavy metals which adsorb on the collector surface, acid leaching is mandatory. The extent of loss of a trace metal through volatilization from the precipitation sample is related to its volatility and also its ambient air concentration. Preservation with a chemical fixing agent is necessary for volatile heavy metals.

7.4 Monitoring Data and Their Interpretation

7.4.1 Observations of Ambient Air Concentrations

Many scientific studies involving determination of atmospheric concentrations of heavy metals have been conducted. Some key references to this literature include: Gordon et al., 1971; Semb, 1978; Bowen, 1979; Kretzschmar and Cosemans, 1979; Peirson and Cawse, 1979; Adams et al., 1980; Galloway et al., 1980; Rahn and McCaffrey, 1980; and Barrie et al., 1981b.

7.4.2 Observations of Dry Deposition Flux

Very few observations of dry deposition flux for heavy metals have so far been reported in the scientific literature. Consequently, knowledge of this parameter is extremely limited. This stems in part from the relative difficulty of making these measurements (compared to obtaining data on bulk or wet-only deposition fluxes) and the somewhat later recognition of the importance of this deposition process in the context of airborne metals.

Table 7-2 provides a summary of reported observations on the dry deposition flux of some of the heavy metals listed in Table 7-1. The paucity of data for any particular element as well as for the heavy metals as a group is strikingly evident from this table. The only general assessment appropriate at this time is the need for more data on dry deposition flux of heavy metals present in the atmosphere.

The data in Table 7-2 have been grouped according to the character of the sampling location: "urban/industrial" for sites under the direct influence of an anthropogenic source, "rural" for sampling sites which are not directly affected by an anthropogenic source but are influenced by regional transport of air pollutants, and "remote" for sampling locations far removed from anthropogenic sources and influenced mostly by long-range atmospheric transport. It should be noted that distinctions between so-called remote, rural, and urban/industrial sites are subjective in nature. Special difficulties can arise in assigning a particular site to either the rural or urban category. It must also be recognized that within an urban environment extremely high and low deposition flux values are possible due to differences in source density and/or magnitude of emission rates.

To date, the most comprehensive compilation of data on atmospheric deposition of heavy metals is the report edited by Galloway et al. (1980). This report is based on a workshop (entitled "Toxic Substances in Atmospheric Deposition: A Review and Assessment") held at Jekyll Island, Georgia, during November 1979. Most of the data presented in Table I-9 of this document are for bulk deposition. However, as the editors correctly point out, for a better understanding of atmospheric processes and more meaningful assessments of the environmental and human health effects of heavy metal deposition, it is important to know the relative contributions of dry and wet deposition mechanisms to the total (bulk) deposition. Field measurements of heavy metals in deposition indicate that the dry-deposited fraction may be substantial. For the several studies reported, the mean dry fraction of the total

TABLE 7-2 OBSERVATIONS OF DRY DEPOSITION FLUX (mg m^{-2} yr^{-1}) OF HEAVY METALS

Location	Metal								Reference
	Cd	Cr	Pb	Mn	Hg	Ni	V	Zn	
Urban/Industrial	<9.4	0.4	<297	<83		<110	<35	<594	Galloway _et_ _al_. (1980)
Rural	<4.7	<2.0	<72	<31		9	<25	<202	Galloway _et_ _al_. (1980)
					0.08- 0.14				Barton _et_ _al_. (1981)
Remote					<2.0				Galloway _et_ _al_. (1980)
					0.02				Weiss _et_ _al_. (1975)[a]

[a] Data derived from a Greenland glacier; total deposition (wet and dry).

deposition lies between 0.3 and 0.6 with the median value for all data, including marine, rural and urban locations, being 0.5 (Galloway et al., 1980).

7.4.3 Observations of Wet Deposition Flux

Very little information exists on wet-only deposition of heavy metals. Jeffries and Snyder (1981), and Galloway et al. (1980) independently reviewed atmospheric deposition of metals (both wet and bulk). Their information for North America, with more recent data added, are given in Table 7-3. No data are available for Co or Sn. Collection of wet-only samples at a "remote" location (American Samoa) has only been reported by Nagourney and Bogen (1981). The remaining "remote" estimates of deposition are based on sampling of the central Greenland snow-pack and represent total deposition. They are, therefore, upper-limit estimates to the wet deposition.

There is a large variability in the data for all parameters in Table 7-3. The different sampling and analytical methodologies used for each study cited contribute to this variation. Nevertheless, certain general conclusions can be drawn. Manganese and iron exhibit similar variations in wet deposition with values in both rural and urban/industrial locations comparable to remote sites. Comparable remote data for Ni and Cr are not available however. Finally, Cd exhibits a 1000-fold greater rural deposition, while Hg shows only a 10-fold elevation. Few estimates of urban/industrial wet deposition of these last two metals are available.

TABLE 7-3 OBSERVATIONS OF WET DEPOSITION FLUX (mg m^{-2} yr^{-1}) OF HEAVY METALS

Location	Metal										Reference
	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	V	Zn	
Urban/Industrial		11	53		115	12		79	54	206	Volchok and Bogen (1971)[a]
			60		120			10		306	Galloway *et al.* (1980)[b]
			46.8	30		4.7		17.1		17.6	Jeffries and Snyder (1981)[a,c]
Rural	0.12		1.8		1.9	2.1				4.0	Struempler (1976)
	15.4	3.6	23.2		24.6	25.3	0.3	9.1		49.9	Andren and Lindberg (1977)
			10		6			1		20	Galloway *et al.* (1980)[b]
	0.43				7.3	4.0				7.6	Lindberg *et al.* (1981)
			3.3	54.1	13.2			<2.2		9.5	Jeffries and Snyder (1981)
Remote				0.18	5.4×10^{-2}	6.0×10^{-2}					Nagourney and Bogen (1981)
	3.7×10^{-3}		1.9×10^{-2}		7.8×10^{-2}					0.10	Boutron (1979a)[d]
	5.7×10^{-4}		2.0×10^{-2}		8.3×10^{-2}	3.5×10^{-2}				9.2×10^{-2}	Boutron (1979b)[d]
	1×10^{-3}		0.19			9.4×10^{-2}	4×10^{-2}				Weiss *et al.* (1975)[d]

[a] 4 to 6 months of data pro-rated to annual value.

[b] Interpretation of data from Lazrus *et al.* (1970).

[c] Mean of 2 stations.

[d] Data derived from Greenland snow and ice cores, and therefore representative of total deposition (wet and dry). Values given can thus be viewed as an upper limit to wet-only deposition rates.

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NOTE: To be able to use the most up-to-date information, not only referenced publications were used, but also unpublished reports and technical notes.

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APPENDIX 1

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APPENDIX 2

Available Deposition Data

(Global, European, and North American)

The contents of this appendix are believed to be correct based on information available to the sub-group at the time of publication of this report. It is intended to be a guide to the reader on the large number and diversity of observational networks and their resultant data sets. However, it must be recognized that these networks are continually being upgraded and the latest status of any particular one should be obtained directly from the listed contact person.

TABLE A2-1 GLOBAL AND EUROPEAN DEPOSITION MONITORING NETWORKS

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
Background Air Pollution Monitoring Network	World Meteorological Organization (WMO)	a) baseline 5-10 b) regional ∿100	remote areas of globe "regionally representative" areas of globe	weekly,monthly	1970s	national laboratories
European Air Chemistry Network (EACN)	International Meteorological Institute, Stockholm, Sweden (IMI)	∿50	Western Europe	monthly	1950s	national laboratories
Long-Range Transport of Air Pollutants Technical Programme Network (LRTAP)	Organization for Economic Co-operation and Development (OECD)	∿80	Western Europe	daily	1972	national laboratories (Norwegian Institute for Air Research at Oslo served as central Q.A. Laboratory)
European Monitoring and Evaluation Program (EMEP)	Economic Commission for Europe (ECE) (U.N.)	∿65	Europe	daily, some weekly	1977	national laboratories (NILU serves at central Q.A. and data handling centre)

TABLE A2-1 GLOBAL AND EUROPEAN DEPOSITION MONITORING NETWORKS (Cont.)

TABLE A2-1 GLOBAL AND EUROPEAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
Background Air Pollution Monitoring Network	o precipitation constituents: sample volume, precipitation amount, pH, SO_4^{2-}, NO_3, conductivity Cl, Na, K, Mg, Ca, NH_4, alkalinity/acidity o suspended particulate matter, total mass o other parameters optional	National Climate Center NOAA Asheville, NC USA 288081	available mag. tape and hard copy	A. Koehler Secretariat WMO, Geneva Switzerland D. Fair NOAA	o wide range of quality in the data (network is run in both very developed and less developed countries). o limited quality assurance program o originally bulk at some locations, but now switching to wet-only throughout network.
European Air Chemistry Network (EACN)	o precipitation constituents: precipitation amount, sulfate, nitrate, chloride, ammonium, sodium, potassium, magnesium, calcium, pH, hydrogen ion/bicarbonate, elect. conductivity o aerosol samples on filters to give same constituents o SO_2 in abosrbing solution	EACN Data Base	available mag. tape and hard copy	L. Granat IMI University of Stockholm Stockholm, Sweden	o some of the precip. measurements are bulk o signigicant changes in methodology, sample location, analytical labs o intensive data assessment currently underway o lab. round-robins have taken place o some of the Swedish sites have been assessed for aereal representativeness
Long-Range Transport of Air Pollutants Technical Programme Network (LRTAP)	o sulfur dioxide o aerosol sulfates o concentrations of sulfate and strong mineral acids in precipitation	Norwegian Institute for Air Research	available mag. tape and hard copy	B. Ottar Director Norwegian Institute for Air Res. Lillstrom, Norway	o some of the precip. sites are bulk o some changes have been made in chem. anal. methods since inception o QC program run by NILU on sample anal. o some sites have supporting measurements (meteorological, other gases-NO_x, NH_3^- occasionally) o there have been intensive measurement periods during lifetime of network.
European Monitoring and Evaluation Program	o sulfur dioxide o aerosol sulfate o sulfate, pH/strong acid in precipitation o other species, particularly nitrogen compounds, optional	Norwegian Institute for Air Research	available as mag tape and hard copy	B. Ottar Director Norwegian Institute for Air Res. Lillstrom, Norway	o some changes have been made in chem. analysis methods o there is a QC program (sample exchange between labs) o data are evaluated for validity by comparing with model predict. and subsequent careful inspection of outliers o some of the precip. sites are bulk.

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
CANADA:						
Canadian Network for sampling Precipitation (CANSAP)	Atmospheric Environment Service Environment Canada	54	Canada	Monthly	April 1977	Water Quality Branch CCIW Environment Canada Burlington
Air and Precipitation Monitoring Network (APN)	Atmospheric Environment Service Environment Canada	8	Canada	Daily	November 1978	Water Quality Branch CCIW Environment Canada Burlington (precip.) o Atmospheric Environment Service (Air)
Great Lakes Precipitation Network (GLPN)	Water Quality Branch Canadian Centre for Inland Waters (CCIW)	15	Great Lakes Basin Ontario	Monthly	May 1969	Water Quality Branch CCIW/IWD Environment Canada Burlington, Ontario
BRITISH COLUMBIA:						
Costal Site Precipitation Monitoring Network	Air Management Branch Ministry of the Environment Province of British Columbia	3	Queen Charlotte and Vancouver Islands	Selected events	September 1980	Environmental Laboratory Ministry of the Environment Vancouver
Northwest British Columbia Precipitation Monitoring Network	Air Management Branch Ministry of the Environment Province of British Columbia	5	Northwest British Columbia	Selected events	September 1980	Environmental Laboratory Ministry of the Environment Vancouver

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
CANADA:					
Canadian Network for sampling Precipitation (CANSAP)	pH (Lab) Conductivity, Acidity/Alkalinity, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+	National Aquatic Data Bank (NAQUADAT)	ASCII or EBCDIC (Tape)	M. Still Atmospheric Env. Ser. 4905 Dufferin St. Downsview, Ontario (416-667-4793)	o QC program, especially for lab analysis o met. data are available at most sites o extreme data outliers not published
Air and Precipitation Monitoring Network (APN)	o precipitation: pH (Lab) Acidity, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+ o air: SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, SO_2	HP 9835	RS 232 9-track tape	L. Barrie Atmospheric Env. Ser. 4905 Dufferin St. Downsview, Ontario (416-667-4785)	o QC program available, especially for lab analysis o met. measurements (class I climat.) at some sites o extreme outliers in data are not published o some changes in air sampling procedures have taken place
Great Lakes Precipitation Network (GLPN)	pH (Lab) Conductivity, Acidity/Alkalinity, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, P, Na^+, K^+, Ca^{++}, Mg^{++}, Cd, Cu, Fe, Pb, Ni, Zn, Si	National Aquatic Data Bank (NAQUADAT) Ottawa	ASCII or EBCDIC (TAPE)	C. H. Chan Canadian Centre for Inland Waters Water Quality Branch 867 Lakeshore Rd. Burlington, Ontario (416-637-4698)	o lab QC program o several-changes in methodology since network inception o some data are bulk o some data screening before reporting
BRITISH COLUMBIA:					
Costal Site Precipitation Monitoring Network	pH (Lab) Total Acidity Strong Acids SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{++}, Ca^{++}	EQUIS Data File B.C., Systems Corp. Victoria, B.C. IBM 360	EBCDIC (TAPE)	M. Kotturi Air Management Branch British Columbia Ministry of the Environ. 200,777 Broughton St. Victoria, B.C. (604-387-5888)	o to continue operation til Dec. 1982 o laboratory QC program o met. data at some sites.
Northwest British Columbia Precipitation Monitoring Network	pH (Lab) Total Acidity Strong Acids SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{++}, Ca^{++}	EQUIS Data File B.C., Systems Corp. Victoria, B.C. IBM 360	EBCDIC (TAPE)	M. Kotturi Air Management Branch British Columbia Ministry of the Environ. 200,777 Broughton St. Victoria, B.C. (604-387-5888)	o to continue operation til Dec. 1982

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
ALBERTA:						
Precipitation Quality Monitoring Program (PQMP)	Air Quality Control Branch Pollution Control Division Alberta Environment	6	Alberta	Monthly	April 1978	Alberta Environmental Centre Laboratory Begreville, Alberta
Precipitation Chemistry in the Oil Sands Area of Northern Alberta Program (AOSERP)	Research Management Division Environment Alberta	14	Oil Sands Area of Northern Alberta	Event (summer only)	May 1981 and summers of 1976-1979	Alberta Environmental Laboratory Begreville, Alberta
MANITOBA:						
Manitoba Network for Precipitation Collection (MNPC)	Environmental Management Division Manitoba Department of Consumer and Corporate Affairs and Environment	2	Mid-eastern Manitoba	Daily	October 1980	Manitoba Government Technical Services Laboratory Winnipeg
ONTARIO:						
Acidic Precipitation in Ontario Study Cumulative Precipitation Sampling Network (APOS)	Air Resources Branch Ontario Ministry of the Environment	34	Ontario	Monthly	September 1980	Laboratory Services Branch Ontario Ministry of the Environment Rexdale, Ontario

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
ALBERTA:					
Precipitation Quality Monitoring Program (PQMP)	pH Conductance Acidity/Alkalinity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{++}, Mg^{++}, Na^+	Hard copy available in Annual Reports		R. Angle Air Quality Control Br. Alberta Environment 9820-106th Street Vegreville, Alberta T5K 2J6 (403-427-5893)	o to be expanded to 10 stations in spring of 1982 o rudimentary QC program at present: is being upgraded o met. and air quality data at some stations o lab. procedures have changed o some data rejection (only extreme outliers) before reporting
Precipitation Chemistry in the Oil Sands Area of Northern Alberta Program (AOSERP)	pH (Lab) Acidity, Conductivity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Ca^{++}, K^+, Mg^{++}	Roscoe System Research Management Division Edmonton	ASCII (TAPE)	Bruce Thompson Research Management Div Alberta Environment 15th Floor, Oxbridge Place 9820-106 Street Vegreville, Alberta T5K 2J6 (403-427-3943)	o lab. QC program o met. measurements at some sites o change in collection and analysis procedures in 1981 o source-oriented (network surrounds two major sources in oil sands area) o bad outliers are rejected
MANITOBA:					
Manitoba Network for Precipitation Collection (MNPC)	pH (Lab) Conductivity, Acidity SO_4^{2-}, $NO_3^=$, Cl^-, NH_4^+, Ca^{++}, Na^+, K^+, Mg^{++}, As, Cu, Pb, Zn, Fe (As volume permits)	Hardcopy		D. Bezak Environ. Management Div. Dept. of Consumer & Corp. Affairs & Environ. Box 7, Bldg. 2, 139 Tuxedo Ave. Winnipeg, Mannitoba R3C 008 (204-895-5273)	o NADP quality control program o met. measurements (surface weather data) at sampling stations o network located in area of two major smelters o some data rejection before reporting
ONTARIO:					
Acidic Precipitation in Ontario Study - Cumulative Precipitation Sampling Network (APOS)	precipitation: pH (Lab) Conductivity, Acidity SO_4^{2-}, $N\text{-}NO_3^-$, Cl^-, $N\text{-}NH_4^+$, Ca^{++}, K^+, Na^+, Mg^{++}, N-TKN, TP, Pb, Ni, Fe, Cu, Zn, Al, Cd, Mn, V air: SO_2, SO_4^{2-}, NO_3^-, some particulate trace metals	Ministry of the Environment Sample Information System (SIS) o IBM 370 Downsview, Ontario	EBCDIC (TAPE)	W. H. Chan Ontario Ministry of the Environment Air Resources Branch 880 Bay Street Toronto, Ontario M5S 1Z8 (416-965-1634)	o QA program, both field and lab o rejection of outliers (based on statistical analysis and inspection of sample chemical composition)

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
Acidic Precipitation In Ontario Study-Event Wet/Dry Deposition Network (APOS)	Air Resources Branch Ontario Ministry of the Environment	20	Ontario	Daily	July 1980	Laboratory Services Branch Ontario Ministry of the Environment Rexdale, Ontario
Acidic Precipitation In Ontario Study - Limnology and Toxicity Unit Network	Water Resources Branch Ontario Ministry of the Environment	7	Southern and Central Ontario	Variable	June 1976	Laboratory Services Branch Ontario Ministry of the Environment Rexdale, Ontario
Nanticoke Environmental Management Program (NEMP)	Air Resources Branch Ontario Ministry of the Environment	6	Nanticoke	Monthly	September 1978 (Partial operation)	Laboratory Servces Branch Ontario Ministry of the Environment Rexdale, Ontario
Ontario Hydro Atikokan Air Quality Monitoring Network	Environmental Studies and Assessments Department Design and Development Division, Ontario Hydro	2	Atikokan	Monthly	December 1981	Laboratory Services Branch Ontario Ministry of the Environment Rexdale, Ontario
Ontario Hydro Air and Precipitation Network	Atmospheric Sciences Section Research Division Ontario Hydro	6	Ontario	Daily	September 1975	Analytic Services Section Ontario Hydro 800 Kipling Avenue Toronto, Ontario

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
Acidic Precipitation In Ontario Study-Event Wet/Dry Deposition Network (APOS)	precipitation: pH (Field) pH (Lab) Acidity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++} air: SO_2, SO_4^{2-}, NO_3^-	Ministry of the Environment Sample Information System (SIS) o IBM 370 Downsview, Ontario	EBCDIC (TAPE)	W. H. Chan Ontario Ministry of the Environment Air Resources Branch 880 Bay Street Toronto, Ontario M5S 1Z8 (416-965-1634)	o QA program, both field and lab o rejection of outliers (based on statistical analysis and inspection of sample chemical composition) o met. and additional air quality data data at some sites
Acidic Precipitation In Ontario Study Limnology and Toxicity Unit Network	pH (Field) Conductivity, Alkalinity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++}, Cu, Ni, Fe, Zn, Mn, Al, Cd, Pb, TKN, TP, Si, DIC, DOC	Ministry of the Environment Sample Information System (SIS) o IBM 370 Downsview, Ontario	EBCDIC (TAPE)	W. Scheider Ontario Ministry of the Environment Water Resources Branch Resources Road Rexdale, Ontario (416-248-3058)	o some bulk precipitation stations o lab, and some field, Q.C. o met. and air quality data at some sites o several changes in methodology since start of operations o data rejection based on bad outliers and poor ionic balance
Nanticoke Environmental Management Program (NEMP)	pH (Lab) Acidity, Conductivity SO_4^{2-}, $N\text{-}NO_3^-$, Cl^-, $N\text{-}NH_4^+$, Ca^{++}, K^+, Na^+, Mg^{++}, N-TKN, TP, Pb, Ni, Fe, Cu, Zn, Al, Cd, Mn, V	Ministry of the Environment Sample Information System (SIS) o IBM 370 Downsview, Ontario	EBCDIC (TAPE)	M. Lusis Ontario Ministry of the Environment, Air Res. Br. 880 Bay Street Toronto, Ontario M5S 1Z8 (416-965-1634)	o source-oriented network o QA program, both field and lab
Ontario Hydro Atikokan Air Quality Monitoring Network	pH (Lab) Acidity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{++}, Na^+, Mg^{++} (Trace metals may be added)	Hardcopy from Ontario Hydro (Also on Ontario Ministry of the Environment APOS Data Base)		A. Hoffer Env. Stud. & Assess. Dept. Design & Development Div. Ontario Hydro 700 University Avenue Toronto, Ontario (416-592-6308)	o source-oriented network o QA program, both field and lab o met. data at one site
Ontario Hydro Air and Precipitation Network	precipitation: pH (Lab) SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Mg^{++}, K^+, Na^+ Acidity, Conductivity air: SO_2, SO_4^{2-}, NO_3^-, HNO_3	Univac 1182 Ontario Hydro 700 University Avenue Toronto	EBCDIC (TAPE) or ASCII (TAPE)	O. Melo Ontario Hydro Research Division 800 Kipling Avenue Toronto, Ontario (416-231-4111)	o lab QC program o air particulates now measured using dichotomous samplers o many changes in methodology since network inception o data rejection based on outliers and ionic balance

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
QUEBEC:						
Le Reseau des Collecteurs de Precipitation du Quebec	Ministry of the Environment Province of Quebec	42	Quebec	Weekly	June 1981 (2 sites as of Aug. 1980	Laboratorie D'Environment Quebec City
Noranda Precipitation Network	Horne Division Noranda Mines Limited	3	Northwest Quebec	Weekly	1977	Noranda Mines Limited Laboratory Noranda, Quebec
NEW BRUNSWICK:						
Environment New Brunswick Precipitation Network	Environmental Services Branch Environment New Brunswick	3 (Additional 2 planned in 1981)	New Brunswick	Monthly Composite	November 1980	Laboratory Services Enviroment New Brunswick Fredericton
NOVA SCOTIA:						
Precipitation Chemistry in Nova Scotia	Environmental Assessment Division, Nova Scotia Department of the Environment	5	Nova Scotia	Weekly	October 1977 (9 sites)	Nova Scotia Department of Health Laboratoy Victoria General Hospital Halifax

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
QUEBEC:					
Le Reseau des Collecteurs de Precipitation du Quebec	pH (Lab) Acidity, Conductivity SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+	IBM 3033 Government of Quebec	EBCDIC (TAPE)	L. Talbot Ministry of the Environment of Quebec 2360 Chemin St. Foye Premier Etage St. Foye, P.Q., GIV 4H2 (418-643-4425)	o four more stations planned o met. data at some stations o lab QC program o some stations (at Abitibi, Temiscaming) near sources o data rejection based on outliers, ionic balance, conductivity ratio
Noranda Precipitation Network	pH (Lab) SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Ca^{++}, Mg^{++}, K^+	Hardcopy		F. Frantisak Noranda Mines Limited Comm. Crt. W., P.O.Box 45 Toronto, Ontario, M5L IB6 (416-867-7306)	o source-oriented network
NEW BRUNSWICK:					
Environment New Brunswick Precipitation Network	Measured Parameters pH (Lab) Acidity, Conductivity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{++}, Ca^{++}	New Brunswick NAQUADAT IBM 3032	EBCDIC (TAPE)	J. Spavold Env. Ser. Br., Envl. New Brunswick, P.O. Box 6000 Fredericton, New Brunswick E3B 5H1 (506-453-2669)	o lab QC program o some met. data at all sites o changes in field and lab methodology in 1982 o suspect data are retained, but flagged
NOVA SCOTIA:					
Precipitation Chemistry in Nova Scotia	pH (Lab) Acidity/Alkalinity Conductivity SO_4^{2-}, $NO_3^=$, Cl^-, Ca^{++}, K^+, Mg^{++}, Na^+, NH_4^+, TN, TP, TOC, Al, As, Cd, Co, Cr, Cu, Mn, Fe, Ni, Pb, Se, Zn	CDC 6600 Dalhousie University Halifax		J. Underwood Environ. Assess. Div. Nova Scotia Dept. of the Env. P. O. Box 2107 Halifax, Nova Scotia B3J 3B7 (902-424-5300)	o lab and some field QC o some met. data are available o changes in sampler location, technique since start of program o data rejected based on visual inspection, outliers, ionic balance, conductivity ratio. Marine sulfate correction is calculated

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
NEWFOUNDLAND:						
Newfoundland Provincial Precipitation Monitoring Network	Air and Industry Division Newfoundland Department of the Environment	3 (1 more planned)	Avalon Penninsula	Weekly	September 1980	Newfoundland Forest Service Laboratories, Canadian Forestry Service, St. Johns, as of Mid-1981
ATLANTIC CANADA:						
Environmental Protection Service, Atlantic Region Precipitation Monitoring Network	Air Pollution Control Div. Environmental Protection Ser. o Atlantic Region Headquarters Darmouth, Nova Scotia	5	3 Nova Scotia (Halifax Vicinity)	Event Monthly (Weekly composite)	December 1978 June 1979 September 1980	Environmental Protection Service Atlantic Region Laboratory Bedford Institute Dartmouth, Nova Scotia
			1 Prince Edward Is.	Weekly	October 1979	
			1 Newfoundland		January 1981	
			(Planned in 1981: 1 Halifax, N.S. 1 Newfoundland)			

TABLE A2-2 CANADIAN DEPOSITION MONITORING NETWORKS (Cont.)

Network	Measured Parameters	Data Storage System	Data Storage Format	Contact	Comments
NEWFOUNDLAND:					
Newfoundland Provincial Precipitation Monitoring Network	pH Conductivity Major Ions Mid-1981	Hardcopy Upon request (Plans for Future Inclusion in NAQUADAT)		L. Hewlett Newfoundland Department of the Environment St. Johns, Newfoundland (709-737-2554)	o QC program being implemented at present o air and met. measurements at some sites o samples with high pH and visible contamination are screened out
ATLANTIC CANADA:					
Environmental Protection Service, Atlantic Region Precipitation Monitoring Network	pH (Lab) SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Ca^{++}, K^+, Mg^{++} (Partial Before 1978)	NAQUADAT (Ottawa) or Hardcopy		J. Machell Environment Canada Environ. Protection Service Queen's Square, 5th Floor 45 Alderny Drive Dartmouth, Nova Scotia E2Y 2N6 (902-426-6132)	o lab QC program o change in pH measurement method in June 1979 o some stations influenced by Halifax emissions o data in NAQUADAT are not screened

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
Department of Energy Environmental Monitoring Laboratory	Department of Energy Environmental Monitoring Laboratory	7 (3) (3) (1)	United States (East Coast) (West Coast) (Central U.S.)	Monthly	1977-	Rockwell International Laboratories Newbury Park, California
Electric Power Research Institute/ Sulfate Regional Experiment Network (EPRI/SURE)	Energy Analysis and Environment Division Electric Power Res. Institute	9 (duplicate collectors at each)	Eastern U.S.	Daily	September 1978-December 1980	Rockwell International Newbury Park, California
		5 (single collectors)		Daily	January 1981-September 1981	
Florida Acid Deposition Study	Florida Electric Power Coordinating Group	14	Florida	12 Weekly 2 Event	July 1981	Environmental Sciences and Engineering Inc. Gainesville, Florida
Great Lakes Atmospheric Network (GLAD)	U.S. EPA	35 6 (bulk)	Great Lakes (incl. Canada)	Weekly	January 1981	U.S. EPA Central Region Laboratory Chicago, Illinois
Hubbard Brook Experimental Forest Ecosystem Study	Likens, Bormann and Pierce Cornell University	Variable 3 to 6 (Bulk and wet only)	Hubbard Brook Experimental Forest New Hampshire	Weekly and Event	1962	Cornell University Ithaca, New York

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS (Cont.)

Network	Measured parameters	Data Storage System	Data Storage Format	Contact	Comments
Department of Energy Environmental Monitoring Laboratory	pH (Lab) Conductance SO_4^{2-}, NO_3^-, Cl^-, $PO_4^{\equiv}$, NH_4^+, Ca^{++}, Mg^{++}, Na^+, K^+ Quarterly Basis: Fe, Cu, Ni, Al, Zn, Mn, Cd, Cr, V, Pb	IBM 360 (Disc) EML New York, NY	EBCDIC (Disc)/ Hardcopy/ Cards	D. Bogen Department of Energy Environmental Monitoring Laboratories New York, NY 10014 (212-620-3637)	o lab QA program
Electric Power Research Institute/ Sulfate Regional Experiment Network (EPRI/SURE)	pH (Lab and Field) Conductivity (Lab and Field) SO_4^{2-}, NO_3^-, Cl^-, $PO_4^{=}$, Ca^{++}, K^+, Mg^{++}, Na^+, NH_4^+, T, DOC Air: SO_2, NO, NO_x, O_3, hydrocarbons SO_4^{2-}, NO_3^-, TSP (2 size fractions)	IBM 3081 Stanford Univer. Stanford, CA Also SAROAD Data Base, EPA Research Triangle Park, NC	EBCDIC or ASCII (TAPE)	P. Mueller Environmental Assess. Dept. Electric Power Res. Inst. 3412 Hillview Avenue Palo Alto, CA 94304 (415-855-2586)	oSURE air Quality Monitor Stations operated near each site o lab QA program o field QA program
Florida Acid Deposition Study	pH Conductivity SO_4^{2-}, NO_3^-, PO_4 , Cl^-, NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+, Air: SO_4^{2-}, NO_3^-	N/A	N/A	C. D. Henderson Florida Power & Light P. O. Box 5291000 Miami, FL 33152 (305-552-4819)	o 24-hr hi-vols at 2 sites every 3rd day o lab QA program o some sites are source-oriented
Great Lakes Atmospheric Network (GLAD)	pH (Lab and Field), Acidity Conductivity (Lab and Field) SO_4^{2-}, NO_2, NO_3^-, Cl^-, Si, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, P, ON, Na^+, Al, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg Mo, Ni, Ag, Sn, Tl, W, Zn, Toxic Arganics (12 sites) Air: SO_4^{2-}, NO_3^-, SO_2, NO, NO_2, O_3	SAROAD Data Base EPA, RTP Research Triangle Park, NC (After March 1982)	ASCII (TAPE)	David Lueck Great Lakes Nat. Prog. Of. U.S. EPA 536 S. Clark St. Chicago, IL 60605 (312-353-1375)	o some sites have collected air quality stations o some sites are source-oriented o lab QA program o some sites have met. datas
Hubbard Brook Experimental Forest Ecosystem Study	pH SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{++}, Mg^{++}, Na^+, TP, DOC, ON, Pb, Cr, Cd, Ni, Zn, Cu, Fe, Si	IBM Cornell University Limited Access to Data		G. E. Likens Section of Ecology and Systematics, Longmuir Lab. Cornell University Ithaca, NY 14835 (607-256-4531)	

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
Kennedy Space Center Precipitation Network	University of Central Florida Under Contract to NASA	7	Kennedy Space Center	Daily (weekdays) 3-day (weekends)	July 1977–October 1981	NASA Laboratories Kennedy Space Center Cape Canaveral, Florida
Multi-State Atmospheric Power Production Pollution Study Precipitation Chemistry Network (MAP3S)	Sponsored by: U.S. Environmental Protection Agency, Principal Organization: Battelle Pacific Northwest Laboratories	9	Eastern U.S.	Event	Late 1976	Battelle Pacific Northwest Laboratory Richland, Washington
National Atmospheric Deposition Program (NADP)	Multi-Agency	100	United States	Weekly	July 1978	Atmospheric Chemistry Lab. Illinois State Water Survey Champaign, Illinois
National Coal Assoc./Bituminous Coal Research Inc., Precipitation Quality Network (NCA/BCR)	Coal Industry	35 Operating (13 Planned)	United States	Weekly	May 1980	Principal: Bituminous Coal Research Inc. Monroeville, Pennsylvania (Others also--12)
Tennessee Valley Authority Deposition Network (TVA)	Air Resources Program Tennessee Valley Authority	9	Tennessee Valley	Biweekly 8 Weeks for Dry	1971 (Partial)	TVA Central Analytical Laboratory Chattanooga, Tennessee
Utility Acid Precipitation Study Program (UAPSP)	Environmental Assessment Department Electric Power Research Institute (Manager) Funded by UAPSP	19 (Duplicate Collectors at 2)	Middle & Eastern United States	Daily	October 1981	Rockwell International Newbury Park, California

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS (Cont.)

Network	Measured parameters	Data Storage System	Data Storage Format	Contact	Comments
Kennedy Space Center Precipitation Network	pH, Conductivity SO_4^{2-}, NO_3^-, F^-, Cl^-, Na^+, K^+, Ca^{++}, Mg^{++}, NH_4^+	Hewlett Packard System 1000 Kennedy Space Center	ASCII	B. Madsen Chemistry Dept. University of Florida Orlando, FL 32809 (305-275-2246)	o source-oriented o some met. data
Multi-State Atmospheric Power Production Pollution Study Precipitation Chemistry Network (MAP3S)	pH (Lab and Field) Conductivity SO_2, SO_4^{2-}, NO_2, NO_3^-, Cl^-, $PO_4^{=}$, NH_4^+, Na^+, K^+, Ca^{++}, Mg^{++}	CDC 6600 Brookhaven National Labs New York	ASCII (TAPE)	M. Terry Dana Battelle Pacific NW Labs Richland, WA 99352 (509-373-2851)	o lab QC program o some sites have met. data o screening of data prior to reporting
National Atmospheric Deposition Program (NADP)	pH (Lab and Field) Conductance SO_4^{2-}, NO_3^-, $PO_4^{\equiv}$, Cl^-, NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+	SAROAD Data Base EPA, Research Triangle Park, NC	ASCII (TAPE)	J. Gibson Natural Res. Ecology Lab. Colorado State Fort Collins, CA 80523 (303-491-5571)	o QC on anal. lab. limited field QA o a few stations have met. data
National Coal Assoc./ Bituminous Coal Research Inc. Precipitation Quality Network (NCA/BCR)	pH Conductivity, Acidity SO_4^{2-}, NO_3^-, F^-, Cl^-, NH_4^+, Ca^{++}, Na^+, K^+, Mg^{++}	Digital 3400 Bituminous Coal Research Inc.	N/A (DISC)	J. Boyer Bituminous Coal Res. Inc. 350 Hochberg Monroeville, PA 15146 (412-327-1600)	o some stles have met. data
Tennessee Valley Authority Deposition Network (TVA)	pH (Lab) Conductance SO_4^{2-}, NO_3^-, Cl^-, $PO_4^{\equiv}$, Fl^-, NH_4^+, K^+, Mg^{++}, Na^+, Ca^{++} Weak and Strong Acid by Gran Titration	IBM 370 (TAPE) TVA (To be validated in 1981)	EBCDIC (TAPE)	W. J. Parkhurst Air Resources Program Tennessee Valley Authority Muscle Shoals, AL 35660 (205-386-2831)	o some sites have met. data o some sites are source-oriented o outliers rejected prior to reporting
Utility Acid Precipitation Study Program (UAPSP)	pH (Lab and Field) Conductivity (Lab and Field) SO_4^{2-}, NO_3^-, Cl^-, $PO_4^{\equiv}$, Ca^{++}, K^+, Mg^{++}, Na^+, NH_4^+, Dissolved NO_2 (6 sites for one year), Weak and Strong Acid by Gran Titration (all sites for one year)	IBM 3081 Stanford Univer. Stanford, CA Also SAROAD Data Base, EPA Research Triangle Park, NC (After July 1982)	ASCII & EBCDIC (TAPE)	P. Mueller Environmental Assess. Dept. Electric Power Res. Inst. 3412 Hillview Palo Alto, CA 94304 (415-855-2586)	o lab and field QC program o external audit QA as of April 82 o data rejection for outliers

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS (Cont.)

Network	Agency	Number of Stations	Area Monitored	Sampling Interval	Start Date	Laboratory
Oxidation and Scavenging Characteristics of April Rains (OSCAR)	U.S. Environmental Protection Agency	Intermediate Density: 37 High Density: 47	Intermediate Density: Eastern U.S. and Canada High Density: Northeast Indiana	Sequential (0.6 mm Intervals)	April 1981	Battelle Pacific Northwest Laboratory Richland, Washington
WMO/NOAA/EPA Network	Air Resources Laboratory National Oceanic and Atmospheric Administration (NOAA)	17	United States	Weekly (Since 1980) Monthly (Prior to 1980)	1972	Atmospheric Chemistry Lab Illinois State Water Survey

TABLE A2-3 SUMMARY OF UNITED STATES WET DEPOSITION NETWORKS (Cont.)

Network	Measured parameters	Data Storage System	Data Storage Format	Contact	Comments
Oxidation and Scavenging Characteristic of April Rains (OSCAR)	pH (Lab and Field) conductivity SO_4^{2-}, NO_3^-, Cl^-, $PO_4^{\equiv}$ NH_4^+, Ca^{++}, Mg^{++}, K^+	CDC 6600 Brookhaven National Labs New York	ASCII (TAPE)	R. Easter Battelle Pacific NW Labs Richland, WA 99352 (509-373-2861)	o one month field study o lab QC program o some sites have met. data o screening of data prior to reporting
WMO/NOAA/EPA Network	pH (Lab and Field) Conductivity SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Mg^{++}, K^+, Na^+	SAROAD Data Base EPA, Research Triangle Park, NC	ASCII (TAPE)	J. Miller NOAA/ARL Silver Spring, MD 20910 (301-427-7645)	o lab QC program o some sites have met. data o now operated as part of NADP network

APPENDIX 3

TABLE OF CONVERSION FACTORS FOR CONCENTRATION AND DEPOSITION UNITS

TABLE A3-1 TABLE OF CONVERSION FACTORS FOR CONCENTRATION AND DEPOSITION UNITS

Ion	Concentration $mg\ l^{-1}$ per $\mu mole\ l^{-1}$	Deposition $kg\ ha^{-1}$ per $mmole\ m^{-2}$
H^+	0.0010	0.010
NH_4^+	0.0180	0.180
Na^+	0.0230	0.230
Ca^{++}	0.0401	0.401
Mg^{++}	0.0243	0.243
SO_4^{2-}	0.0961	0.961
NO_3^-	0.0620	0.620
Cl^-	0.0355	0.355

EXAMPLE for SO_4^{2-}

0.0961 $mg\ l^{-1}$ of SO_4^{2-} equal 1 $\mu mole\ l^{-1}$
0.961 $kg\ ha^{-1}$ of SO_4^{2-} equal 1 $mmole\ m^{-2}$