# ATMOSPHERIC SCIENCES AND ANALYSIS
# WORK GROUP 2

UNITED STATES — CANADA

# MEMORANDUM OF INTENT
# ON
# TRANSBOUNDARY AIR POLLUTION

FINAL REPORT
NOVEMBER 1982

# WORK GROUP 2

# ATMOSPHERIC SCIENCES AND ANALYSIS

## FINAL REPORT

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Submitted to the Coordinating Committee 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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We are pleased to transmit under cover of this letter the FINAL REPORT* of Work Group 2 (Atmospheric Sciences and Analysis) as required in our terms of reference and the work plans. We believe this report satisfies, in a scientifically responsible manner, our objectives under the Memorandum of Intent.

Lester Machta

Lester Machta
U.S. Chairman
Work Group 2

H L Ferguson

Howard L. Ferguson
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* the FINAL REPORT has four supporting technical papers. These are:

| | |
|---|---|
| 2F-A | Atmospheric Sciences Subgroup Report |
| 2F-M | Regional Modeling Subgroup Report |
| 2F-I | Monitoring and Interpretation Subgroup Report |
| 2F-L | Local and Mesoscale Analysis Subgroup Report |

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# FOREWORD

This is the final report prepared by the Atmospheric Sciences and Analysis Work Group (2). This group is one of five established under the Memorandum of Intent signed by the governments of Canada and the United States on August 5, 1980.

This final report, the main product of Work Group 2, which is supported by four technical documents represents the currently available information relevant to transboundary air pollution, particularly acidic deposition.

The information in these reports will be used by both governments to develop a consensus on the nature and extent of transboundary pollution.

Any portion of these reports is subject to modification and refinement as further advances in scientific understanding become available.

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# INTRODUCTION

# 1. INTRODUCTION

In 1968 Oden[1] suggested that acidity in precipitation in Sweden was largely attributable to emissions of sulfur compounds in Central Europe and England. By 1972 Rodhe et al[1] had developed the first quantitative analysis of the long range transport of sulfur in Europe. They showed that distances of transport frequently exceed 1000 kilometers, the residence time of sulfur in air was 2-4 days and the fields of deposition were roughly symmetrical and slightly displaced to the northeast from sources of emission.

In 1978, the Governments of Canada and the U.S.A. established a Bilateral Research Consultation Group on the Long Range Transport of Air Pollutants to co-ordinate the exchange of scientific information on acid precipitation. This group documented the transboundary exchange of sulfur and nitrogen oxides between the U.S.A. and Canada in 1979. In the fall of 1978, the United States Congress passed a resolution calling for bilateral discussions with Canada to preserve and protect mutual air resources. On August 5, 1980, the two governments signed a Memorandum of Intent "to develop a bilateral agreement on transboundary air pollution including the already serious problem of acid rain". To provide a suitable technical and scientific foundation for the

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[1] From Cowling, E.B. (1982). Acid precipitation in historical perspective. Environmental Science and Technology, Vol. 16, No. 2, pp. 110-123.

formulation of such an agreement, bilateral work groups were established to prepare scientific reports on specific aspects of the problem. The specific aspect that Work Group 2 was to address was atmospheric science and modeling. This Work Group was established to provide information, based on co-operative atmospheric modeling and analysis of monitoring and other data, which would lead to a further understanding of the transport of air pollutants between source regions and sensitive areas. The complete Terms of Reference for the Work Group and its membership are contained in Appendices 1 and 2, respectively.

The purpose of this report is to provide as complete a response as possible to all the scientific and technical areas identified in the Terms of Reference and as specified in the approved phased Work Plans. The Work Group has devoted its efforts to developing source-receptor relationships based on quality controlled modeling results and other analyses of data. During the past year, the Work Group has:

(1) documented, evaluated, intercompared and applied eight regional-scale models to the North American Continent;

(2) assessed the appropriateness of the methods and assumptions used in these regional models to quantify source-receptor relationships on an annual basis over eastern North America;

(3) attempted to define the applicability and limitations of the models to predict the result of changes in annual emission rates in this region; and

(4) used data to estimate the usefulness of the models and the validity of the annual source-receptor relationships.

Much is known about the physical process of atmospheric transport and transformation and deposition of acidic substances and their precursors, but some uncertainties remain. The extent to which these uncertainties affect the reliability of model results is an important question in designing appropriate control strategies.

In the interests of brevity and clarity, some simplifications have been made in the analyses of results presented and discussed in this report but a major effort has been made to review the main features of all currently available research findings, both published and unpublished, in order to specify the range of uncertainty that characterizes the results presented in this report.

Although many substances may undergo transboundary atmospheric transport and have harmful effects upon either atmospheric or surface receptors, acidic deposition has been the phenomenon of primary concern for the Work Group. Emphasis has also been placed on the development of a "transfer matrix" which is a form of model output which generally relates the contribution of source areas to a sensitive receptor area.

For the analysis of transport, transformation and deposition to be useful, a designation of the pollutant or pollutants believed to be causing the damage to man or his environment is required. Relatively more information is available for sulfur and its species than for oxides of nitrogen. For this reason, and others, Work Group 2 has focussed its efforts primarily on sulfur emissions and depositions over larger time and space scales in eastern North America.

It is clearly recognized that many of the chemical transformations of acid-related substances in the atmosphere are non-linear. The significance of these non-linear processes on the source-receptor relationships obtained from the Work Group 2 models, which make linear approximations, depends upon the specific applications of these models. For example, the chemistry determines the proportion of each form of sulfur that can be deposited at a given downwind distance. If total sulfur, that is, sulfur dioxide plus sulfate, is of primary interest, the chemistry involved in sulfur dioxide to sulfate conversion acquires a secondary role. On the other hand, if the deposition of hydrogen ion and other ionic species must be specified, then atmospheric chemistry would play a crucial role in determining the contributors to the acid rain impact. In fact, a demand for distinct ionic species cannot be adequately satisfied by the chemistry module of any current long range transport model.

There are other specifications which would have to be satisfied before these models are able to provide reliable detailed control strategy advice for control options involving specific point sources. For this level of application the significance of episodic deposition events which contribute a large part of the total seasonal or annual deposition must be understood. Similarly the role of deposition in snow leading to spring "snow melt shock" in streams would need to be clarified.

The Work Group has placed a high priority on addressing all issues raised by the peer and other external reviews of the working papers that preceded this final report. The working documents were reviewed by 46 individuals or groups. Based on an analysis of these diverse peer reviews by an independent contractor[1], the Work Group concluded that

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[1] Munn, R.E. (1982). Synthesis of Peer Reviews: Conclusions and Recommendations. Institute for Environmental Studies, The University of Toronto, Ontario, Canada.

the reviews provided a representative cross-section of scientific opinion on these interim publications.

Chapters 2 to 5 of this report summarize the current state-of-the-art of the application of operational atmospheric long range transport models with particular reference to eastern North America. They trace the modeling sequence from emissions through atmospheric transport, dispersion and chemical transformations to deposition on the earth's surface. Chapter 6 deals with the monitoring data which form the basis for model development and testing. Chapters 7 and 8 provide an overview of the current models, and their limitations and applications, focussing primarily on sulfur. Chapters 9 and 10 address other major pollutants which can be transported over long distances and the significance of local and mesoscale processes in the context of transboundary air pollution. Chapter 11 provides conclusions and recommendations concerning the "research modeling and monitoring elements of an agreement" as required by the Terms of Reference.

Since this Final Report is intended as a general reference for the use of non-scientists as well as scientists, an attempt has been made to avoid technical complexity and a Glossary of Terms is included. The detailed analyses which form the technical basis for this report will be found in the four Sub-Group Reports* which are being published simultaneously. Technical readers interested in specific sections are urged to refer to these companion documents.

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* The four supporting technical papers are:
2F-A Atmospheric Sciences Subgroup Report
2F-M Regional Modeling Subgroup Report
2F-I Monitoring and Interpretation Subgroup Report
2F-L Local and Mesoscale Analysis Subgroup Report.

# EMISSIONS

# 2. EMISSIONS

## 2.1 Emission Inputs to Models

Emissions inventories in the U.S. and Canada have traditionally been prepared on an individual point and area source basis as well as for aggregations of sources over various geographical units like square grids, counties, Air Quality Control Regions, states and provinces. It is generally thought that emissions inventories are more accurate for larger geographic units than for smaller units; however LRT models usually require smaller geographic aggregations of sources because of the way in which sources are parameterized and the desire to simulate sub-regional features of the concentration and deposition fields. Emissions inventories for the major pollutants like sulfur dioxide, nitrogen oxides, particulates, carbon monoxide and hydrocarbons have traditionally received the most emphasis because of concern over the adverse health and welfare effects of these pollutants. However, the acid deposition problem has prompted interest in the inventories of other potential acidifying or neutralizing substances like primary sulfates, ammonia and calcium. Most recently, there has been renewed interest in the emissions inventories of heavy trace metals like manganese and vanadium because of their potential role as tracers of emissions from a source in a specific category.

Modelers use emissions data in various ways. These include point and area sources which are (1) used within a given grid cell or geographic area as a single source emitting at one level in the atmosphere, (2) used and stratified vertically or (3) used as discrete puffs with masses proportional to the emission rate and time of travel.

The grid sizes vary from 70 by 70 kilometers to 190 by 190 kilometers.

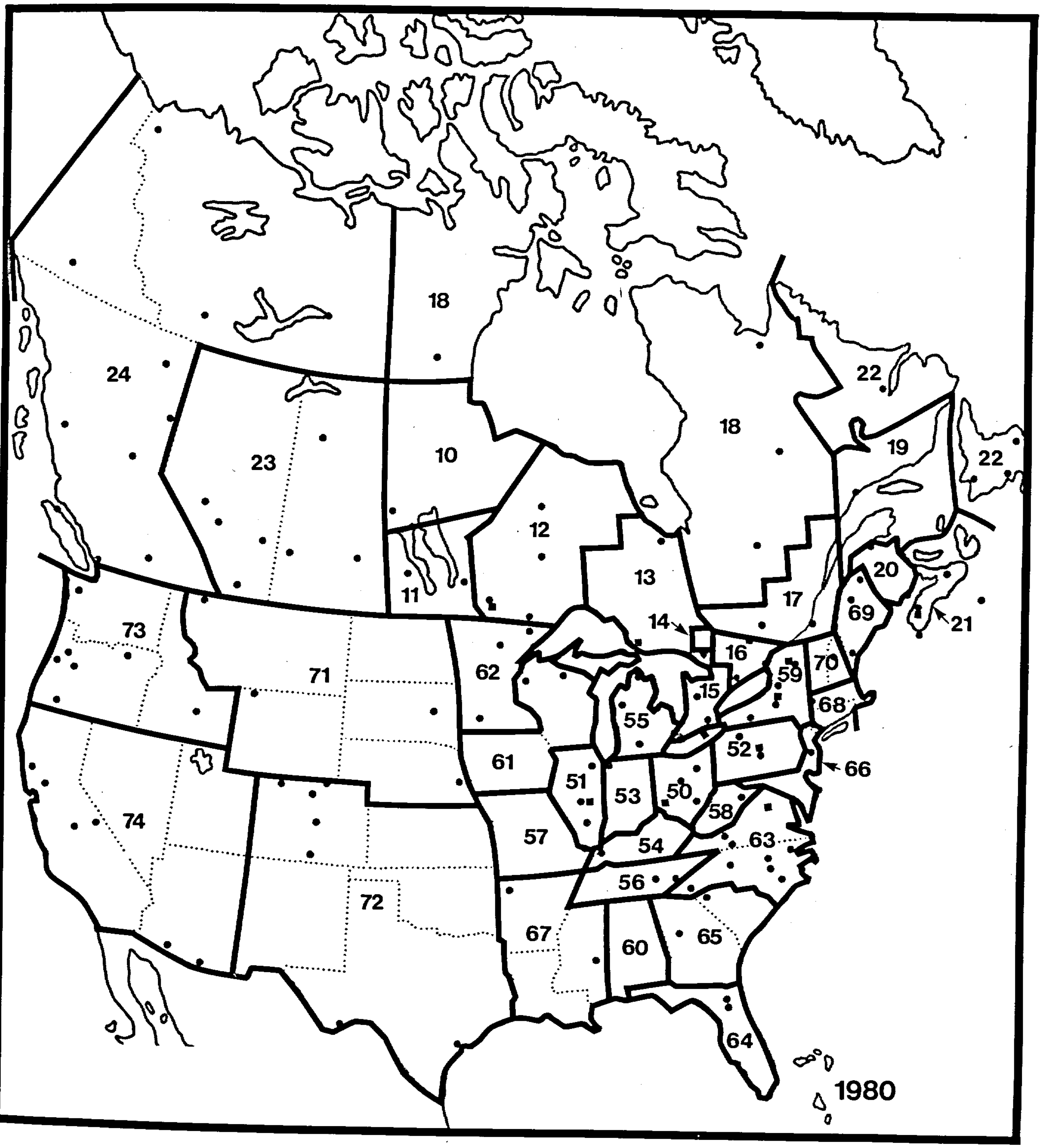
## 2.2 Agreed Upon Sulfur Dioxide Emissions Inventory (1978)

### 2.2.1 Canada

The best estimate Canadian sulfur dioxide emissions inventory for the base year 1978 was developed by the Canadian part of Work Group 3B for use in model validation. Point sources were located by their latitude - longitude and area sources specified on a 127 km to 127 km grid spacing.

For the final phase, it was decided that the emission source regions to be used in the development of an MOI transfer matrix should be resolved spatially on a province/subprovince and state/multi-state level as shown in Figure 2.1; there are 15 source regions in Canada and 25 in the U.S. The emissions of sulfur dioxide in Canada summarized by province and source region are shown in Table 2.1.

Table 2.2 shows the historical trend in Canada for emissions of sulfur dioxide. It can be seen that the emissions of sulfur dioxide increased from 1955 to 1965 but decreased from 1965 to 1978. There has been a significant increase in the sulfur dioxide emissions from utilities over the time period shown but the emissions from copper-nickel smelting peaked in 1965 and have since been decreasing (the emissions from this sector are lower than current levels because of the prolonged work stoppage at the Inco Smelter in Sudbury in 1978).



North American source regions
used for the transfer matrices

Figure 2.1

TABLE 2.1 Canadian sulfur dioxide emissions for 1978
by province and modeling source region
(emissions in kilotonnes of sulfur dioxide/year)

| Region Number | Province(s) and Subregion Name | Region Emission Total | Province Emission Total |
|---|---|---|---|
| 10 | Manitoba - Northern | 473.5 | 502.0 |
| 11 | Manitoba - Southern | 28.5 | |
| 12 | Ontario - Northwestern | 17.9 | 1610.0 |
| 13 | Ontario - Northeastern and Algoma | 183.9 | |
| 14 | Ontario - Sudbury* | 689.1 | |
| 15 | Ontario - Southwestern and Toronto | 667.6 | |
| 16 | Ontario - Southeastern | 51.5 | |
| 17 | Quebec - Montreal and St. Lawrence Valley | 454.6 | 1073.5 |
| 18 | Quebec - Northern | 539.6 | |
| 19 | Quebec - Gaspe Bay | 79.3 | |
| 20 | New Brunswick | 191.5 | 191.5 |
| 21 | Prince Edward Island | 169.9 | 8.7 |
| | Nova Scotia | | 161.2 |
| 22 | Newfoundland - with Labrador | 59.5 | 59.5 |
| 23 | Saskatchewan | 560.9 | 41.5 |
| | Alberta | | 519.4 |
| 24 | British Columbia with | 247.7 | 244.6 |
| | Yukon/N.W.T. | | 3.1 |
| | Canadian Subtotal | 4415.0 | 4415.0 |

Data from Environment Canada (1981)

* typically emissions from this source are 829 kilotonnes per year but were lower in 1978 due to a prolonged work stoppage.

TABLE 2.2 Historical emissions of sulfur dioxide for Canada (in kilotonnes)

| INDUSTRIAL SECTOR | YEAR<br>1955 | <br>1965 | <br>1978 |
|---|---|---|---|
| Cu-Ni Smelters | 2887.4 | 3902.0 | 1673.0 |
| Power Plants | 56.3 | 261.8 | 718.0 |
| Other Combustion | 1210.1 | 1129.6 | 885.0 |
| Transportation | 83.5 | 48.7 | 77.8 |
| Iron Ore Processing | 109.7 | 155.8 | 167.0 |
| Others | 189.9 | 1095.3 | 894.2 |
| TOTAL | 4536.9 | 6593.2 | 4415.0 |

Data from Environment Canada (1981)

### 2.2.2 United States

The U.S. sulfur dioxide emissions inventory representative of 1978, given for each eastern state as total emissions for the utility and non-utility sectors, was developed by contractors to EPA; utilities by E.H. Pechan and Associates based on 1978 fuel consumption, plant flue gas desulfurization equipment and other fuel data (for example, fuel sulfur content and ash sulfur retention); and non-utilities by the Mitre Corporation. Although the non-utility emission estimates are not specifically for 1978, the U.S. part of Work Group 3B has recommended their use in the absence of better information. Table 2.3 lists the sulfur dioxide emission totals for the 25 U.S. source regions used. This table also summarizes emissions by state. The U.S. source regions are numbered 50 through 74 (see Figure 2.1).

A disaggregation of the emissions for the eastern U.S. was prepared by the Modeling Subgroup. The power plants, identified by Pechan and Associates as among the 200 largest utility emitters for 1978, were located by the latitude and longitude. The remaining utility emissions for the states were distributed as state-wide percentage changes in the 1979 emissions of plants not included in the top 200 emitters for 1978. The 1979 utility emissions estimates and plant locations were supplied by the Ontario Ministry of the Environment. These emissions were calculated in a manner similar to that used by Pechan and Associates for 1978 calculations.

TABLE 2.3 United States sulfur dioxide emissions for 1978 by State and modeling source region (emissions in kilotonnes of sulfur dioxide/year)

| Region Number | State | State Emission | | | Region Emission Total |
|---|---|---|---|---|---|
| | | Utility | Non-Utility | Total | |
| 50 | Ohio | 2203.8 | 575.1 | 2778.9 | 2778.9 |
| 51 | Illinois | 1190.0 | 367.4 | 1557.4 | 1557.4 |
| 52 | Pennsylvania | 1316.7 | 656.7 | 1973.4 | 1973.4 |
| 53 | Indiana | 1225.2 | 492.9 | 1718.1 | 1718.1 |
| 54 | Kentucky | 1085.6 | 113.2 | 1198.8 | 1198.8 |
| 55 | Michigan | 727.4 | 332.3 | 1059.7 | 1059.7 |
| 56 | Tennessee | 937.2 | 138.2 | 1075.4 | 1075.4 |
| 57 | Missouri | 918.2 | 189.4 | 1107.6 | 1107.6 |
| 58 | West Virginia | 813.7 | 132.9 | 946.6 | 946.6 |
| 59 | New York | 471.6 | 535.8 | 1007.4 | 1007.4 |
| 60 | Alabama | 495.4 | 159.8 | 655.2 | 655.2 |
| 61 | Wisconsin | 410.3 | 154.9 | 565.2 | 907.6 |
| | Iowa | 241.0 | 101.4 | 342.4 | |
| 62 | Minnesota | 176.6 | 103.2 | 279.8 | 279.8 |
| 63 | Virginia | 202.0 | 148.3 | 350.3 | 875.9 |
| | North Carolina | 359.9 | 165.7 | 525.6 | |
| 64 | Florida | 539.6 | 188.6 | 728.2 | 728.2 |
| 65 | Georgia | 552.4 | 101.1 | 653.5 | 919.1 |
| | South Carolina | 178.5 | 87.1 | 265.6 | |
| 66 | Maryland | 199.9 | 96.9 | 296.8 | 760.5 |
| | Delaware | 50.4 | 34.7 | 85.1 | |
| | New Jersey | 104.7 | 228.4 | 333.1 | |
| | District of Columbia | 9.4 | 36.1 | 45.5 | |

TABLE 2.3 (continued)

| Region Number | State | State Emission Utility | Non-Utility | Total | Region Emission Total |
|---|---|---|---|---|---|
| 67 | Arkansas | 53.4 | 47.5 | 100.9 | 617.6 |
| | Louisiana | 57.8 | 213.6 | 271.4 | |
| | Mississippi | 187.3 | 58.0 | 245.3 | |
| 68 | Massachusetts | 234.6 | 183.4 | 418.0 | 575.2 |
| | Connecticut | 23.7 | 106.0 | 129.7 | |
| | Rhode Island | 3.1 | 24.4 | 27.5 | |
| 69 | Maine | 7.8 | 74.5 | 82.3 | 82.3 |
| 70 | Vermont | 0.3 | 13.2 | 13.5 | 86.9 |
| | New Hampshire | 47.4 | 26.0 | 73.4 | |
| 71 | Nebraska | 37.9 | 22.3 | 60.2 | 581.3 |
| | North Dakota | 78.1 | 25.4 | 103.5 | |
| | South Dakota | 33.0 | 8.0 | 45.0 | |
| | Montana | 28.1 | 166.9 | 195.0 | |
| | Wyoming | 96.1 | 81.5 | 177.6 | |
| 72 | Oklahoma | 13.0 | 76.3 | 89.3 | 1698.1 |
| | Kansas | 154.0 | 84.9 | 238.9 | |
| | Colorado | 77.5 | 41.5 | 119.0 | |
| | New Mexico | 81.8 | 389.1 | 470.9 | |
| | Texas | 242.4 | 537.6 | 780.0 | |
| 73 | Washington | 69.9 | 301.3 | 371.2 | 470.3 |
| | Idaho | 0 | 49.4 | 49.4 | |
| | Oregon | 0.1 | 49.6 | 49.7 | |
| 74 | California | 117.1 | 470.1 | 587.2 | 2220.4 |
| | Nevada | 38.4 | 287.6 | 326.0 | |
| | Utah | 30.2 | 175.2 | 205.4 | |
| | Arizona | 60.1 | 1041.7 | 1101.8 | |
| | Continental U.S. Subtotal | | | 25881.7 | 25881.7 |

The non-utility emissions were disaggregated within each state by scaling the non-utility sources in the MAP3S sulfur dioxide inventory prepared by Brookhaven National Laboratory (BNL) to the totals given by the Mitre Corporation. In the BNL MAP3S inventory, point sources are located by their latitude and longtitude. Area emissions are presented as county totals located at the area centroid of the county. Work Group 3B has approved this disaggregation for use in the Work Group model evaluation.

The western U.S. emissions distribution was provided by Work Group 3B. The large point sources, except utilities, were taken from the 1978 National Emissions Data System files (NEDS) and were identified by latitude and longitude. The utilities emissions were as estimated by Pechan and Associates. All other emissions were extracted from NEDS and presented on an Air Quality Control Region (AQCR) basis.

The western emissions were not available in time for some of the final model runs. Thus, different emissions estimates for the western U.S. sources were used by the participating modelers.

An analysis of sulfur dioxide emission trends during 1940-1975 in the eastern U.S. has been made recently for EPA. This analysis (Table 2.4) shows that sulfur dioxide emissions have not increased steadily over the entire period for the entire eastern U.S., but have in fact first increased and then decreased with the exception of the Southeast Region (IV), where the sulfur dioxide emissions have steadily increased. A more detailed analysis of utility sulfur dioxide emissions trends, in the highest utility emitting states, shows a rather steady decline in utility emissions in the period 1974 through 1980.

TABLE 2.4 Historical emissions of sulfur dioxide in the United States by region (in kilotonnes)

| REGION | SECTOR | YEAR<br>1955* | <br>1965* | <br>1978 |
|---|---|---|---|---|
| I<br>(Northern States) | Electric Utilities | 561 | 476 | 317 |
| | Other Sources | 884 | 714 | 427 |
| | TOTAL | 1445 | 1190 | 744 |
| II<br>(New York, New Jersey) | Electric Utilities | 1252 | 990 | 576 |
| | Other Sources | 1627 | 1510 | 764 |
| | TOTAL | 2879 | 2500 | 1340 |
| III<br>(Mid-Atlantic States) | Electric Utilities | 1154 | 1573 | 2592 |
| | Other Sources | 2943 | 3239 | 1106 |
| | TOTAL | 4097 | 4812 | 3698 |
| IV<br>(Southeastern States) | Electric Utilities | 1179 | 2437 | 4337 |
| | Other Sources | 1341 | 1800 | 1012 |
| | TOTAL | 2520 | 4237 | 5349 |
| V<br>(Upper Midwestern States) | Electric Utilities | 3735 | 5568 | 5934 |
| | Other Sources | 4240 | 6337 | 2027 |
| | TOTAL | 7975 | 11905 | 7961 |
| OTHER STATES<br>(Mississippi River States and Texas) | Electric Utilities | 1011 | 632 | 2428 |
| | Other Sources | 3161 | 2111 | 4361 |
| | TOTAL | 4172 | 2743 | 6789 |
| GRAND TOTALS | Electric Utilities | 8892 | 11676 | 16184 |
| | Other Sources | 14196 | 15711 | 9698 |
| | TOTAL | 23088 | 27387 | 25882 |

*Method differs from that used for 1978 data.

### 2.2.3 Data Used For Model Evaluation and the Transfer Matrices

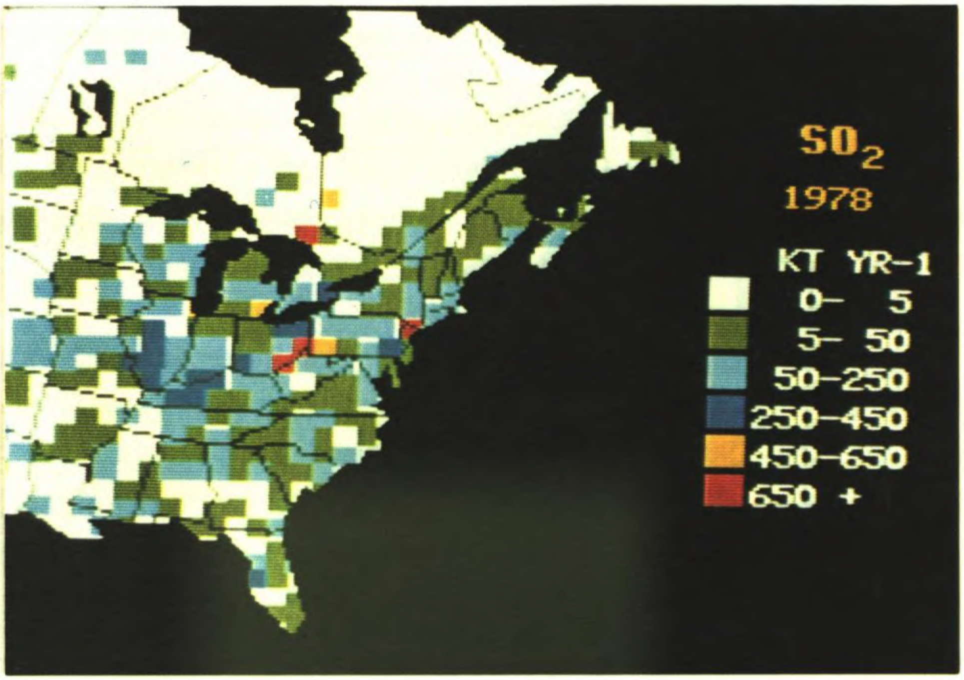
When the agreed upon sulfur dioxide emissions inventory is displayed on a grid basis (see Figure 2.2) the clustering of the high emission areas, along the Ohio River and elsewhere in the U.S., is readily apparent as are the high emission areas in Canada.

Figure 2.2 shows both the 1978 and the 1980 gridded values for sulfur dioxide. The 1978 distribution was used for model evaluation purposes and the 1980 distribution was used to produce the transfer matrices.

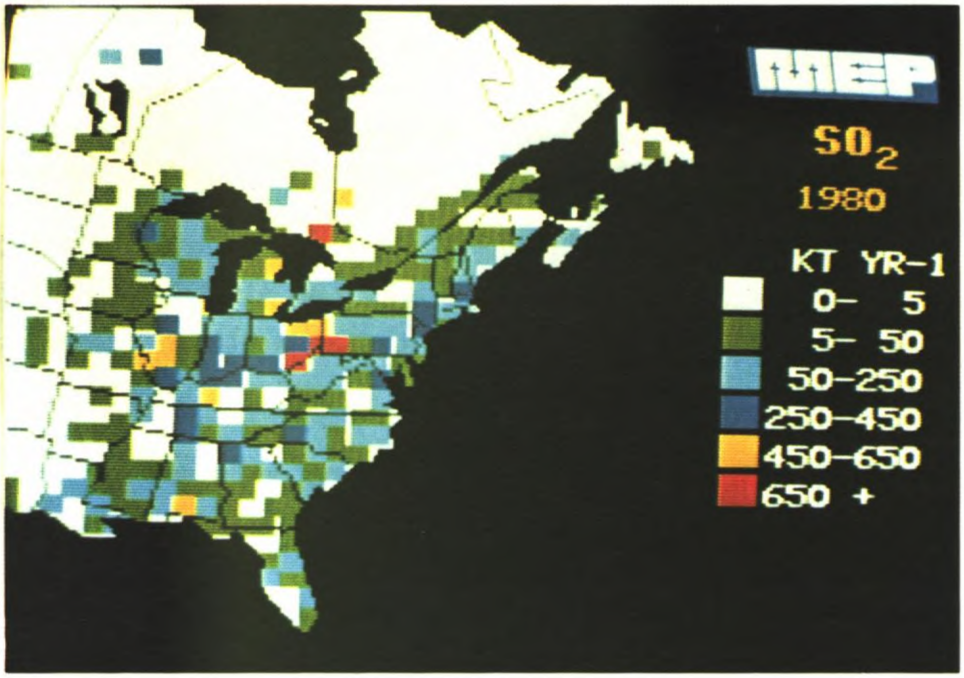
### 2.2.4 Uncertainty and Aggregation

Work Group 3B has provided estimates of uncertainty in the 1980 U.S. and Canadian emissions in their final report and feels that these estimates should apply reasonably well to the 1978 sulfur dioxide emissions.

The participating modelers agreed to group the 40 source regions used in the transfer matrix into 11 aggregated regions to facilitate analysis of the modeling results. Table 2.5 lists the 11 aggregated areas which are shown on Figure 2.3 with the location of the selected sensitive areas.



(Used for Model Evaluations)



(Used for Transfer Matrices)

Figure 2.2 Sulfur dioxide emissions in kilotonnes per year representative of 1978 and 1980 on a grid basis (127 kilometers) [Source: MEP, 1982].

TABLE 2.5 Source region groupings for presentation of the modeling results

| Region Number | Region Name | Source Areas Included |
|---|---|---|
| 1 | Maritime Provinces | 20, 21, 22 |
| 2 | Quebec | 17, 18, 19 |
| 3 | Ontario | 12, 13, 14, 15, 16 |
| 4 | Western Provinces | 10, 11, 23, 24 |
| 5 | Northeastern States | 59, 68, 69, 70 |
| 6 | Eastern Midwest States | 50, 52, 58 |
| 7 | East Coast States | 63, 66 |
| 8 | Southern and Gulf Coast States | 60, 64, 65, 67 |
| 9 | Central States | 51, 53, 54, 56, 57 |
| 10 | Western Midwest States | 55, 61, 62 |
| 11 | Western States | 71, 72, 73, 74 |

The eleven aggregated emissions regions in North America and selected sensitive areas

Figure 2.3

**Sensitive Receptors**

1 Boundary Waters BW
2 Algoma ALG
3 Muskoka MUSK
4 Quebec QUEB
5 Southern Nova Scotia SNSC
6 Vermont/New Hampshire VT
7 Adirondacks ADIR
8 Pennsylvania PENN
9 Smokies SMOK

## 2.3 Status of Emissions Inventories for Other Compounds

In Canada, national emission inventories on a provincial basis have been produced for a variety of base years (1970-1978) for the major anthropogenic sources of mercury, copper, nickel, antimony, lead, manganese, vanadium, cadmium, cobalt, and tin. National emissions inventories for the U.S. for some of the above elements have also been produced in past years.

Work Group 3B has agreed to provide best estimate primary sulfate and nitrogen oxide inventories in their final report. They have also agreed to exchange and review volatile organic compound (VOC) emissions on a province and state-level and emissions for selected trace elements.

Efforts have been initiated in both the U.S. and Canada to develop inventories of other compounds like ammonia and it is expected that Work Group 3B will review these results after March 1982.

# TRANSPORT PROCESSES

# 3. TRANSPORT AND DIFFUSION PROCESSES

## 3.1 Description of the Processes

After a pollutant leaves the point of emission, be it a point source (such as a stack) or an area source (such as a city), it is affected by physical and chemical processes in the atmosphere. This chapter will deal with two important physical processes: the transport and the dispersion of the pollutant by large scale atmospheric flows. The chapter will also discuss how the models incorporate these two processes in the simulations.

Atmospheric flows are almost always turbulent, exhibiting a wide range of spatial and temporal scales of motion. Atmospheric turbulent eddies range from a few centimeters to several thousands of kilometers with time scales from a few seconds to several days. These eddies are mainly responsible for the transport and dispersion of pollutants. It is assumed that the pollutants do not alter the state of motion of the atmosphere.

A puff of pollutants released into the atmosphere is dispersed mainly by eddies which are comparable in size to the puff. Larger eddies bodily move the puff while smaller eddies simply redistribute the mass within the puff, smoothing out sharp gradients. In the initial stages the puff is dispersed by smaller eddies; but as it grows in size it is affected by larger eddies. When it reaches a size of several hundred kilometers, it is dispersed by eddies at the synoptic scale (synoptic scale eddies are three dimensional eddies synonymous with the high and low pressure weather systems).

In view of the wide range of the scales of motion in the atmosphere, atmospheric flows are conveniently studied by statistical methods. These methods study the impact of a puff released at a given point and time, on a receptor at a different point and time, by examining the probability that the puff will reach the receptor. The probability function depends upon the atmospheric flows and other processes such as scavenging and chemical reactions along the path.

Several methods are employed to determine this probability function. One approach assumes the shape of the function, as is the case in the statistical long range transport models. As a result of the distances involved in long range transport modeling, some of the assumptions underlying a statistical model (such as stationarity and homogeneity) may be questionable. Another approach attempts to overcome this problem by tracing the path of each puff, carrying out a mass balance along the path, and finally summing the contributions from all puffs. This method is generally referred to as the "Lagrangian" approach.

The atmosphere has a vertical extent of approximately 10 kilometers. The lowest one kilometer or so contains the three dimensional turbulence arising from the frictional interaction of the wind with the surface and through solar heat input. The lowest layer is called the mixed layer and is very often capped by a sharp inversion layer which inhibits transport from the mixed layer to the upper layers. The mixed layer height exhibits a diurnal cycle, being at its peak value (∿ 1 kilometer) during the early afternoon in eastern North America. With sunset the mixed layer shows a pronounced height change to a value near zero. Cooling at the surface during clear nights establishes a stable layer close to the ground. Most of the mixing in this layer takes place due to mechanical turbulence alone (that is, turbulence caused by friction).

Most of the time the pollutants are emitted into the mixed layer. It is thus reasonable to assume, for long range transport where dispersion mechanisms in the first few kilometers of travel are unimportant, that the puff of pollutants is well mixed vertically. An exception to this occurs when a puff is released above the mixed layer (emissions from tall stacks during the night). In this case the puff can travel a long distance with virtually no mixing. Such a puff will eventually intersect the mixed layer at some point downwind and become well mixed vertically. The mixed layer also exhibits spatial and temporal changes. Thus the puff may become entrained into the mixed layer in a random manner during its transport.

An added complexity in the transport of the puff arises at the lower boundary (earth's surface) where the wind speed is zero. This implies that the 'mean' wind (mean is defined as a time average) exhibits strong variations in the vertical within the mixed layer. During the day, the strong shear is confined only to the lowest layers. In this situation the mean wind is virtually uniform vertically through most of the mixed layer except very near the surface. It approaches the geostrophic wind above the mixed layer through a change within the capping inversion. During the night, on the other hand, a ground based inversion is often observed within which the mean wind exhibits strong vertical shear.

The implication of wind shear is that the puff may be differentially transported at different vertical levels causing expansion and thus shifting of the position of its centre of mass. Unless the wind shear is considered in models the mean path (trajectory) of the puff can be in error.

Transport out of the mixed layer into the upper levels can occur by the ventillating effects of clouds, large scale vertical motions, and by penetrating convection during the day time. These effects are important if one wishes to properly account for the distribution of mass within the mixed layer.

The transport and dispersion of pollutants over long distances is a very complex process. It is not possible to include all of these details in an 'operational' model. Models must make simplifying assumptions. These assumptions are described in the following section.

## 3.2. Treatment by the Models of Transport and Diffusion Processes

The manner in which the eight LRTAP models simulate transport and diffusion will be briefly described in the following paragraphs. For a more detailed treatment, the reader is referred to the report of the Regional Modeling Subgroup (Report 2F-M) and to the individual model profiles (Reports 2-5 to 2-12).

### 3.2.1 Movement of the Pollutant with the Wind

To carry out the essential task of simulating the movement of the pollutant with the wind, the models use either statistically derived winds, observed winds or winds derived from pressure fields at one or more heights in the layer between the surface and 850 millibars (about 1500 meters above ground) where most long range transport is believed to take place. Some of the models (ENAMAP, ASTRAP) reported here use an average wind in this layer while others (MOE, RCDM-3, CAPITA, MEP, UMACID, AES) use winds considered to be representative of a transport level.[1]

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[1] See Chapter 7, Table 7.2 for a full description of these models.

Because LRT models are generally used to generate long-term average concentrations and depositions, integration of the results with time is needed. Some models (AES, ENAMAP, CAPITA, MEP, UMACID) advect the pollutants from each source every 6 hours or so, using synoptic data, and integrate over long time periods while others (ASTRAP, MOE, RCDM-3) use mean monthly or annual wind fields or wind roses.

### 3.2.2 Dilution of the Pollutant by Atmospheric Turbulence

As it is moving along with the wind, the pollutant is also being dispersed and diluted by atmospheric turbulence which may be described as horizontal and vertical fluctuations of the wind about its mean speed and direction.

The treatment of the horizontal dispersion of the pollutant varies greatly in complexity among the models. The simplest approach is to assume horizontal uniformity within the plume or puff of pollutants, with the width of this plume or puff remaining constant with time (AES). This assumes that the horizontal dispersion occurs instantly at the time of emission throughout the emission grid cell. A slightly more complex treatment is to allow the width of the plume to vary with time, but still maintain horizontal uniformity. An example of this approach is the ENAMAP model. More detail may be introduced by allowing the concentrations to vary horizontally by using, for example, a Gaussian distribution whose standard deviations may or may not vary with time (MOE, MEP). The ASTRAP and UMACID models simulate horizontal dispersion by calculating the distribution of plume centerlines about the mean path or trajectory of the pollutants. The most complex treatments of horizontal dispersion are by the Eulerian models which use the horizontal wind components and/or an eddy diffusivity at each grid point. The RCDM-3 model uses analytical solutions to the Eulerian diffusion equation for large scale motions. The CAPITA model treats horizontal dispersion by a Monte Carlo technique, using repeated random perturbations of the movement of the pollutants about the mean flow.

As in the case of horizontal diffusion, the treatment of vertical diffusion and mixing height varies greatly among the models. Most models assume a uniform concentration in the vertical below a specified height because pollutants are very often uniformly mixed from the surface to the top of the mixed layer (usually several hundred to 2000 meters deep). In some models, the mixing height is constant in time and space (MOE) or it may vary daily, monthly, seasonally and/or spatially (RCDM-3, UMACID, AES, ENAMAP, MEP). The CAPITA model treats vertical diffusion as a random vertical perturbation. The ASTRAP model uses a vertical diffusivity which may be varied with time and height. Mixing heights (the top of the surface mixed layer) and noctural ground-based inversions are simulated by zero vertical diffusivity at the appropriate height above the ground.

## 3.3 Conservation of Mass in the Models - Use of the Lagrangian or Eulerian Framework

LRT models conserve the mass of the pollutant, be it sulfur or nitrogen, by solving the equation of the continuity of mass. When the equation is solved in a co-ordinate system that moves along with an air parcel, the model is said to be Lagrangian. If the conservation of mass equations are solved in a fixed co-ordinate system through which air masses are advected and diffused, the model is said to be Eulerian. Lagrangian models relate relatively easily to the processes going on in a specific air parcel, but can be difficult to relate to observations in a fixed sampling network. On the other hand, the formulation of the processes occurring in the moving air mass is more complex in an Eulerian than in a Lagrangian framework, but output can be more readily compared with observations. In addition, important statistics such as frequency of precipitation are derived from Eulerian (point) observations, but are often used in the Lagrangian sense. The relationship between the Lagrangian and Eulerian statistics is not always straightforward.

The majority of the models that are described in this report are Lagrangian in nature, but the RCDM-3 is an analytical-Eulerian model. The CAPITA model has both Eulerian and Lagrangian characteristics.

## 3.4 Limitations and Recommendations

In the statistical, or, analytical models (MOE and RCDM-3), the mean wind direction and the spread of the long-term long range plume from a source are assumed to have a certain predetermined behaviour. These assumptions are based on our experience with homogeneous and stationary turbulent flows. Simple translation of this experience to large scale flows, which are non-stationary and non-homogeneous (that is, the topography and diurnal pattern of turbulence changes along a puff trajectory), may not be valid.

The trajectory models (AES, MEP, UMACID, CAPITA, ENAMAP-1, and ASTRAP) derive the mean trajectory and the spread of a plume from the trajectories of individual puffs. In these models transport is dealt with more rigorously, but several difficulties are encountered in computing individual puff trajectories properly.

First, the wind fields for the large scale flows are derived from upper level wind velocity measurements, spaced approximately 400 kilometers apart, and surface wind measurements, spaced approximately 150 kilometers apart. This means that information at scales smaller than 150 kilometers for the surface and 400 kilometers for the upper levels are lost. This not only introduces errors in individual trajectories, it also confines the predictions of the models to a space resolution of at best 150 kilometers. Also, the trajectories in the vicinity of fronts may have gross errors because of these scale limitations. Since most precipitation events are of a frontal nature, considerable uncertainty exists in the model's ability to predict the movement of the specific pollutant parcel undergoing wet removal. Some models (MEP and CAPITA) attempt to treat subgrid scale effects by allowing dispersion about each trajectory.

Second, the wind fields are normally observed with a time resolution of 12 hours. The modelers interpolate the wind fields to finer time scales, but regardless of the interpolation scheme used, the dynamics of the flow are not reproduced at a scale smaller than 12 hours. Thus processes affected at scales of less than 12 hours may not be properly treated by the models. This has implications in the chemistry, deposition and source-receptor relationships.

Third, the wind fields used by the modelers are derived from a balance of inertia, pressure, and coriolis forces. Sometimes only the pressure fields are available and the modelers generate their own wind fields from a balance of pressure to coriolis forces. This does not account for the frictional effects at the surface. Some models make an empirical adjustment to reflect the frictional effects. However, these empirical adjustments are based on site specific studies and are not expected to be valid everywhere. One model (AES) uses multi-level gridded winds produced from the observed values by objective analysis techniques which include more complex meteorological effects.

Fourth, only one model (UMACID) uses the effects of vertical wind shear in the dispersion module. As pointed out earlier, wind shear can affect the individual trajectory by shifting the centre of mass of the puff.

Fifth, all models define the effective transport wind differently. Some assume it to be the surface wind, whereas others assume it to be at a height near 1500 meters. Some other assume a mixed layer average wind. There is no consensus about the proper definition of of the effective transport wind.

The above difficulties are severe for individual trajectories. They are less severe for the statistics of an ensemble of trajectories. For instance, over a long averaging time it is the relative spread of the ensemble of trajectories which determines the spread of pollutants from the mean. Therefore, some of the assumptions used by modelers may not be severe in defining a long-term long range plume from a source if deposition and chemical reactions are neglected. However, when deposition and chemical reactions are important such assumptions would introduce some errors. This also limits our ability to properly define the impact of a given source region on a given receptor.

Some models use a constant mixed layer height. Other models use mixing heights which vary in space on a monthly to seasonal time frame. The MEP and ASTRAP models introduce a diurnal variation to the mixed layer height. However, these models do not differentiate between the transport of the masses above the mixed layer and within the mixed layer. The mass remaining within the mixed layer may travel in a different direction from the mass above the mixed layer. The two masses could eventually decouple themselves, so that transporting them as a single "slab" is not a valid assumption. Also, if these masses were to be treated properly the number of trajectories to be computed would become unmanageably large. Trajectory models will not be very efficient for this purpose. Eulerian models may be more suitable.

It has been noted that mass transported above the mixed layer can be decoupled from the surface layer. Thus dry deposition of this mass will be virtually zero. Some models (MOE) account for this indirectly by assuming a smaller deposition velocity. Also, the mass above the mixed layer travels faster than below so that a single slab model could introduce errors in the spread of the trajectories.

Most models ignore mass transported vertically by large scale vertical motions. Clouds are capable of processing a large volume of mixed layer pollutants. Since sulfur dioxide to sulfate conversion is fairly rapid within clouds, ignoring mass transport by clouds would certainly result in an underestimation of the sulfate in precipitation. The MOE model accounts for this by assumming an apparent washout coefficient which is derived from the fact that the rate of removal of sulfate by precipitating clouds would be nearly equal to the rate of entrainment of sulfur dioxide by the clouds. This implicitly assumes rapid conversion of sulfur dioxide to sulfate within clouds. Ignoring vertical mass transport also affects the distribution of mass within the mixed layer. It should be noted that large scale mean vertical velocities are of the order of 1 centimeter per second which is comparable to the dry deposition velocity of sulfur dioxide and much larger than the dry deposition velocity of sulfate.

Transport of mass along a single trajectory is influenced by all the small scale phenomena described above. None of the models considered here explicitly treat these phenomena, but the errors associated with the neglect of small scale processes are likely to be less severe when averaged over an ensemble of trajectories. The following are some recommendations to alleviate some of these problems in the current models:

1. In order to assess the effects of the coarse time and space resolution of the network of radiosonde stations that is used with the present LRT models, a denser network of atmospheric sounding stations should be established covering an area of about 500 by 500 kilometers with a spacing of about 100 kilometers. The vertical distribution of wind and temperature should be sampled about 8 times per day, and the sampling should extend to a height of at least 4 kilometers. This network should be able to detect some of the smaller eddies that are undetected by the present network, as well as provide information on wind shear and fluctuations in the surface mixed layer.

2. In conjunction with the above meteorological data, air and precipitation sampling should be carried out using a pollutant or tracer which is released within the fine meteorological network. An inert tracer should be used in order to avoid chemical transformations. Air sampling should also be carried out by aircraft within and above the surface mixed layer. If possible, the tracer should be released at different heights. Sampling should be carried out under as many meteorological conditions as possible, including convective overturning.

3. Using the above data, LRT models should use the present coarse resolution meteorological data to forecast the downwind concentrations of the tracer. The present LRT and mesoscale models should also be run using the finer resolution data. The results should be compared with those using the coarse meteorological data, and the observed data, to determine what improvement, if any, results from the use of the fine meteorological grid data. This may resolve where more meteorological detail needs to be put into the present models.

4. Existing data sets containing fine resolution meteorological data and information from tracer studies should be examined carefully to see if they can provide the sort of information that items 1 to 3 above are intended to address.

5. Models need to be devised to account properly for the effects of the variability of mixed layer height in space and time as well as the other meteorological and chemical processes that contribute to acid deposition.

# ATMOSPHERIC CHEMISTRY

# 4. ATMOSPHERIC CHEMISTRY

## 4.1 Introduction

Increases in atmospheric acidification result from the oxidation of sulfur, nitrogen, and carbon compounds to form the strong mineral acids $H_2SO_4$ and $HNO_3$ and weak organic acids. Therefore, the oxidation of $SO_2$, NO, and $NO_2$ must be among the processes appearing in the long range transport LRT models if they are to predict meaningful wet and dry deposition patterns for individual species such as $SO_2$, $NO_2$, $HNO_3$, and $H_2SO_4$. That is because the rates for wet and dry removal of $SO_2$ and $NO_2$ are vastly different from $H_2SO_4$ and $HNO_3$, respectively. The chemical forms significantly influence the residence time and transport distances of these sulfur and nitrogen compounds. Also, the extent of the adverse ecological effects may be strongly dependent upon the chemical forms.

## 4.2 Linearity vs. Non-Linearity

The LRT models described in Chapter 7 attempt to account for the formation of $H_2SO_4$ through a simple, linear rate law, which is:

$$\begin{aligned} d[H_2SO_4]/dt &= d[SO_4^{2-}]/dt \qquad (4\text{-}1) \\ &= k_S[SO_2] \end{aligned}$$

In words, equation 4-1 states that the overall formation rate in the atmosphere of $H_2SO_4$ is equal to the rate for $SO_4^{2-}$ formation, which is in turn equal to a constant ($k_S$) times the $SO_2$ concentration. The constant $k_S$ includes the combined rate of $SO_2$

oxidation for all major pathways, where each is represented as a linear process. For example, the oxidation rate of $SO_2$ by an HO radical in the gas phase to form $H_2SO_4$ has the form

$$d[H_2SO_4]/dt = k_2[HO][SO_2] \tag{4-2}$$

If the HO concentration in the atmosphere is constant, then the rate can be expressed as

$$d[H_2SO_4]/dt = k_2^{'}[SO_2] \tag{4-3}$$

where $k_2^{'}$ is a pseudo first-order rate constant. This rate is linear in $SO_2$ concentration. That is, changes in $SO_2$ concentration will directly effect the $H_2SO_4$ formation rate. Thus, for the rate of $H_2SO_4$ formation to have a linear dependence on the ambient $SO_2$ concentration:

(a) the rate expression must have a first-order dependence on $SO_2$ ambient concentration,

(b) the $SO_2$ must not be a limiting reactant (that is, its concentration must greatly exceed those of the oxidizers so that it is not completely consumed), and

(c) $k_2^{'}$ must remain constant.

If all the major processes are linear, then their rates are additive and $k_S$ is the sum of the pseudo first-order rate constants for these processes. However, if one or more major $H_2SO_4$ formation processes cannot be expressed in a linear form such as in equation 4-3, then $k_S$ is not constant and equation 4-1 is, in principle, not an adequate representation for modeling the $H_2SO_4$ formation in the atmosphere.

The phenomenon of non-linearity refers to the variation of $k_S$ as a result of complex interactions of chemical and physical properties of the atmospheric system. The extent to which $k_S$ varies, as a function of those properties not treated by the modeling systems, is extremely relevant to the credence placed on the linear relationship between $SO_2$ and $SO_4^{2-}$ formation.

In order that the LRT models account for the formation of $HNO_3$ and organic acids, they must use similar linear expressions, such as:

$$d[HNO_3]/dt = d[NO_3^-]/dt \tag{4-4}$$

$$= k_N[NO_2 \text{ or } NO_x]$$

$$d[\text{organic acids}]/dt = k_0[\text{hydrocarbons}].$$

## 4.3 Summary of Possible Acidification Pathways

The major pathways leading to acidification of the air, suspended particles, dews, fog droplets, cloud nuclei, and raindrops are shown in Figure 4.1. Gas-phase photochemical and non-photochemical reactions produce free radicals which may react directly with $SO_2$, $NO_2$, and organics to produce acids, or which may react to form long-lived oxidants. Some of the long-lived oxidants may react directly in the gas phase with organics to form organic acids (for example, the $O_3$-olefin reaction), but they do not react at significant rates with $SO_2$ and $NO_2$. Of the long-lived oxidants formed, $H_2O_2$ is highly soluble, $HNO_2$ is soluble when $pH > 4$, $O_3$ is slightly soluble, and $NO_2$ is practically insoluble in water. Since $SO_2$ is also soluble when $pH > 3$, reactions with dissolved long-lived oxidants could be a major acidification pathway for wet suspended particles, dews, fog droplets, cloud nuclei and raindrops. Also, transition metal ions [especially

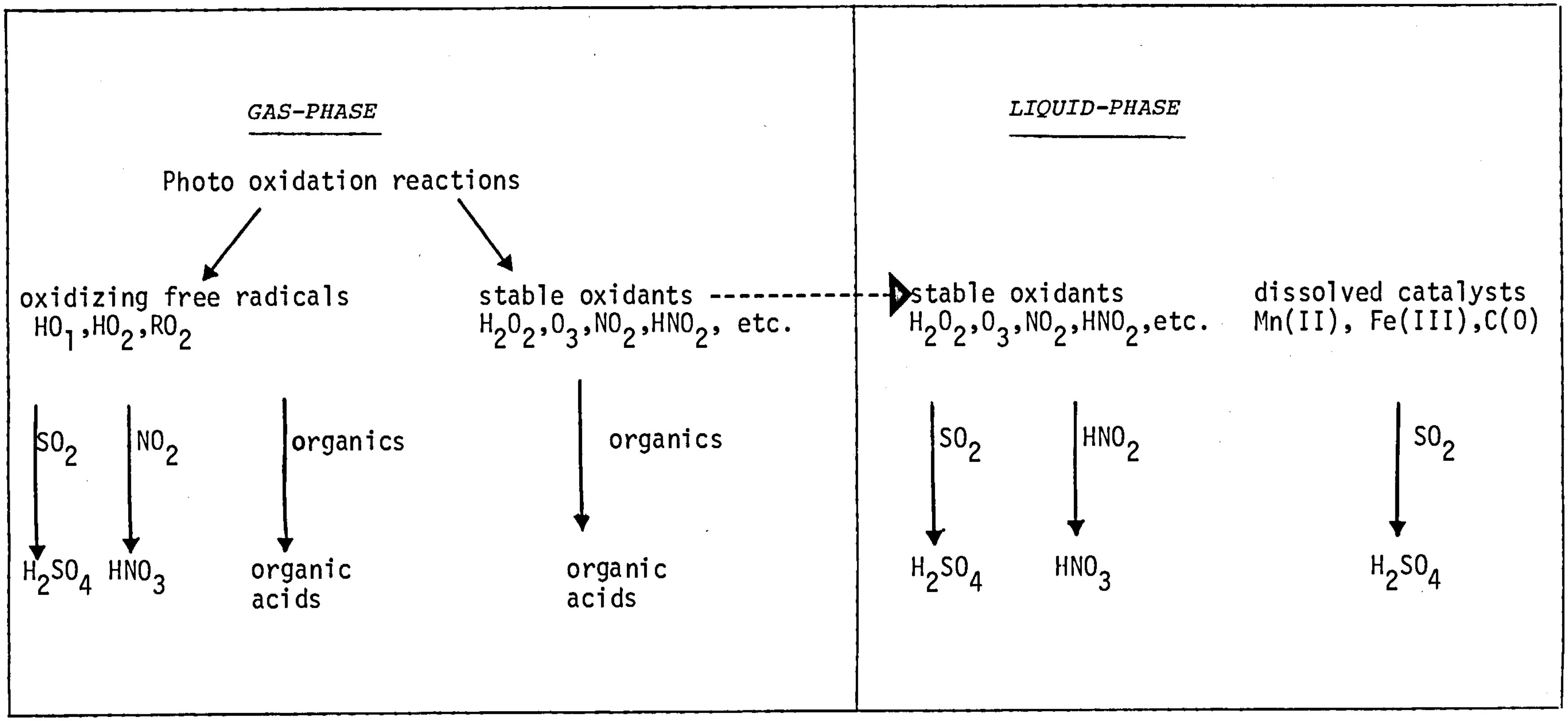

Figure 4.1 Major Pathways for Acidification in the Atmosphere

Mn(II) and Fe(III)] and carbon catalyze the oxidation of dissolved $SO_2$ to form $H_2SO_4$ in the absence of oxidants. The aqueous-phase may be acidified by the reaction of dissolved $HNO_2$ with oxidants, but since limited data exists on ambient $HNO_2$ concentration levels, the importance of this reaction is unknown. The relative importance of the gas-phase and the aqueous-phase pathways for various geographical regions has not been established; but there are indications that the aqueous-phase pathway is dominant for $H_2SO_4$ formation. The relative importance of the pathways for $HNO_3$ formation is not known, but it appears that the overall $HNO_3$ formation rate is greater than 5 times that for $H_2SO_4$.

### 4.3.1 The Photochemical Oxidation Cycle

Of the four major acidification (oxidation) pathways shown in Figure 4.1, the first three depend upon free radicals produced directly and indirectly in the photochemical oxidation cycle for polluted atmospheres. This cycle (Figure 4.2) is governed by the following basic features. Free radical attack on atmospheric volatile organic compounds (VOC) is initiated by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After the initial free radical attack, the VOC's decompose by various paths resulting in the production of peroxyl radical species ($HO_2$, $RO_2$, $R'O_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds (R is a fragment of an organic molecule). The peroxyl radicals react with NO, converting it to $NO_2$, and in the process produce hydroxyl/alkoxyl radical species (HO, RO, R'O, etc.). Alkoxyl radicals can be further oxidized, forming additional peroxyl radicals and partially oxidized products, thereby completing the inner cylical loop reaction process illustrated in Figure 4.2; or they may attack the VOC pool (this is the major path for hydroxyl radical) present in the polluted atmosphere, thereby completing the outer loop

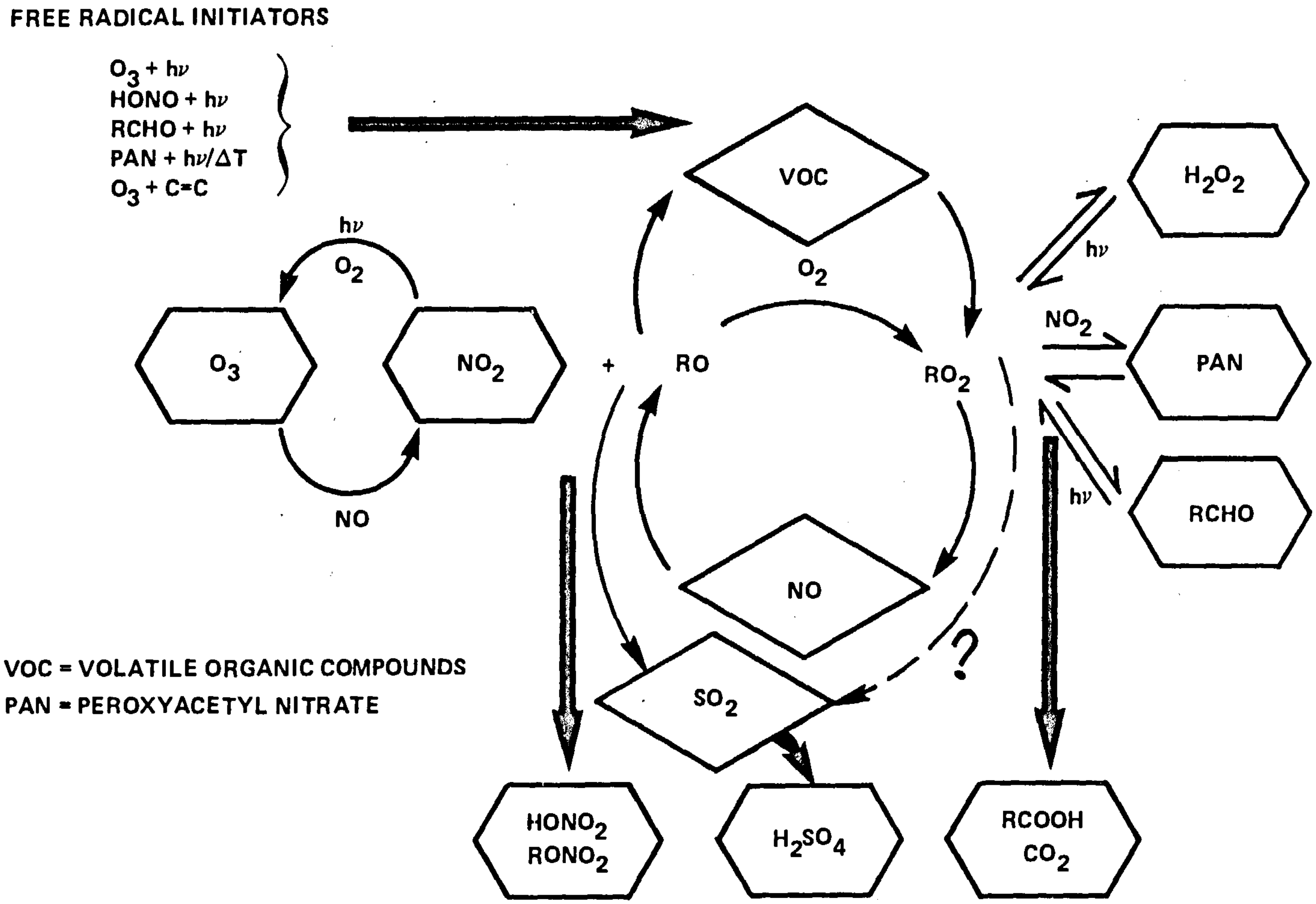

FIGURE 4.2 Schematic of the polluted atmospheric gas-phase photooxidation cycle

reaction process. The resultant effect in either case is the conversion of NO to $NO_2$ with a commensurate oxidation of reactive organic carbon to form organic oxidation products, $CO_2$, and $H_2O$.

The complex mixture of organic compounds present in the polluted atmosphere react with initiator radicals at different rates dependent upon their molecular structure, the result being varying yields of free radical species, ozone, $NO_2$, $H_2O_2$, peroxyacetyl nitrate (PAN) and other partially oxidized organic products as a function of VOC composition and VOC-$NO_x$ levels.

Hydroxyl radical (HO) reactions seem to be the dominant gas-phase mechanism by which carbon monoxide, hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmosphere.[1,2,3] Interestingly enough, this highly reactive transient species, quite contrary to its organic free radical counterparts, shows limited variations in concentration with changes in atmospheric VOC and $NO_x$ levels, a result readily explainable upon review of the free radical production and consumption sources. In the case of the hydroxyl radical, ambient conditions which enhance its production also tend to consume the radicals at an equivalent rate. The result is a faster cycling in the VOC-$NO_x$ oxidation but very little perturbation in the HO steady state concentration. Under similar conditions an enhanced production of organic free radicals, mainly the peroxyl species, is not offset by an increased consumption, and this results in increased steady state concentrations. Hence, the concentration of the organic free radicals is subject to variations due to changes in VOC and $NO_x$ levels, in contrast to the HO concentration.

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[1] See References on page 4-21.

## 4.3.2 Free Radical (Gas Phase) Oxidation

The features of the free radical oxidation of $SO_2$ are presented in Table 4.1.

Based on limited rate constant data for the $SO_2$-free radical reactions, Calvert[3] determined from computer model simulations that the hydroxyl radical dominated the rate of $SO_2$ oxidation in the clean troposphere, while in polluted atmospheres the rate of $SO_2$ oxidation showed equivalent contributions from the hydroxyl, hydroperoxyl ($HO_2$) and methylperoxyl ($CH_3O_2$) radicals. Figure 4.3 depicts the estimated time dependent rates of $SO_2$ oxidation by free radical species in a polluted air mass. Typical rates of $SO_2$ oxidation were of the order of 1.5% per hour and 4.0% per hour for clean and polluted atmospheres, respectively, during July at mid-northern latitudes. The major difference in these rates is a result of higher concentration levels of free radicals in the hydrocarbon-rich polluted atmospheres. In a similar manner, Altshuller[4] predicted the rates of homogeneous oxidation of sulfur dioxide to sulfate in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen[5]. A sample result from this study showing the altitudinal, latitudinal and seasonal dependence of the average diurnal rate of $SO_2$ oxidation in the clean troposphere is presented in Figure 4.4. For the polluted troposphere, the rates shown in Figure 4.4 may be up to about a factor of 3 greater due to the higher $HO_2$ and $RO_2$ concentrations. Altshuller has concluded that the gas-phase oxidation rate of $SO_2$ is important for low latitudes at all seasons, and at high latitudes only during the summer.

Recent laboratory measurements[6,7,8] suggest that the rate of reaction of $SO_2$ with $HO_2$ may not be as great as estimated by Calvert[3]. But even these results may not be totally conclusive since preliminary experimental work by Calvert has indicated that the

Table 4.1  Features of sulfur dioxide oxidation in the lower polluted troposphere

| | Strong Dependence on Parameters | | | | | | $SO_2$ Oxidation | | |
|---|---|---|---|---|---|---|---|---|---|
| | Formation | | | Reaction with $SO_2$ | | | | | |
| Oxidizers | Sunlight | Temp. | Humidity | Sunlight | Temp. | Mass of Liq. water | Rate Function | Linear (24-hr average) | Oxidizer Transported Long-Distance |
| Gas phase | | | | | | | | | |
| 1. HO | Yes | No | No | No | No | No | $= k_1[SO_2][HO]$<br>$= k_1'[SO_2]$[sunlight intensity],day<br>= 0, night | No | No |
| 2. $HO_2$ | Yes | No | No | No | No | No | $= k_2[SO_2][HO_2]$<br>$= k_2[SO_2]$(complex function),day<br>= 0, night | No | No |
| 3. $RO_2$ | Yes | No | No | No | No | No | $= k_3[SO_2][RO_2]$<br>$= k_3[SO_2]$(complex function),day<br>= 0, night | No | No |
| Aqueous phase[a] | | | | | | | | | |
| 4. $H_2O_2$ | Yes | No | No | No | No | Yes | $\propto (LWC)\ k_4[H_2O_2][SO_2 \cdot H_2O]$ | No | Yes |
| 5. $O_3$ | Yes | No | No | No | Yes | Yes | $\propto (LWC)\ k_5[O_3][SO_2 \cdot H_2O]/[H^+]$ | No | Yes |
| 6. $NO_2$ | Yes | No | No | No | Yes | Yes | ? | No | Yes |
| 7. $HNO_2$ | Yes | No | No | No | Yes | Yes | $= k_7[SO_2 \cdot H_2O][HNO_2]/[H^+]^2$ | No | Yes |
| 8. Mn(II) | No | No | No | No | Yes | No | $= k_8[Mn(II)]$ | ? | Yes |
| 9. Fe(III) | No | No | No | No | Yes | No | $= k_9[SO_2 \cdot H_2O][Fe(III)]/[H^+]$ | ? | Yes |
| 10. C(O) | No | No | No | No | Yes | No | $= k_{10}[C(O)]$ | ? | Yes |

a. $SO_{2(gas)} \leftrightarrow SO_2 \cdot H_2O$ (absorption/desorption)
$SO_2 \cdot H_2O \leftrightarrow H^+ + HSO_3^-$ (dissociation/association)

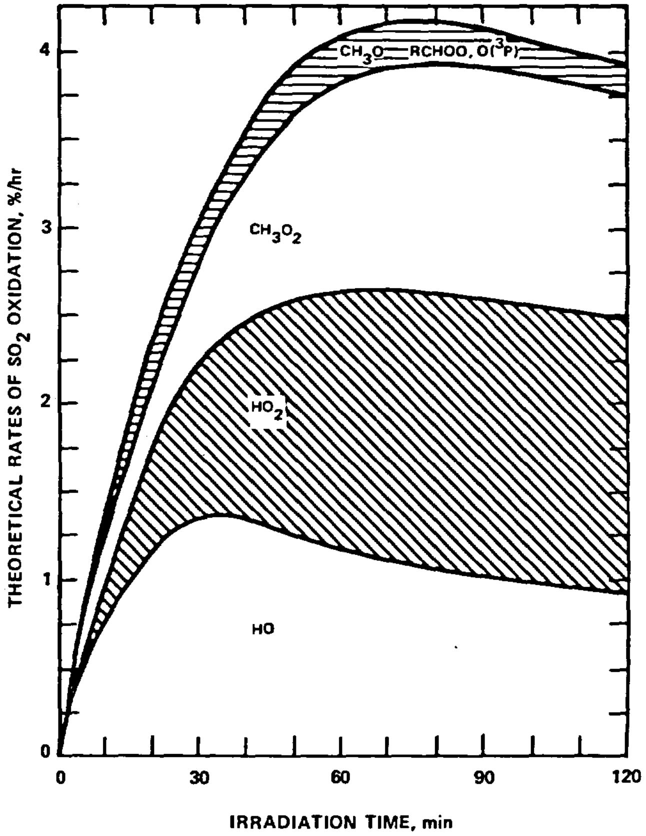

Figure 4-3. The theoretical rate of reaction (percent per hour) of various free-radical species with $SO_2$ is shown for a simulated sunlight-irradiated (solar zenith angle of 40°) polluted atmosphere. The initial concentrations (in ppm) were as follows: $SO_2$, 0.05; NO, 0.15; $NO_2$, 0.05; CO, 10; $CH_4$, 1.5; $CH_2O$, 0; $CH_3CHO$, 0. The relative humidity was 50 percent, and the temperature was 25° C.

Note: The rate constants for $HO_2$ and $CH_3O_2$ radical reactions with $SO_2$ are not well established.

Source: Calvert et al. (1978).

reactions of $SO_2$ with $CH_3O_2$ may be accelerated by trace levels of NO. Therefore, in the theoretical estimates of $SO_2$ oxidation rates, by Calvert, and by Altshuller, only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established $SO_2$ oxidation rates of the order of 1.5% per hour for both clean and polluted atmospheres during July at mid-northern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order of 0.4% per hour. However, field measurements of the rates of $SO_2$ oxidation indicate that maximum $SO_2$ oxidation rates of the order of 10% per hour (diurnally averaged rates of the order of 1-2% per hour) are typical of many atmosphere pollution scenarios, which suggests that aqueous-phase reactions are important.

Since the production of the oxidizing radicals HO, $HO_2$, and $RO_2$ is a complex process that is dependent upon sunlight intensity and precursors, it follows that the gas-phase oxidation rate of $SO_2$ is non-linear. The adequacy of its representation as a linear process is dependent in a complex manner upon the transport time scale, the geographical distribution and type of sources, and the removal time scale.

There are potential pathways for radical production at night. These pathways involve the $O_3$-olefin reaction to produce radicals that can oxidize $SO_2$ to $H_2SO_4$. They also involve the formation of an $NO_3$ radical, which may participate in the formation of organic nitrates and $HNO_3$. The radicals which have a direct photochemical dependence cannot be transported on a regional scale because of their very short lifetimes. Those radicals, which are produced through thermal reactions, may be transported regionally and the radicals may be present during the night.

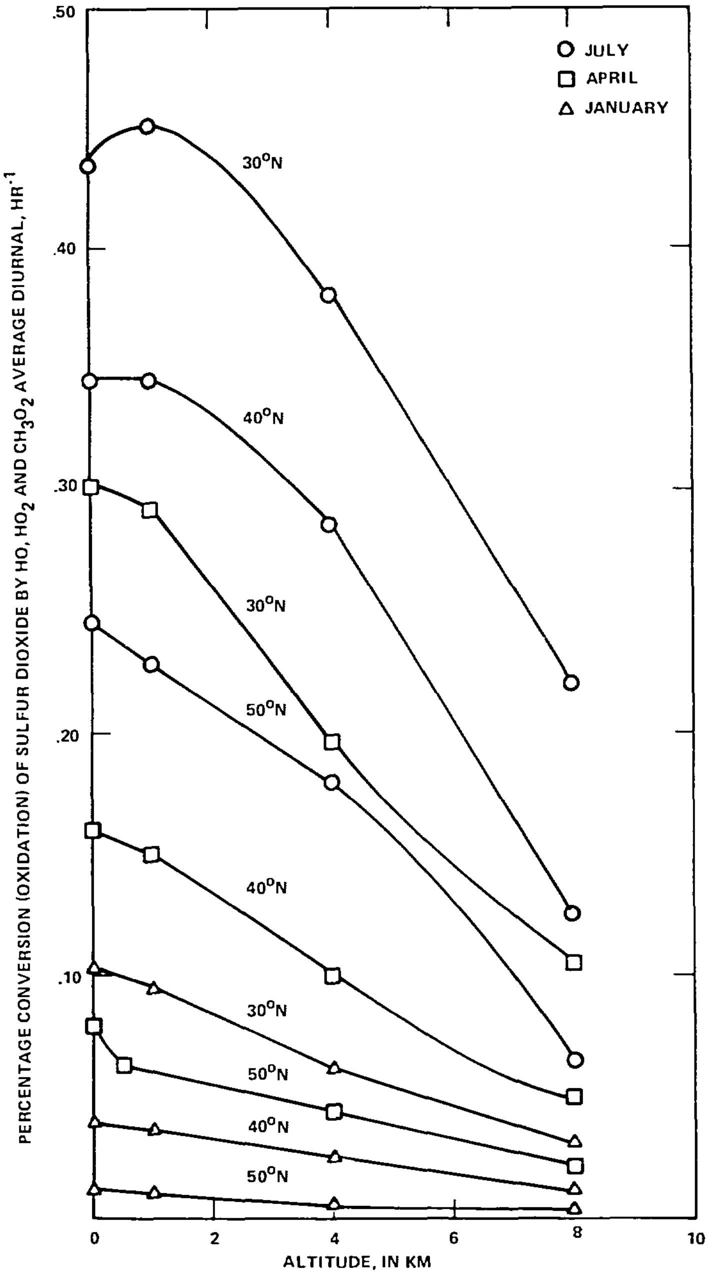

Figure 4.4 Daily average $SO_2$ oxidation as a function of altitude for various latitudes and months. (from Altshuller, 1979)

### 4.3.3 Aqueous-phase Oxidation

The relative magnitudes of the contribution of gas-phase and aqueous-phase formation of $H_2SO_4$ vary as a function of season. At southern latitudes for all seasons it is likely that the gas-phase photooxidation pathway is important. At northern latitudes for all seasons, it is likely that the aqueous phase $SO_2$ oxidation pathways (wet particles, fogs, clouds, precipitation) is important and in the winter is dominant. At this time, the significance of the aqueous phase $NO_2$ oxidation pathways to form $HNO_3$ is not known. The knowledge of aqueous oxidation rates of dissolved $SO_2$ is barely adequate for simple (clean) systems, inadequate for N-oxides and N-oxy acids systems, and practically non-existent for complex sulfur dioxide/N-oxides/N-oxy acids/organic/catalyst/oxidizer systems. Studies of these systems are made difficult by the need for high-purity reagents, the type of chemical reactors required, and the lack of sensitive instrumentation/methods to determine the reaction rates at the low pollutant concentrations (ambient values).

The dissolved $SO_2$ oxidation reaction rate expressions (see Table 4.1) for $H_2O_2$, $O_3$, and $HNO_2$ are known and are non-linear. Each of the three rates depends upon the liquid water content (LWC) of the atmosphere, which leads to gross non-linearity in the $H_2SO_4$ formation rate due to its extreme spatial-temporal variation in the atmosphere over short time periods. The $H_2O_2$ reaction rate expression has first order dependence on the $H_2O_2$ and $SO_2$ concentrations in the gas phase and has no dependence on the pH of the water until the pH declines to about 2. Thus, this reaction in cloud and raindrops will continue to acidity atmospheric water at a constant reaction rate until either the gas-phase $H_2O_2$ or the $SO_2$ is completely consumed. The indications[9,10] are growing that this reaction is the important one for acidifying rainfall and atmospheric particles. It is estimated that this reaction accounts for about 75% of the $H_2SO_4$ formed in the atmosphere[11].

The $O_3$ reaction rate expression has an additional non-linearity; it is dependent upon the inverse of the $H^+$ concentration. This causes the reaction to become unimportant as the atmospheric water's pH declines to about 4. This reaction can be as important as the one for $H_2O_2$ only at pH's greater than about 7, which are unlikely in the eastern U.S. and Canada. The $HNO_2$ rate expression has a dependence on the inverse squared $H^+$ concentration, causing it to be unimportant except in unusual circumstances where the $HNO_2$ concentration is greater than about 10 ppb. This might occur in urban air masses and combustion source plumes during the night. Generally, these reactions are not thought to be significant if $H_2O_2$ is present in the atmosphere.

The $SO_2$ catalyzed oxidation rate equations due to Mn(II), Fe(III), and C(0) are presented in Table 4.1. The Mn(II) and C(0) reaction rates are independent of $SO_2$ concentration, and they depend only on the concentration of the catalyst in the liquid water. So, these acidification reaction rates will not change as the $SO_2$ concentration is lowered. For this reason, these reactions are non-linear. The Fe(III) catalyzed reaction rate has a first order dependence on $SO_2$ concentration, but is non-linear since it has an inverse hydrogen ion dependence. Thus, the three most significant catalyzed reactions are non-linear. Their importance in $H_2SO_4$ formation is not known. While the rate for the Mn(II) reaction is very high, it is not known whether Mn(II) is sufficiently distributed in cloud and raindrops for it to be effective. That is, most of the Mn(II) may be in only a small number of the droplets, making it unavailable for oxidizing large quantities of $SO_2$.

Important aqueous phase reactions also include those bases such as ammonia, calcium carbonate and calcium oxide. These basic chemicals react in water to remove $H^+$ resulting in a decrease in acidity. However, they may also cause an increase in the amount of sulfate formed leading to an increase in the total amount of sulfur wet deposited as sulfate and sulfite.

Comparison of the relative importance of the gas-phase and the aqueous-phase pathways for $H_2SO_4$ is difficult due to the different parameters that control each. The instantaneous rate expressions given in Table 4.1 must be integrated over periods of events if either the $SO_2$ or oxidizing agent is depleted. For example, if $SO_2$ and $HO_2$ enter a convective cloud, the formation of $H_2SO_4$ through their reaction will cease if either reactant is totally consumed. Such a reactant is called the "limiting reactant" since its concentration governs the net amount of product formed.

## 4.4 Chemical Knowledge and LRT Models

To date, the detailed chemical knowledge presented above has not been incorporated into regional transport models. The MOI LRT models only use linearized approximations of the non-linear $H_2SO_4$ and $HNO_3$ formation rates. Regional Eulerian grid models are capable of employing non-linear chemistry, but they are presently insufficiently developed for assessment use.

Rodhe et al.[12] have formulated a simple non-linear chemistry box model for atmospheric acidification. Their work is useful in demonstrating the influence of non-linearity on acid formation and removal rates, but the model possesses serious deficiencies which limit its usefulness for assessment applications. Specifically, its major deficiencies are:

(a) The use of ethylene as a surrogate for VOC in polluted atmospheres is not sufficient to represent the variety of reactive VOC present in polluted atmospheres;

(b) The chemical mechanism does not provide an adequate representation of VOC-$NO_x$ oxidation cycle as presently understood for polluted atmospheres; and

(c) The representation of diffusion and deposition in the model may introduce unrealistic conditions which affect the chemistry in ways which are not representative of the real atmosphere.

## 4.5 Implications and Conclusions

At this time, there are growing indications that, generally in the northeast U.S., the gas-phase reaction pathway accounts for about 25% and the aqueous-phase reaction pathway about 75% of $H_2SO_4$ formation in the atmosphere which is dry and wet deposited. The gas-phase oxidation of $SO_2$ is due to reactions with the photochemically generated radicals HO, $HO_2$, and $RO_2$. On the regional scale, this $H_2SO_4$ formation pathway suggests the following implications:

1. The reaction rates are non-linear with regard to $SO_2$ because the free radical concentrations are not constant over time and space. The LRT models, therefore, may not correctly predict the quantity and the deposition patterns of $H_2SO_4$ formed through the gas-phase reactions;

2. Since the gas-phase rates are first order in $SO_2$, a reduction in $SO_2$ concentration will result in a direct reduction in $H_2SO_4$ formed in the gas phase if the free radicals' temporal-spatial concentrations remain constant;

3. The rates are first order in free radical concentrations. If a reduction in free radical concentration (through oxidant precursor control) can be obtained, then this will result in a direct reduction in $H_2SO_4$ formed in the gas phase;

4. Reduction in both $SO_2$ and free radical concentrations will result in a compounded reduction of $H_2SO_4$ formation in the gas phase; and

5. Since LRT models do not presently employ chemical mechanisms to predict concentration fields of free radicals, which have important spatial-temporal variations, it is unlikely that they can correctly predict the present quantity and deposition pattern of $H_2SO_4$ formed through gas-phase reactions.

The likely effects of these types of reduction of $H_2SO_4$ formation in the gas phase are presented in Table 4.2.

The aqueous-phase oxidation of $SO_2$ in wet particles, cloud nuclei, fogs, dew and raindrops is thought to be due mainly to $H_2O_2$, with some contribution from $O_3$. On the regional scale, this $H_2SO_4$ formation pathway suggests the following implications:

1. The reaction rates are non-linear in regard to $SO_2$ because the atmospheric liquid water content is not constant over time and space. The $O_3$ reaction possesses an additional non-linearity due to a dependence on the inverse $H^+$, which causes the reaction to cease being important for $pH < 4$.

2. Since the LRT models do not employ the $H_2O_2$ and $O_3$ concentration fields, which have important spatial-temporal variations, it is unlikely that they can correctly predict the present quantity and deposition patterns of $H_2SO_4$ formed through the aqueous-phase reactions.

3. The rates are first order in $SO_2$. However, $H_2O_2$ oxidation of $SO_2$ should be viewed as limited by the reactant present at the lower concentration. If $SO_2$ concentration in water exceeds that of $H_2O_2$ in water, then a reduction in $H_2O_2$ will yield a direct reduction of $H_2SO_4$ formation. In this case, a reduction in $SO_2$ concentration will produce no significant

Table 4.2 Effect of reduction of $SO_2$ and oxidizer concentrations on the $H_2SO_4$ formation rate

| | Effect of Action | | |
|---|---|---|---|
| Oxidizer | A. Reduce Only $SO_2$ | B. Reduce Only Oxidizer | C. Reduce Both |
| Photochemically generated radicals | direct reduction[a] | direct reduction | compounded reduction |
| $H_2O_2$ (aqueous) | | | |
| a. $[SO_2] > [H_2O_2]$ | no significant reduction | direct reduction | no additional benefits over B as long as $[SO_2] > [H_2O_2]$ |
| b. $[SO_2] < [H_2O_2]$ | direct reduction | no significant reduction | no additional benefit over A as long as $[SO_2] < [H_2O_2]$ |
| $O_3$ (aqueous), $[H_2O_2] > 1$ ppb | no significant reduction | no significant reduction | no significant reduction |
| $O_3$ (aqueous), $[H_2O_2] < 1$ ppb | | | |
| a. $[SO_2] > [O_3]$ | less than direct reduction | less than direct reduction | compounded reduction |
| b. $[SO_2] < [O_3]$ | less than direct reduction | less than direct reduction | compounded reduction |

[a] Assumes that this action does not cause the free radical concentrations to increase.

benefit. If the $SO_2$ concentration in water is less than that for $H_2O_2$ in water, then reduction of $SO_2$ will result in direct reduction of $H_2SO_4$ formation. It also follows that $H_2O_2$ reduction will be ineffective in this case.

4. It is reasonable, in the eastern U.S. and Canada, that there are large areas in which $SO_2$ concentrations are greater and are less than those of $H_2O_2$. If such data correspond to greater and lower concentrations of $SO_2$ in water than $H_2O_2$ in water, then a single pollutant reduction strategy may lead to non-uniform reduction in $H_2SO_4$ deposition patterns.

5. Since the LRT models do not utilize the oxidant spatial-temporal concentration fields and the specific oxidation reactions, it is unlikely that they will correctly predict the resulting changes in dry and wet $H_2SO_4$ deposition patterns due to reductions in concentrations of $SO_2$, $H_2O_2$, or both.

The likely effects of these types of reductions on $H_2SO_4$ formation in the aqueous phase are presented in Table 4.2.

The above implications are based on non-linear microscale chemistry that applies to individual events of duration less than one day. While clearly inadequate for describing events, it is possible that the long term (monthly or greater) averages derived from the linear LRT models described in Chapter 7 may give similar results as non-linear models for total sulfur deposition. This behaviour would require other processes either to dominate or to compensate for the non-linear chemical processes. However, the influence of such processes has not been examined or studied to date.

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# DEPOSITION PROCESSES

# 5. DEPOSITION PROCESSES

## 5.1 Introduction

The purpose of this chapter is to examine the manner in which current knowledge of atmospheric deposition processes is incorporated into the MOI long range transport models under discussion.

"Deposition processes" include all the mechanisms by which atmospheric constituents are removed from the atmosphere and deposited at the earth's surface. Their role may be demonstrated by a simple example: if pollutant-sulfur emissions were not subjected to removal processes, the average concentration of sulfur in the global troposphere would be increasing by approximately 10 $\mu g$ S $m^{-3}$ $y^{-1}$ (assuming no escape to the stratosphere) - something that is not observed. In view of the importance of removal processes, with regard both to cleansing the atmosphere and delivering material to surface ecosystems, it is desirable that models be able to simulate the most important processes in a quantitative manner, and be able to reproduce major features of actual observed deposition fields in time and space.

In this chapter, the processes of deposition and those factors which have an important influence on deposition are reviewed briefly; methods of incorporating deposition processes into the MOI long range transport models are examined; and finally some conclusions are drawn regarding the adequacy of deposition representation in MOI models. Throughout the discussion emphasis is given to those substances and processes which are of greatest importance in the acid deposition issue.

This chapter is not meant to be a comprehensive review of the subject of deposition. The recent scientific literature abounds with theoretical, experimental and modeling studies of deposition. MOI

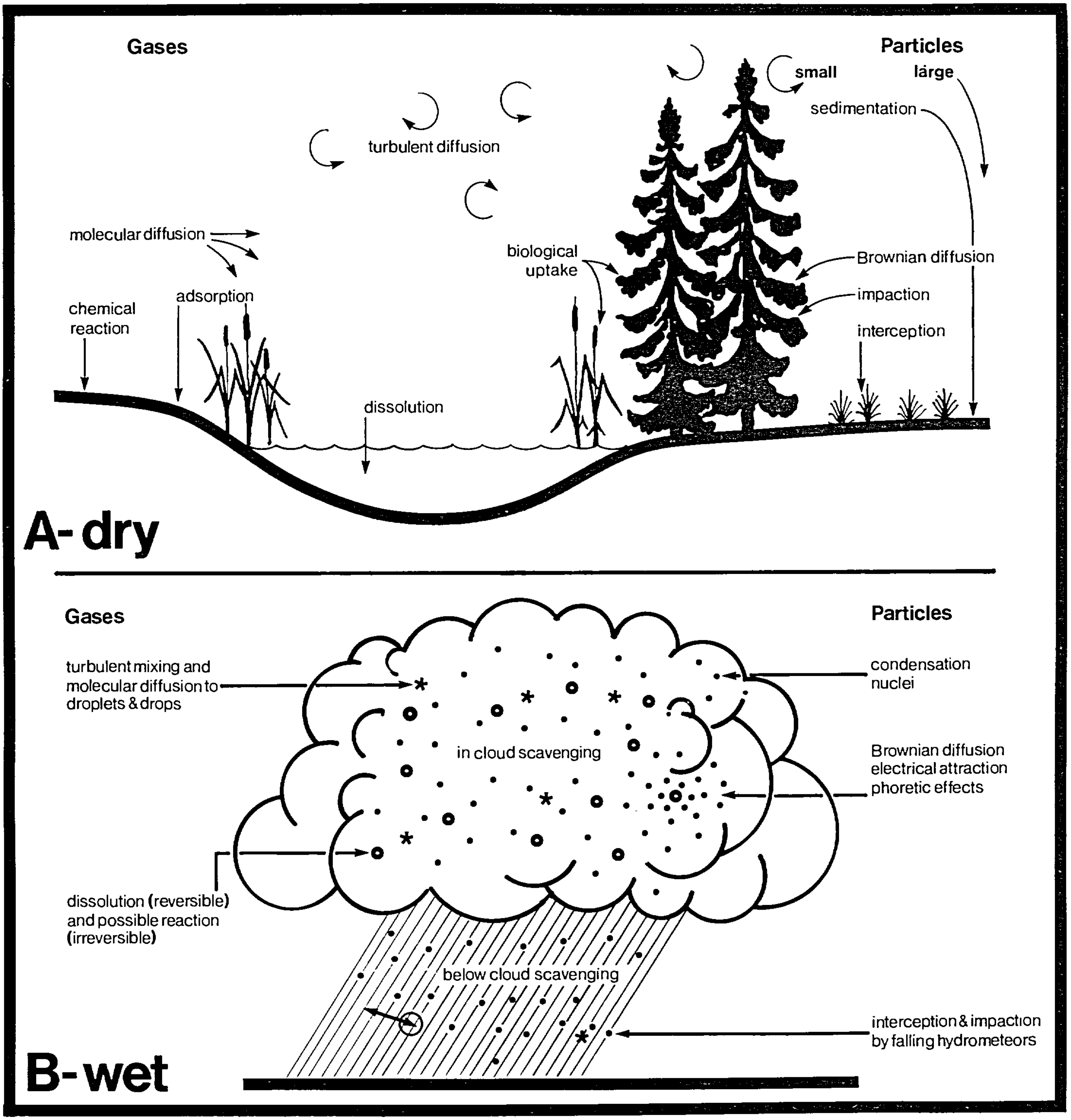
Report 2F-A contains supporting papers with material pertinent to the topic of this chapter, and two chapters of the recent EPA Critical Assessment Document (CAD) on Acid Deposition provide in-depth reviews of the wet and dry deposition topics. (Executive summaries of these two chapters are included in MOI Report 2F-A). Rather, the intent is to provide guidance on the adequacy of deposition simulation in those LRT models selected for use in the context of the MOI, in view of the competing demands for accurate portrayal of scientific knowledge, and immediate application in the policy development area.

## 5.2 Current Understanding of Deposition Processes

Deposition processes may be classified into two types: wet and dry. Wet deposition processes involve precipitation and deliver pollutants to the surface in an irregular but somewhat concentrated form. Dry deposition processes do not involve precipitation, and they provide for a slower but more continual deposition. Figure 5.1 shows schematically the several wet and dry deposition processes.

Dry deposition of gases and particles smaller than a few micrometers occurs by turbulent mixing and transport to the near-surface region. Within millimetres of the surface, a region of quasi-laminar flow may exist through which gases are transferred by molecular diffusion and particles by Brownian diffusion. Uptake at the surface is accomplished by chemical reaction, adsorption, dissolution or foliar uptake in the case of gases, and by impaction on and interception by surface elements in the case of small particles. The deposition of larger particles is assisted by sedimentation.

Wet deposition involves the incorporation of substances into precipitation elements and subsequent fall to the surface. Small particles may serve as condensation nuclei for cloud droplets which



# Schematic diagram of the deposition process

**Figure 5.1**

subsequently grow to form precipitation-sized particles. Gases are transferred to the near-surface region of both cloud and precipitation elements and are incorporated by dissolution and adsorption. Small particles may be scavenged in a similar fashion in clouds. Particles are also collected by falling raindrops and snowflakes through processes of interception and impaction.

The discussion here pertains primarily to the atmospheric constituents which are involved in the acidic deposition phenomenon: sulfur, as $SO_2$, $SO_4^{2-}$; nitrogen, as NO, $NO_2$, $HNO_3$, $NO_3^-$, $NH_3$, $NH_4^+$, PAN; and hydrogen ion, $H^+$. Although other atmospheric pollutants, e.g. trace metals and organic materials, are removed by similar mechanisms, the efficiencies of the removal processes involved will depend on their physical and chemical properties; thus, they might behave somewhat differently.

Figure 5.2 shows schematically the pathways by which the various acidic constituents are deposited. Dry deposition is an important pathway for the gases $SO_2$, $HNO_3$, $NH_3$ and PAN; some evidence exists that the deposition of particulate $SO_4^{2-}$, and perhaps $NO_3^-$ and $NH_4^+$, may rival that of the corresponding gaseous precursors on occasion. Wet deposition is an important pathway both for the gases $SO_2$ and $NH_3$, via the mechanism of in-cloud chemical reactions, and for $HNO_3$ and the particulate forms $SO_4^{2-}$ and $NH_4^+$. In the case of the dry deposition of gases and $NH_4^+$, chemical or biological reactions are required at the receptor in order to release hydrogen ion; whereas, in the case of precipitation, the free hydrogen ions associated $SO_4^{2-}$ and $NO_3^-$ and are delivered directly to the receptor. It is important to note that non-acidic constituents, including alkaline ones such as calcium carbonate, are delivered to the surface by a similar range of processes and that from a receptor response point of view, it is the total loading from the atmosphere which must be taken into account.

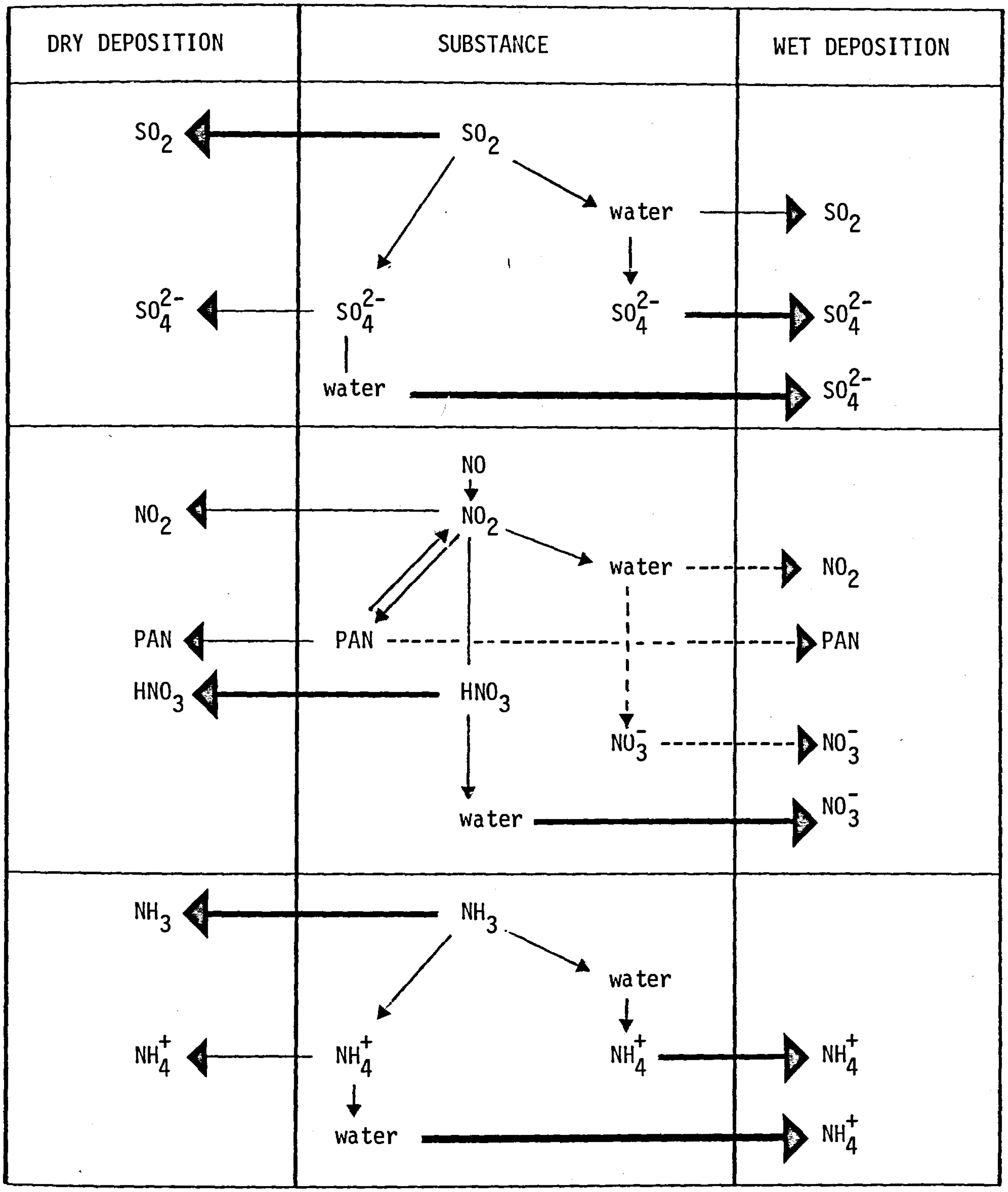


Figure 5.2 Schematic diagram of possible deposition pathways for the major acidic species. The middle column depicts processes or steps along the pathway prior to deposition. The horizontal arrows depict deposition processes for the various species: to the left indicates dry deposition; to the right indicates wet deposition. Heavy lines represent important pathways and broken lines represent uncertain ones.

The effectiveness of a particular dry deposition process or pathway (series of processes) is governed by a number of factors which include the chemical and physical properties of the substances, ambient atmospheric conditions, and properties of the receiving surface. When the lower atmosphere is well mixed, material is transported effectively to the near-surface region; however, when stable conditions prevail, such as typically at night, vertical mixing is inhibited and deposition reduced. A layer of quasi-laminar flow over smooth surfaces also frequently inhibits deposition, particularly for small particles (e.g., the vast majority of sulfate-containing particles). Microscale surface roughness promotes particle deposition, while wet, alkaline and physiologically active surfaces promote the deposition of $SO_2$. Clearly, the importance of dry deposition will be a function of both time (time of day, season), stability and location (surface type).

The effectiveness of wet deposition depends on the ease with which materials are incorporated into precipitation elements, and on what might be termed the precipitation regime. $HNO_3$, $NH_3$ and $SO_2$ are soluble enough to be readily taken up by cloud and rain drops (although for $NH_3$ and $SO_2$ this is a function of pH), and $SO_4^{2-}$ particles are efficient cloud condensation nuclei. The main wet deposition pathways for sulfur are through $SO_4^{2-}$ particles serving as condensation nuclei for cloud droplets, and $SO_2$ being taken up into cloud and rain drops and subsequently oxidized to $SO_4^{2-}$.

The importance of "precipitation regime" derives from such factors as frequency of precipitation, type of storm, and relative contributions of rain and snow to the total precipitation. In general, for a given atmospheric loading condition, more frequent precipitation will result in greater wet deposition. Storm type, to a large extent, governs the scavenging regime. For example, a summer convective storm which draws up air from surrounding regions will be conducive to in-cloud scavenging by nucleation and $SO_2$ uptake and oxidation. On the other hand, continuous precipitation falling through a polluted air mass would be expected to scavenge primarily below cloud. In northern regions, where dry snow is frequent, many scavenging processes, except those for $HNO_3$ and below-cloud interception of particles, are probably inefficient. As in the case of dry deposition, wet deposition will be a function of time (season) and location (but in relation to the precipitation regime rather than to the underlying surface).

## 5.3 The Simulation of Deposition in MOI Models

The deposition processes are included in long range transport models using formulations which are well founded in the scientific literature and which simulate either the total dry or wet deposition pathway or the portion of it which is perceived to be dominant. The basic approach is to compute the deposition as the product of two factors: the first is a coefficient that provides a measure of removal rate, and the second is a measure of atmospheric concentration or mass.

In the case of dry deposition the total pathway, which includes all contributing processes, is simulated in the form

$$D_D = v_d \, c_a$$

where $D_D$ is the dry deposition (dimension $ML^{-2}T^{-1}$), $v_d$ is a deposition velocity ($LT^{-1}$), and $c_a$ is the ambient atmospheric concentration ($ML^{-3}$). $v_d$ depends on the many factors noted in the previous section. The most basic approach is to use a constant value of $v_d$ for each compound (AES, MOE, RCDM-3). Various degrees of sophistication can be achieved by including a functional dependence of $v_d$ on time of day (ASTRAP, ENAMAP-1, MEP, UMACID); on season (ASTRAP, ENAMAP-1, MEP, UMACID); on stability (ENAMAP-1); or on land-use (ENAMAP-1, UMACID).

Wet deposition is treated in a similar manner, but the removal rate coefficient may have a number of formulations. The AES model selects a value of the scavenging ratio W (dimensionless) for $SO_2$ and for $SO_4^{2-}$, and wet deposition is determined as

$$D_W = W\ p\ c_a$$

where $D_W$ is the wet deposition ($ML^{-2}T^{-1}$) and p is the precipitation rate ($LT^{-1}$).

The ASTRAP model uses a fractional depletion f such that

$$D_W = f\ M_1$$

where f is proportional to the half power of precipitation rate and $M_1$ is the mass transferred to a grid square during a time step.

The ENAMAP-1, MEP, MOE, and UMACID models use scavenging rate coefficients which are functions of precipitation rate, viz:

$$D_W = k_W M_2$$

where $M_2$ is the column mass ($ML^{-2}$) and $k_W$ is scavenging rate coefficient ($T^{-1}$), which may be written in the form

$$k_W = \beta p^a$$

Here $\beta$ is a model-dependent constant, and a is equal to 1, 1, 0 and 0.625 respectively, for the four models.

The RCDM-3 model uses an expression for the fraction of ambient $SO_2$ and $SO_4^{2-}$ removed per unit time, which is a function of a scavenging coefficient, precipitation rate, and average durations of wet and dry periods.

The CAPITA model makes use of a total (i.e., wet plus dry) removal rate coefficient for $SO_2$ and $SO_4^{2-}$. Here total deposition $D_T$ is computed as

$$D_T = \lambda M_2$$

where $\lambda$ is the removal rate coefficient ($T^{-1}$) which may be expressed as a probability of removal per time step, with a seasonal dependence.

A comparison of the deposition formulations in MOI models with current scientific knowledge shows that the simulations are done in a simplified way. Nevertheless, the main requirements relevant to the long range transport of sulfur emissions are fulfilled - that is, depletion of the atmospheric load and deposition at the surface. In most models a distinction is made between wet and dry deposition, and between $SO_2$ and $SO_4^{2-}$.

In the case of dry deposition the complete pathway is simulated (that is, atmosphere plus near-surface layer plus surface). Micrometeorological theory and measurements have provided a sound basis for the parameterization of atmospheric transfer commonly used in models. Experimentation has provided confidence in this approach for gases, but difficulties remain in the case of particle deposition. One of the major unknowns for both particle and gas deposition is the behavior of different surface types. The efficiency of the deposition pathway depends upon such factors as time of day, season, stability and surface type. Several of the models have included some of these functional dependences on the appropriate model scale.

The models also simulate the overall wet deposition pathway. However, in this case there are two additional difficulties. The first is that scientific knowledge is less advanced, for example about nucleation scavenging and the in-cloud scavenging and oxidation of $SO_2$. The second is that precipitation is by nature episodic; the time scale of precipitation and scavenging processes is of the order of minutes to a few hours, generally less than the input-data resolution or time step in models. In view of this discrepancy, models must attempt to simulate the average behaviour or the dominant processes, in a system where great variability occurs. Wet deposition depends upon the constituent being studied and a number of variables related to storm type. These latter factors are both time (season) and space (location) dependent. Models have begun to attempt to include some of these dependences, for example by the various formulations of scavenging rate coefficient. However, this is an area where considerable refinement is anticipated in the next few years.

In summary, it appears that large-scale models are inherently limited in their capability to simulate a variety of processes which are of smaller time and space scales. Thus, effective parameterization of the most important features of the several processes is required. With this in mind it appears that dry deposition is more amenable to such a treatment, and in fact, dry deposition simulation is progressing well, with a number of temporal and spatial dependences being included in some models. Wet deposition is more complex, has a shorter characteristic time scale, and is therefore more difficult to simulate. One might expect that wet deposition simulation could be improved with a more complete knowledge of the temporal and spatial distribution of storm type and dominant scavenging mode throughout the study region.

Despite (1) the simplified formulations that have been used to incorporate wet and dry deposition processes into large-scale models and (2) the deficiencies of our scientific knowledge of the microphysics and chemistry in a number of important areas, it is encouraging to be able to reproduce the right order of magnitude of the large time and space scale features of the wet sulfur deposition fields. The current degree of scientific effort applied to this area provides a reassuring outlook for improvements in deposition modeling during the next few years.

## 5.4 Summary and Recommendations

The following items are most crucial to our further understanding of acid deposition, and to our ability to simulate the processes in models.

### 5.4.1 Dry Deposition

The state of the science is such that advances are required in the experimental and measurement areas before there is likely to be much further improvement in simulation. However, it is recommended that dry deposition simulation in current models incorporate information that is available on the temporal and spatial dependences of $v_d$. Very high priority must be given to developing and implementing dry deposition measurement techniques. Also of high priority is the need for high quality atmospheric concentration measurements of important sulfur and nitrogen species, with which dry deposition may be calculated. Research is required in the following areas: improved understanding of particle deposition (including the time dependence of particle size distribution); the magnitude of surface resistance to deposition as a function of time and space; deposition measurements for almost all species, as well as more for $SO_2$.

### 5.4.2 Wet Deposition

Wet deposition is an area in which our understanding of important processes is still incomplete and which is generally simulated poorly in large-scale models. A basic discrepancy exists between the nature of precipitation processes - episodic, stochastic, small time and space scales - and the manner in which wet deposition is necessarily included in models - limited by model time and space steps and input data resolution. A major effort is required either to reproduce the small scale characteristics of wet deposition, or to find a better way to represent the dominant processes on larger scales. It is strongly recommended that research efforts be increased to investigate the $SO_2$-uptake-oxidation-deposition pathway, relationships with the chemistry of other compounds in clouds (including catalysis), the role of $SO_4^{2-}$ - nucleation scavenging, and the so-called non-linear and saturation aspects of aqueous-phase chemistry. Current scavenging formulations in large-scale models require a more realistic physical basis, in some cases, and more and better scavenging parameter values which show storm-type and precipitation rate dependence. Finally, it would seem that improved statistics of the temporal and spatial variability of precipitation events and the development of storm-type climatologies for eastern North America would improve our ability to simulate wet deposition in the large-scale models.

### 5.4.3 Model Development and Testing

Appropriate data are lacking with which to develop and test modified deposition simulations; effort is required to specify carefully the requirement, and to compile such data. At present, model results can be compared with air concentration measurements of $SO_2$ and $SO_4^{2-}$, and wet deposition of total S (or $SO_4^{2-}$ and $SO_2$, if special precautions are taken), but not against dry deposition. Because of the difficulties in simulating wet deposition in the large-scale models, it is advisable to compare model outputs with air concentration measurements, in addition to those of wet deposition.

The following are issues which require resolution through additional research effort: the differing real-world process and simulation model "scales"; the inadequate resolution of the data input fields for the process simulation; and the necessity of validating models using output fields of low resolution against point measurements.

As more sophisticated deposition models are developed (e.g. for scavenging) efforts should be made to incorporate them into the LRT models.

### 5.4.4 Modeling Deposition

Most current LRT models simulate only sulfur deposition; whereas, the net impact of atmospheric deposition is finally determined by the total input of all constituents. Scientists agree that total sulfur deposition, and not nitrate deposition, has been the major contributor to the long term lowering of pH in some poorly buffered waters, but that nitrate deposition can contribute to episodic acidity of surface waters during spring runoff.

Although it is acknowledged that the modeling of sulfur is of primary importance for assessing the acidification of aquatic ecosystems, it is understood that modeling of other constituents must be undertaken to provide a complete picture of acidic deposition.

# MONITORING DATA — DISPLAY, ANALYSIS AND INTERPRETATION

# 6. MONITORING DATA - DISPLAY, ANALYSIS AND INTERPRETATION

## 6.1 Introduction

The preceding four chapters have discussed the pathways of the chemical species of interest (especially the acidic compounds of sulfur and nitrogen) from their emission at source through transport and dispersion in the atmosphere and how they are transformed before being deposited onto the earth's surface. This chapter will review and discuss the actual observations made by monitoring the atmosphere and the deposition on a routine basis with networks, and by shorter term studies or experiments using airborne observational platforms and/or special ground stations and networks. The data so collected provide an essential input to:

(a) understanding the physical and chemical processes described in Chapters 3, 4 and 5;

(b) the parameterization of these processes in LRT models;

(c) the improvement and verification of models, and

(d) studies of the effects of acidic deposition and other pollutants on the ecosystem, man-made structures and human beings.

In addition, these data are useful in their own right in the more general sense of:

(a) documenting the existence of long range transport of pollutants and the link with acid deposition in various parts of the world,

(b) providing, by means of interpretive analysis, another tool (in addition to modeling) to assist in the development of appropriate remedial action, and

(c) establishing the existence of trends.

Future monitoring data will play a key role in assessing the effectiveness of actions taken, as a result of any treaty or agreement between Canada and the United States, to limit or reduce emissions.

The basic working document for this chapter is the report prepared by the Sub-Group on Monitoring and Interpretation (MOI Report No. 2F-1). That report contains large sections on monitoring techniques and the available data sets but these will not be summarized here: the reader is referred to that report for details. What will be summarized here are some of the most important analyses that have been carried out using monitoring data. Topics to be covered in this chapter are: temporal and spatial variations, simple wind sector analyses at selected stations, regional box budgets and time trends.

## 6.2 Spatial Variations

The geographical variation of pollutant concentrations in air and precipitation is controlled by the following factors:

(i) the distribution of the pollutant sources;

(ii) the meteorological regimes which disperse the pollutant;

(iii) the efficiency of removal processes (that is, chemical transformation, precipitation scavenging and dry deposition) as reflected by the residence time of the pollutant in the atmosphere; and

(iv) in the case of particles and soluble gases, the precipitation patterns near and downwind of the sources.

The configuration of pollutant sources in North America for sulfur dioxide is discussed in Chapter 2. A more complete description of other pollutants, such as primary sulfate and nitrogen oxides, can be found in the final report of Work Group 3B. In eastern North America man-made sources of sulfur dioxide exceed natural sources by at least a factor 10. Although less is known about natural sources of nitrogen oxides, they also are believed to be substantially less than man-made. However, on a global basis natural and man-made emission for both sulfur dioxide and nitrogen oxides are estimated to be of roughly equal magnitude.

While the natural emissions tend to be widely distributed around the globe (with low emission density), the man-made emissions are strongly concentrated in a few highly industrialized regions in eastern North America and Eurasia. On a global basis the distribution of acidity of precipitation shows that the regions of lowest pH occur over and immediately downwind of these industrial regions, indicating a strong causal relationship.

### 6.2.1 Global Variations

Some observations from remote stations around the world indicate that at remote oceanic sites, exposed west coasts and in the polar regions, the pH of precipitation is generally less than 5.6 (the carbon dioxide - clean water equilibrium value, sometimes used as the "clean rain" reference value). On the other hand, at continental sites in semi-arid regions, with low population density and little industry producing acidic pollutants, the wind blown dust which is generally high in alkaline substances results in rain with pH values much greater than 5.6. It is important to understand the reasons for the, sometimes observed, high acidity in remote locations so that the source-receptor relationships in the regions of maximum acidic deposition can be placed in their proper context.

Historically, the earliest remote measurements which suggested relatively high values of acidity were obtained at the Mauna Loa Observatory (3400 meter altitude on the island of Hawaii). Confirmation that this was not due to local volcanic emissions was obtained by upwind measurements on the island of Kauai. Both here and at other remote sites around the world, median annual values of about pH = 5.0 and on rare occasions individual events as low as pH = 3.8 to 4.0 have been confirmed. A recent paper attempts to explain how such low pH values may arise. Sparse observations in remote locations indicate that (excluding the neutral sulfate contribution from sea-spray) the acid sulfate aerosol concentrations range from 0.5 to 1.0 μg of sulfate per cubic meter in the lower troposphere. In the absence of any significant alkaline material in the cloud air (very likely at remote oceanic sites) then, depending upon the cloud liquid water content, the resultant pH could range from 3.7 to 5.1. It is interesting to note that observations above the general level of the earth's surface at a few mountain sites or with aircraft in both remote and polluted regions indicate that the pH tends to decrease (i.e. the acidity increases) with height and pH values of 4.0 or less can occur in the lower parts of clouds. Sulfate aerosols are small (< 1.0 micrometer) and have long residence times because of small fall velocities, while alkaline particles are usually larger (> 10 micrometers) and have much shorter residence times and higher fall velocities. Thus, the higher one goes in the atmosphere the greater is the expected average ratio of acidic to alkaline materials. Similarly, at sites distant from sources of these materials, the very low total particulate content of the atmosphere tends to be dominated by neutral to acidic rather than alkaline particles.

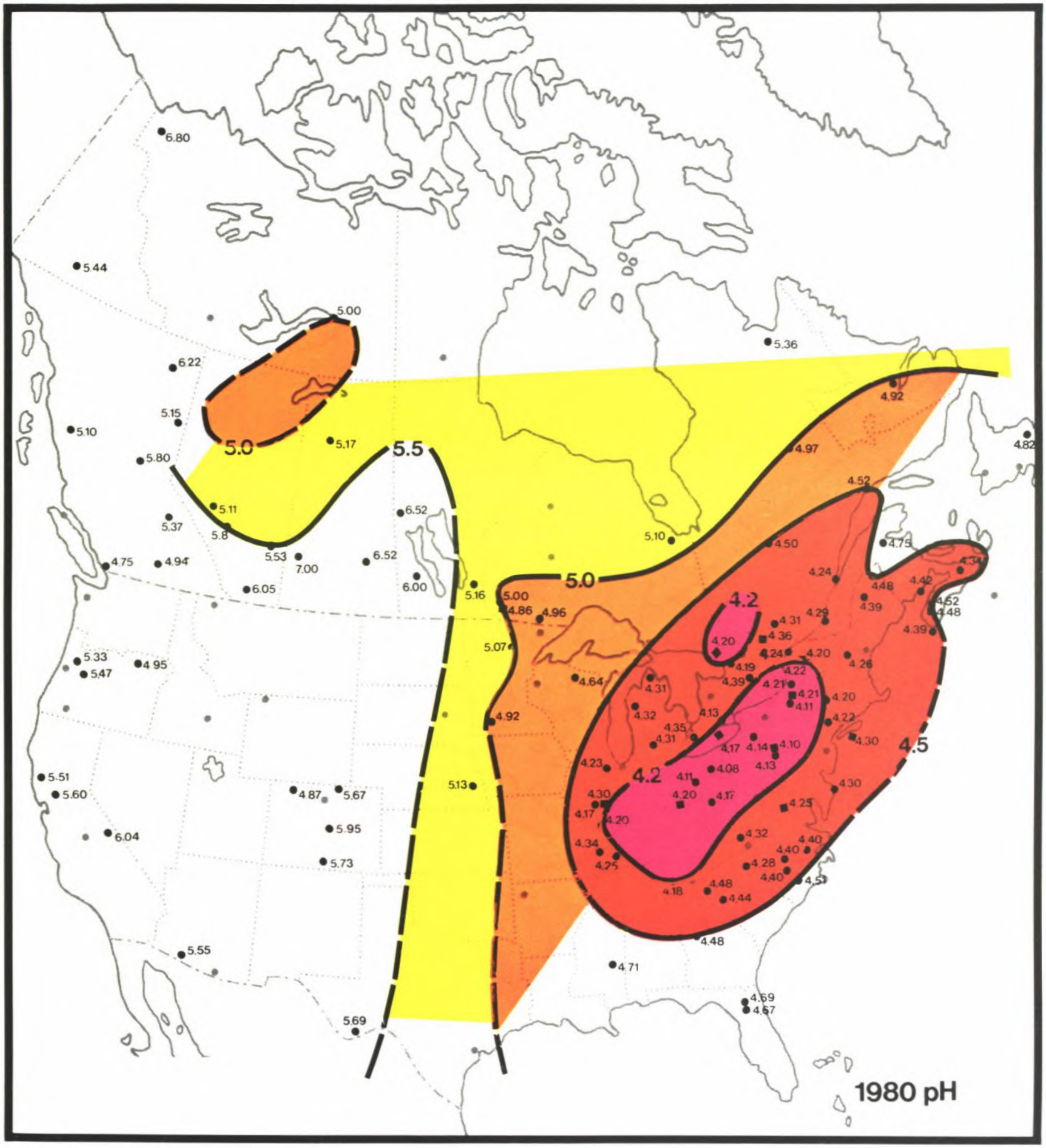
What is not so clear is the source of the sulfate that is found as part of the global background. Two sources have been suggested. One is natural emissions of sulfur from the oceans (especially in tropical regions), coastal areas and swamps. The other is the very long range transport of anthropogenic emissions. There is some evidence to support both of these, but more analysis is required to establish whether either, both, or some other sources, are the most significant contributors.

The implications of these observations for eastern North America can be summarized as follows. While the low pH values observed on occasion in remote areas are perhaps at first surprising, reasonable explanations for their occurrence have been offered. The extreme low pH (or high acidity) values in remote locations may on occasion be lower than the annual averages in the most heavily impacted region of eastern North America (see Section 6.2.2). But when considering the overall significance of these observations, particularly for assessing effects, a comparison of median values of acidity is more appropriate and these are at least three times higher in eastern North America than at remote locations. There is undoubtedly a contribution to the deposition of acidity in eastern North America associated with North American natural sources and also the world wide background (either from natural sources or ultra long range transport from man-made sources far upwind). In principle, all atmospheric LRT models could take this into account and in fact three have done so (see Chapter 7) by estimating empirically an additional contribution from these sources. However, this background is generally considered to be small in comparison with the regional man-made contribution over the large region which is heavily affected and its impact may thus be expected to be correspondingly small. Nevertheless, further observations and data analysis are needed to determine more precisely what the relative importance of "global" acidity is in the eastern North American context.

### 6.2.2 North American Variations

Maps of the spatial distribution of pH and the most important (from the effects point of view) chemical species in precipitation over North America have been prepared using data from the major U.S. and Canadian national networks (see Report 2F-I, Figures 4.2 to 4.17). These maps are based on some 90-100 observing stations - a network sufficiently dense to give the major features of the large-scale fields with confidence in the east. Concentrations of the major acid-related ions (hydrogen ion, sulfate, nitrate, and ammonium ion) in precipitation for the year 1980 were prepared separately. Using the more detailed precipitation amount fields for the same year, based on the denser meteorological networks, the deposition field was prepared by multiplying the precipitation concentration field by the precipitation amount field. The resultant pH, the per cent of normal precipitation and the deposition fields are shown in Figures 6.1 to 6.6.

When the sulfate deposition pattern is compared with the sulfur emission data shown in Figure 2.2 a very dramatic spatial concurrence is apparent with the maximum deposition located over and immediately downwind of the region of maximum emissions in eastern North America. The zone of elevated deposition also extends for a considerable



Precipitation amount- weighted mean annual pH in North America for the calendar year 1980

Figure 6.1

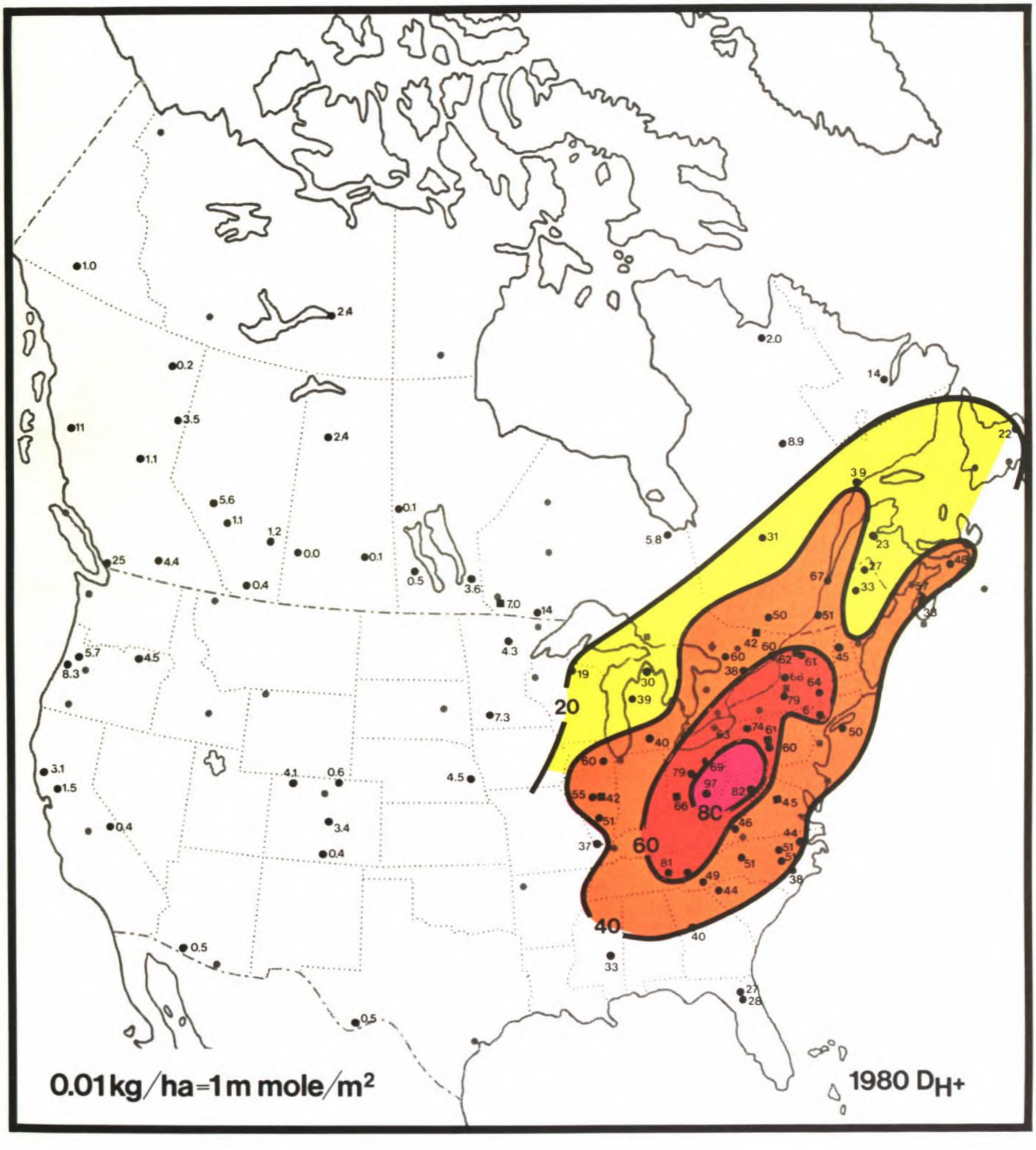
**Legend**

| Canada | United States |
|---|---|
| ● CANSAP | ● NADP |
| □ APN | □ MAP3S |
| ◆ OME | |

(See also Table 6.1)

Percent of normal precipitation in North America in 1980

Figure 6.2



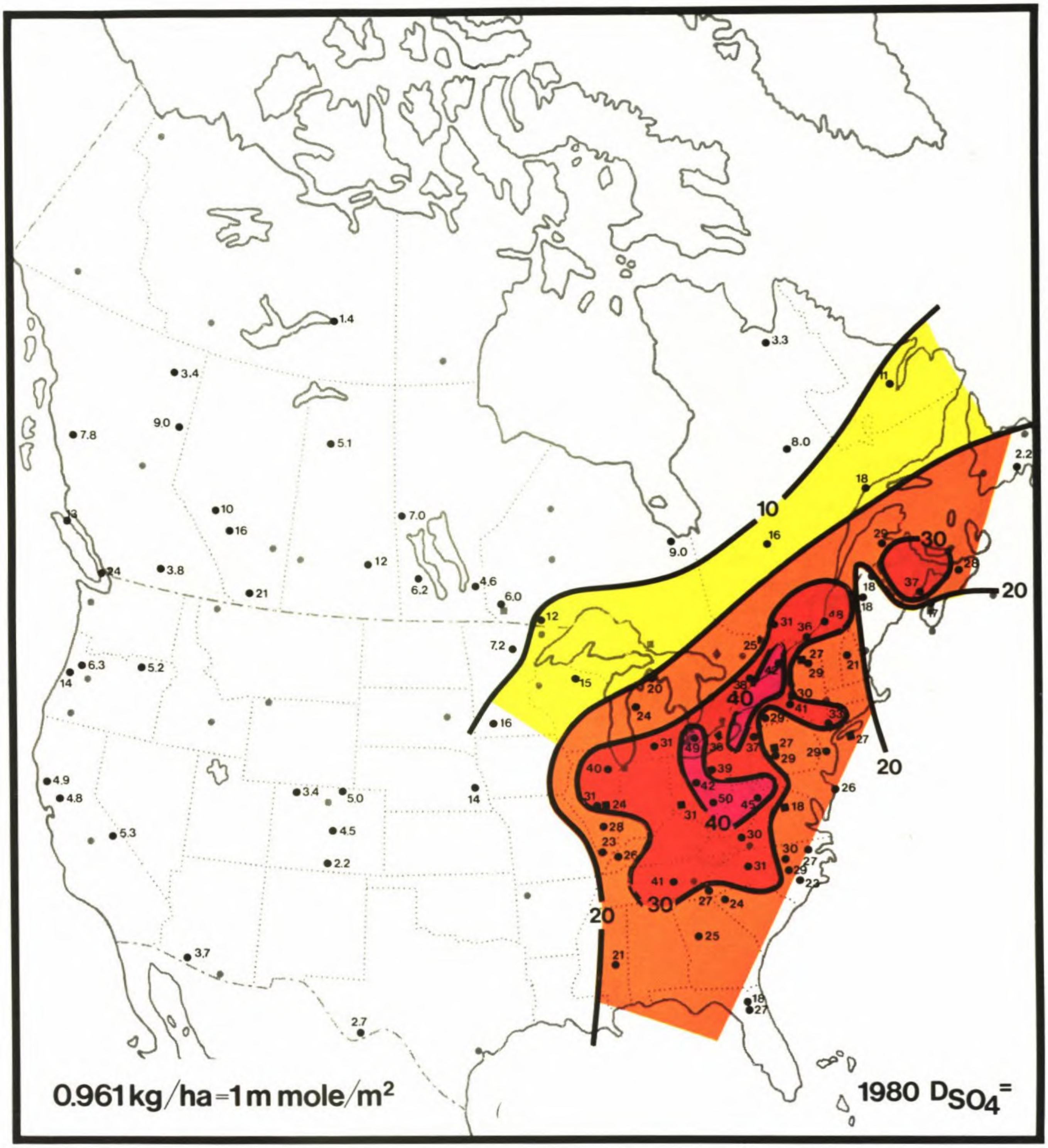
**Precipitation amount- weighted mean hydrogen ion deposition for 1980 (m moles per square meter)**

**Figure 6.3**

**Legend**

| Canada | United States |
|---|---|
| ● CANSAP | ● NADP |
| □ APN | □ MAP3S |
| ◆ OME | |

(See also Table 6.1)



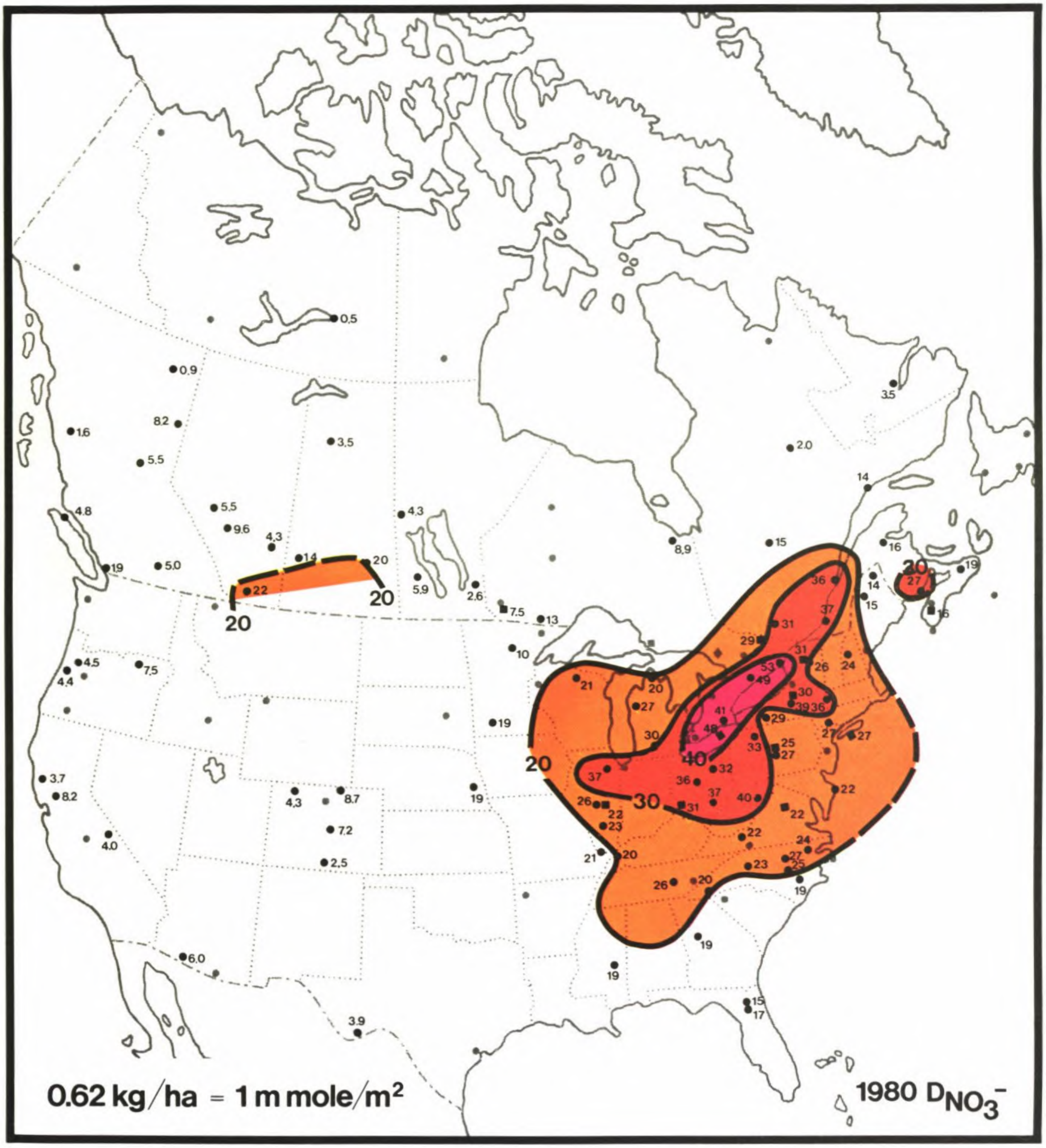
# Precipitation amount- weighted mean sulfate ion deposition for 1980 (m moles per square meter)

## Figure 6.4

**Legend**

| **Canada** | **United States** |
|---|---|
| ● CANSAP | ● NADP |
| □ APN | □ MAP3S |
| ◆ OME | |

(See also Table 6.1)



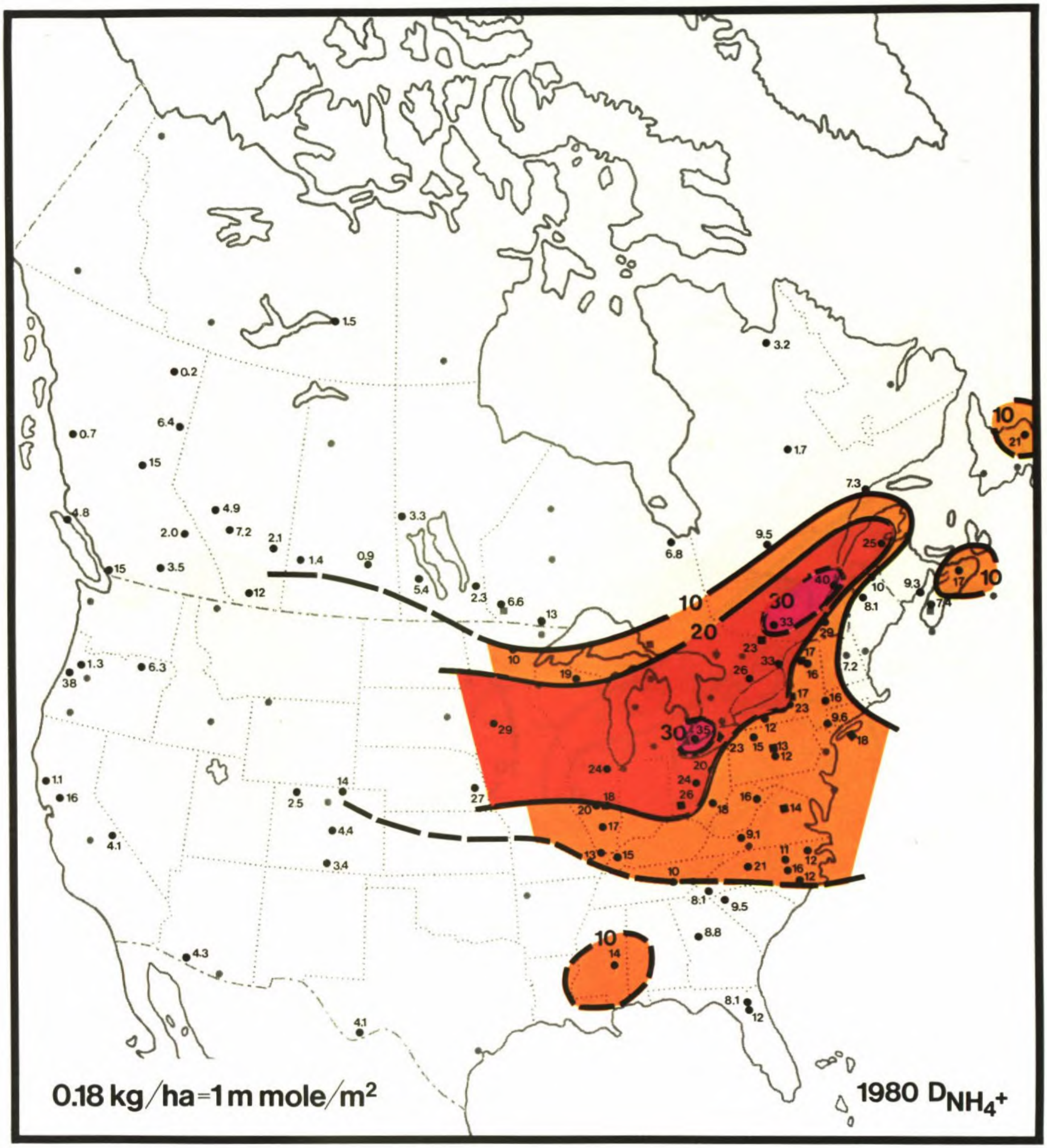
Precipitation amount- weighted mean nitrate ion deposition for 1980 (m moles per square meter)

**Figure 6.5**

**Legend**

| Canada | United States |
|---|---|
| ● CANSAP | ● NADP |
| □ APN | □ MAP3S |
| ◆ OME | |

(See also Table 6.1)



## Precipitation amount- weighted mean ammonium ion deposition for 1980 (m moles per square meter)

## Figure 6.6

**Legend**

| Canada | United States |
|---|---|
| ● CANSAP | ● NADP |
| □ APN | □ MAP3S |
| ◆ OME | |

(See also Table 6.1)

distance downwind, that is, to the east and northeast. The pH map shows a similar pattern with the lowest values coinciding closely with the greatest sulfate, nitrate and hydrogen ion deposition.

## 6.3 Temporal Variations

The geographical variability was discussed in the previous section mainly on the basis of annual averages. This is just one of the many important time scales and has automatically smoothed out temporal variations on all shorter time scales and resulted in the fairly smooth spatial continuity shown in the maps. However, the pollutant concentrations in air and precipitation are highly variable over a very wide range of time scales. This is not surprising when one considers the total experience of a pollutant as it moves between a source and a receptor. Among the most important factors influencing its behaviour and hence contributing to the variability of the composition of the air and precipitation are:

- fluctuations and trends in anthropogenic and natural emissions (see Chapter 2 and the Work Group 3B report);
- the dynamic variability within individual rain systems, their motion and hence the trajectories followed by the polluted air parcels (see Chapter 3), as well as the air motions during dry periods;
- the variability associated with dry deposition and chemical conversions in the dry air before pollutants encounter precipitating weather systems, and the cloud processes and reactive chemistry within such systems (see Chapters 4 and 5); and
- the variability of storm types and their mean tracks on a seasonal and annual basis and possible shifts in these patterns on the climatological scale.

Several figures illustrating examples of the time variability determined from observations of concentrations of major ions in precipitation and of sulfur dioxide and sulfate in air are given in Report 2F-I. From these, typical ranges of variability can be summarized as shown in Table 6.1. The variability in measured concentrations is much larger than the variability of the emissions over the same time scale and must, therefore, be due mainly to the other contributing factors listed above.

TABLE 6.1 Typical ranges of variability of hydrogen ion, sulfate, nitrate and ammonia for various time scales in polluted regions at a single observing station.

| Time scales of variation | Typical range of variability about average |
|---|---|
| minutes to hours | factor of 10 |
| day to day | factor of 5 |
| month to month | factor of 2 |
| year to year | factor of 1.5 |
| decade to decade | unknown |

### 6.3.1 Time Trends

Several authors have attempted to use historical monitoring data in Europe and North America to establish trends in deposition with varying and sometimes conflicting results or interpretations. For instance, one group of researchers claim that, when the deposition patterns in North America are examined over a decade (1955-1965), there is some evidence of a trend in the shape and size of the various deposition contours. For example, while the value of the lowest pH at the centre has not changed much over a decade, the surrounding region of moderate acidity has expanded outwards especially to the south and southwest. This is a source of continuing controversy. The general conclusion is that historical air and precipitation data have sufficient uncertainty in them to make it difficult to draw any conclusions regarding long term temporal trends in either the acidity itself or the precursor emissions. This is not to say that trends do not in fact exist, but if they do, the available data are incomplete and too unreliable to quantify their existence.

The next step, after looking at long-term historical deposition, is to evaluate shorter periods where high quality deposition data do exist. These data are compared to sulfur emissions values for the same period. Swedish investigators have done this with the data from the European network and found that various geographical groupings of stations appear to suggest different trends over various extended time intervals. They offer the plausible suggestion that these differences mainly reflect interannual variations in the atmospheric transport patterns. If true, the variability imposed on the deposition trends by changing airflows, even averaged over the period of a year, has a strong bearing on the use of deposition data to detect benefits from emission reductions. Improvements resulting from emission restrictions could be exaggerated or minimized even over five year intervals. One would then be forced to rely on the use of long range transport models (particularly their meteorological components) to demonstrate benefit and, as is argued, such models possess considerable uncertainty at present. It should be noted that the year-to-year variability of pollution concentration in precipitation may be attributed to factors other than transport differences. There may be, for example, chemistry complications or other factors like the amount of sunlight (or dry deposition) that vary from year to year. During some lengthy periods, at some stations, the trends of sulfate concentration in precipitation are even opposite to those of emissions of sulfur dioxide in northern Europe. These periods and stations have been quoted as demonstrating our lack of understanding of the behavior of sulfur. But other periods and groups of stations have pollution deposition trends which are at least qualitatively in phase with

European sulfur dioxide emissions. For example, over the entire period of record, both the average deposition (or concentration in precipitation) at all stations and the emissions of sulfur dioxide have increased. Nevertheless, the absence of a good year-to-year or pentade-to-pentade parallelism between emissions and concentration of pollutants demonstrates the complexity of the entire system.

On the other hand looking at the nitrogen oxides, the slowly rising nitrogen oxide emissions in North America seem to parallel the increase in the nitrate concentration in precipitation. Although the trends in both emissions and pollutant concentration of nitrogen oxides have been relatively small, they appear to be somewhat more regular, and in phase, than the trends in sulfur oxides. It should be remembered that the conversion of gaseous nitric oxide (NO) and nitrogen dioxide ($NO_2$) to nitrates is believed to be much faster than sulfur dioxide to sulfate and that sources at ground level constitute a larger fraction of the nitrogen oxides emissions than the sulfur oxides emissions. Therefore, it is expected that a greater proportion of the nitrogen emissions would be deposited over eastern North America. However, analyses of monitoring data cannot completely support this contention, because only a small fraction of the emitted nitrogen is wet deposited. It is unknown how much of the large balance is dry deposited or exported from the continent.

### 6.3.2 The Annual Cycle

The most obvious and consistent temporal variation at nearly all monitoring stations is the annual cycle in sulfate concentration and, to a lesser extent, acidity in precipitation. Several examples are given to illustrate this cycle. Monthly values of four chemical species in precipitation from the Pennsylvania State University MAP3S site over a three year period have been subjected to a rigorous statistical analysis. This data shows a significant annual cycle for all species except ammonium ion ($NH_4^+$). At Chalk River just west of Ottawa, Canada, a marked seasonal variation shows up for the hydrogen and sulfate ion, but the nitrate ion remains fairly constant throughout the year.

Only one network operating in North America, has been routinely monitoring air concentrations of sulfur dioxide and sulfate at regionally representative rural locations for several years; it is the Air and Precipitation Network (APN) in Canada. Data from 4 sites in 1979 have been analyzed. It should be noted that the three eastern stations are within or downwind (most of the time) of the major emission source regions. The fourth station (ELA-Kenora) is upwind (most of the time) of the emissions. For sulfur dioxide, all stations show a seasonal variation with a winter maximum and a summer minimum. All eastern stations show a summer maximum in sulfate, an oxidation product of sulfur dioxide, indicating a summer maximum in the conversion rate of sulfur dioxide to sulfate. At ELA-Kenora the seasonal variation is different with both species having a maximum in winter. Here the southward depression of the westerlies over the mid-continent and the Arctic high pressure areas over central-northern Canada result in the maximum frequency of easterly winds which can transport both sulfur dioxide and sulfate to Kenora from the eastern source regions at concentrations greater than summer levels.

### 6.3.3 Wet versus Dry Deposition

The data from the APN sites can also be used to estimate the relative importance of wet and dry deposition of acidic species. Using the most recent techniques to estimate dry deposition rates from the air concentrations, and calculations of wet deposition rates as the product of the precipitation amount and the precipitation concentration. At the station closest to the sulfur sources (that is, Long Point) wet and dry deposition rates are approximately equal most of the year. At sites more distant from emissions, wet deposition is greater than dry by up to a factor of 5 for most of the year. The ratio of dry to wet is higher in winter than in summer since, in winter, ground level sulfur dioxide concentrations are highest and precipitation amounts are lowest.

## 6.4 Special Studies

The previous two sections have discussed some of the information that can be gained from operating routine monitoring networks. However, there are other approaches to gaining a fuller understanding of the pathways and processes between emission and deposition, namely special studies carried out with intensive, more detailed observations over limited geographical areas and shorter periods of times. These studies have often involved aircraft to obtain data within the atmosphere's surface mixed layer and in clouds. Some of the major studies carried out in the last few years are discussed in Report 2F-I although in most cases the data analysis is far from complete. Some of the emerging findings from these studies include a) the role of clouds in speeding up the production of sulfuric acid from sulfur dioxide, b) the role of cloud nucleation as an important in-cloud sulfate scavenging mechanism, and c) the observed acidity of cloud water, implying a mechanism that produces additional acid in the clouds. The implications of some of these results have been discussed in Chapter 4.

## 6.5 Single Station Sector Analysis

As pointed out in Section 6.4.1 there is a strong geographical concurrence of the regions of highest sulfur deposition with the emission source regions. This relationship can be further investigated by analyzing the data from monitoring stations according to wind sector. The principle is very simple. At a given station the surface wind, or if available the wind at a more representative transport height (say, one or two kilometers above the ground), is classified according to wind direction (usually by the eight compass points). The air or precipitation concentrations are then stratified into these sectors and the mean value, frequency distribution or other statistical characteristics of the data obtained. It is then possible to relate the observations for a given sector to the pollutant sources upwind in that same sector. Since it is unlikely that the air arriving at a station has followed a straight line path over the whole region of interest such an analysis might identify the wrong contributing upwind sources. A refined, and more realistic approach, is therefore to calculate the pathway followed by the air parcels using one of the models discussed in Chapter 7 and to classify by sector according to air parcel history during the previous 24 to 48 hours (the typical time required for the air parcel to traverse the major emission and receptor regions of interest). Errors in trajectory calculations tend to be random and thus, when averaged over a large number of cases, tend to cancel out giving a more reliable mean value.

This technique was first applied in southern Norway where the results clearly identified the major emission source regions in western Europe as lying in those wind sectors associated with the greatest deposition of acidity. In North America the technique has been used at several locations where the appropriate daily sampling of air and precipitation concentrations is carried out. The results of these studies are given in Section 4.4 of MOI Report 2F-I and are briefly summarized here, first for air concentrations and then for precipitation.

### 6.5.1 Air Concentrations

A study in Toronto, Ontario, during the summer of 1976 showed that all the episodes of high sulfate, ozone and low visibility occurred with winds in the sector between west and south, with summertime sulfate concentrations averaging about 10 times those with winds in other sectors. A similar study in July 1976 and in July 1975 showed that in upper New York State the highest sulfate concentrations were associated with winds from direction of the upper Ohio River valley.

In a more recent study, to quote the abstract, "Particulate sulfate in air was monitored daily from June 1978 to December 1979 at Whiteface Mountain, N.Y. The daily sulfate concentrations were related to surface-air trajectory ensembles to assess the relative contribution from the U.S. and from Canada. During the study period the site was influenced approximately equally by continental polar and maritime tropical air masses. However, the maritime air masses from the U.S. were the principal conveyors of high sulfate concentrations at this site and transported 4 to 5 times more sulfate than did the polar continental air from Canada".

In Canada data from the three eastern stations in the Air and Precipitation Network (APN) consistently show the highest concentrations of particulate sulfate and nitrate and sulfur dioxide gas with air arriving from the southerly and southwesterly sectors. At the westerly site near Kenora, Ontario, just north of the Minnesota border, average air concentrations are much lower for all species and the highest values that occur are more evenly spread around the compass.

### 6.5.2 Precipitation Concentrations

For concentrations in precipitation, similar results have been reported. In the Muskoka-Haliburton area of southern Ontario (about 150 kilometers north of Toronto) the majority of the hydrogen ion (75-80%), sulfate ion (70-80%) and nitrate ion (57-86%) in wet deposition is associated with air trajectories from the southwesterly and southerly octants. The Canadian APN network shows results for wet deposition that are very similar to those for air concentrations. At Whiteface Mountain, and Champaign, Illinois, precipitation events were sampled during 1978. For Whiteface, concentrations of the dominant ions were highest with precipitation events associated with trajectories from the southwest and northwest sectors, leading to strong maxima in the deposition from these sectors. On the other hand at Champaign, only the southwest sector showed a large peak in deposition. In a recently published study for Bermuda, precipitation has been monitored on an event basis since May of 1980. With air arriving from the sector southwest through north (that is, the North American continent) the average rainfall pH is 4.4; for the remaining directions the average is about 5.0. For the west sector about 50% of the rain events had a pH of less than 4.5. In the remaining sectors only 5% of the rain events had a pH of less than 4.5.

In summary, these independent studies all indicate a very strong association of highest air and precipitation concentrations of sulfate (and nitrate) and lowest pH with air arriving from the region of greatest emissions in North America. In effect this analysis produces the simplest form of source-receptor relationship that can be generated. It is, therefore, useful for identifying in a general and qualitative way which source regions are responsible for the air concentration and deposition at a given site. While the sector(s) of origin can be identified, this analysis cannot distinguish between nearby and more distant sources. The modeling described in Chapters 7 and 8 expands upon this sector analysis principle in a quantitive way to arrive at such estimates.

## 6.6 Mass Budget Studies

This approach uses existing data, averaged over appropriately large time and space scales to examine the fluxes of constituents of interest into and out of a selected portion of the atmosphere. An inherent assumption is that on these large scales a steady state condition exists and that the concept is most useful where emissions and the climatological regime is reasonably homogeneous. It does not take into account enhanced local deposition that may take place near strong emission sources, and hence the removal terms may be overestimated by an unknown, but probably small, amount.

Several global budget estimates have been made over the last 20 years, but only in the last few years have regional budgets been prepared for eastern North America using data from the 1970's (the detailed results of various fluxes are given in Table 4.5.1 of Report 2F-I). Some of the most important findings of these studies follow.

Man-made sulfur emissions in eastern North America 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" terms, 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 the proximity to emission sources; that is, dry deposition is greater in the eastern USA where emissions are larger. Approximately 30-40% 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 eastern USA emissions.

In this last finding are the beginnings of the transfer matrix concept, to be discussed more fully in Chapter 8, that indicates the relative importance of various sources to receptors; in this case only two, namely Canada and the USA on a gross scale. Numerical modeling can produce such relationships on a finer space scale involving many source and several receptor regions.

# SIMULATION MODELING

# 7. SIMULATION MODELING

## 7.1 Introduction

Previous chapters describe the mechanisms of transport, dispersion, transformation, and deposition of the major pollutants associated with acidic deposition. Some of these mechanisms have been formulated mathematically in long range transport models to allow preliminary estimates of the deposition on sensitive receptors resulting from emissions from source areas. This chapter will discuss the attributes of some of these models and their evaluation against measured data.

It is not possible (due to practical modeling considerations as well as our incomplete understanding of the phenomena) to provide models for all the pollutants of interest or to incorporate all the processes mathematically into operational regional models. For example, deficiencies in both emission inventories and in our understanding of the transformation and deposition processes preclude the development of quantitative models for acid nitrate deposition. Nor is it possible to incorporate the detailed atmospheric chemical interactions between $SO_2$, $NO_x$, VOC, oxidants, and their acidic reaction products (see Chapter 4). Models described here, therefore, contain simplifying assumptions which are based upon our current understanding of the phenomena of long range transport.

Eight models for sulfur oxides have been selected by Work Group 2 based on criteria set in the earlier phases of the program. They represent the types of operational models currently available. The models are "linear" in the sense that chemical transformations and scavenging are expressed as first order processes where the rate constants are assumed to be independent of the emissions and the co-pollutant concentrations. These simplifications of the physical/chemical processes, some of which are known to be non-linear, will introduce some errors into the model results and make the models generally inappropriate for local scale episodic analyses. The model profiles are summarized in a tabular form in Section 7.2 and detailed profiles are available as supporting technical material for this report.

A set of criteria for evaluating models against observed data has been developed during the workshops held by the Regional Modeling Subgroup. These evaluation criteria were derived from the basic recommendations of the Workshop on Dispersion Model Performance sponsored by the American Meteorological Society. The theoretical framework for the evaluation criteria is developed in the Regional Modeling Subgroup report (2F-M) while the results of the model evaluation are briefly described in Section 7.3. Due to uncertainties in the input emission inventory, the precipitation data used by the models and the measurement data used for validation, a ranking of the models in terms of their absolute performance cannot be made at this time.

The assumptions of linearity in the transformation and wet deposition processes that are incorporated into all eight models may also be questioned. The non-linearity of several of the processes is described in Chapters 4 and 5. However, non-linear chemistry modules have either not been available or have not been incorporated into the current long range transport models. The question, that is the subject of individual judgment, is whether or not the linear models of sulfur transport represent a reasonable first approximation over the long term. It is not clear that non-linear effects will invalidate the general seasonal and annual results of these linear models. The question of whether or not the linear models of sulfur transport represent a reasonable first approximation over the long term and large space scales has not been resolved by the Work Group. Although Chapter 8 will deal with this subject in greater detail, a complete analysis of the impact of non-linearity is beyond the scope of this report. Additional sensitivity analyses and evaluations against measurement data are expected to shed more light on this matter.

## 7.2 Regional Modeling Approach

Eight long range transport models (Table 7.1) developed by Canadian and U.S. scientists were applied by the Regional Modeling Subgroup of Work Group 2 using standardized input data sets. This section discusses the general attributes and data input requirements of these models and the differences in the modeling techniques employed.

The techniques of simulating the transport, dispersion, transformation, and deposition of pollutants are quite varied since:

(1) the best modeling techniques are not clearly discernible (that is, each technique has advantages and disadvantages);

(2) the nature of all relevant physical and chemical processes is not fully understood;

(3) each modeler makes various assumptions to simplify the complex processes; and

(4) each model was developed independently.

This wide range in modeling techniques will become evident in the discussion in the subsequent section and from Table 7.2.

Table 7.1 Long range transport models assembled by Work Group 2

| | Model Name | Acronym | Work Group 2 Report Number* |
|---|---|---|---|
| 1. | Atmospheric Environment Service Long Range Transport Model | AES | 2-5 |
| 2. | Advanced Statistical Trajectory Regional Air Pollution Model | ASTRAP | 2-6 |
| 3. | Centre for Air Pollution Impact and Trends Analysis-Monte Carlo Model | CAPITA | 2-12 |
| 4. | Eastern North American Model of Air Pollution | ENAMAP-1 | 2-7 |
| 5. | Meteorological and Environmental Planning, Ltd. Transport of Regional Anthropogenic Nitrogen and Sulfur (TRANS) Model | MEP | 2-11 |
| 6. | Ontario Ministry of the Environment Long Range Transport Model | MOE | 2-8 |
| 7. | University of Illinois Regional Climatological Dispersion Model | RCDM-3 | 2-9 |
| 8. | University of Michigan Atmospheric Contributions to Interregional Deposition Model | UMACID | 2-10 |

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* These report numbers were assigned in the early Phases of the work and some model profiles have been revised since that time.

It should be noted that the following descriptions of the model input data requirements, model parameterizations, and model outputs address specific Work Group 2 applications. Over a series of applications, the nature of the available input data, the time and cost constraints, and the desired model output often dictate the form of the model parameterizations. Thus the constants used in the Work Group 2 model parameterizations, and presented in Table 7.2, may differ from those used in previous phases and are subject to change for subsequent applications.

Each of the models simulates the transport, dispersion, transformation and deposition of sulfur compounds. Monthly-averaged concentrations and depositions, as well as monthly source-receptor relationships, are generated by most of these models for central and eastern North America. The ASTRAP, CAPITA, ENAMAP-1, MEP, RCDM-3, and MOE models are source-oriented which facilitates generation of concentration and deposition fields, while the AES and UMACID models are receptor oriented. The AES, ASTRAP, CAPITA, MOE, and RCDM-3 models have included various parts of western North America in the modeling domain.

### 7.2.1 Input Data Requirements

Most models utilize gridded sulfur dioxide point and area source emissions as input and, with the exception of the ASTRAP and MEP models, treat the total emissions within a given grid cell as one virtual point source emitting pollutants at one level or within one layer (Table 7.2). The emission grid resolution varies from model to model within the range of 70 to 190 kilometers. The MOE model incorporates individual point sources and area emissions totalled by county as effective point sources. The ASTRAP and MEP models distribute the emissions vertically as a function of the stack characteristics. In addition to sulfur dioxide, the AES, ASTRAP, CAPITA, ENAMAP-1, MOE, and UMACID models are capable of including primary sulfate emissions. The MOE model assumes a constant

Table 7.2 Summary of Regional Model Attributes

| ATTRIBUTE | AES | ASTRAP | CAPITA | ENAMAP-1 |
|---|---|---|---|---|
| a. Model Type | Lagrangian - box | statistical - trajectory | Monte Carlo | puff - trajectory |
| b. Receptor Grid (cells);<br>Grid Resolution (km)* | 52 x 37;<br>127 x 127 | user specified; receptor point locations | 52 x 37;<br>127 x 127 | 46 x 41;<br>70 x 70 |
| c. Model Domain | North America and adjacent oceans | North America and adjacent oceans | North America and adjacent oceans | eastern and central North America |
| d. Model Output | monthly $SO_2$ and $SO_4^{2-}$ concentrations and dry and wet S depositions | monthly $SO_2$ and $SO_4^{2-}$ concentrations and dry depositions and bulk S wet deposition | monthly $SO_2$ and $SO_4^{2-}$ concentrations and dry and wet depositions | monthly $SO_2$ and $SO_4^{2-}$ concentrations and dry and wet depositions |
| e. Input Requirements* | | | | |
| 1. Emissions | 1. annual and seasonal $SO_2$ grids (127 km) | 1. 3-D annual and seasonal $SO_2$ for 6-layer grids (127 km) plus stack parameters of major point sources | 1. annual $SO_2$ grids (95 km for northeastern U.S. and southeastern Canada and 190 km elsewhere) | 1. annual $SO_2$ grids (70 km) |
| 2. Winds | 2. 0000 and 1200 GMT rawinsonde winds and temperatures at 1000, 850, 700, and 500 mb levels | 2. 0000 and 1200 GMT rawinsonde wind profiles | 2. 1500, 1800, and 2100 GMT surface winds and 0000 and 1200 GMT rawinsonde wind profiles | 2. 0000 and 1200 GMT rawinsonde wind profiles |
| 3. Precipitation | 3. daily amounts | 3. 6-h amounts | 3. 6-h probabilities | 3. 3-h amounts |

*Grid dimensions in the models using polar stereographic projections (AES, ASTRAP, CAPITA, MEP, and UMACID) are fractions of the U.S. National Meteorological Center and Canadian Meteorological Centre grid spacing (381 km at 60°N; less at lower latitudes).

Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | MEP | MOE | RCDM-3 | UMACID |
|---|---|---|---|---|
| a. Model Type | Lagrangian | statistical | analytical | puff - trajectory |
| b. Receptor Grid (cells); Grid Resolution (km)* | user-specified; point receptors | user-specified; point receptors | 70 x 70;<br>80 x 80 | 41 x 32;<br>80 x 80 |
| c. Model Domain | eastern North America | North America | North America | eastern and central North America |
| d. Model Output | monthly concentration and dry and wet depositions of sulfur | long-term $SO_2$ and $SO_4^{2-}$ concentrations; annual dry and wet sulfur depositions | monthly concentration and dry and wet depositions of sulfur | estimates of source contributions to downwind concentrations and contributions of upwind sources on receptors at 6-h time steps |
| e. Input Requirements*<br>1. Emissions | 1. seasonal, annual 127 x 127 gridded North American emissions | 1. point sources and area sources as effective point sources | 1. emissions and emission centroids of source areas | 1. total annual $SO_2$ rates for 80 km grid squares |
| 2. Winds | 2. 6-h surface pressures | 2. long-term statistics: mean west to east at 10 m $s^{-1}$, $\sigma_u$=10 m $s^{-1}$, and $\sigma_v$=6 m $s^{-1}$ | 2. monthly, seasonal, and annual resultant winds and persistence factors from rawinsonde stations | 2. rawinsonde and pibal winds at 12-h intervals |
| 3. Precipitation | 3. 3-h amounts | 3. estimated statistics of durations of wet and dry periods (Eulerian and Lagrangian) and average precipitation rate during wet periods | 3. spacially averaged annual and seasonal dry and wet period durations for each state/province | 3. 3-h amounts |

*Grid dimensions in the models using polar stereographic projections (AES, ASTRAP, CAPITA, MEP, and UMACID) are fractions of the U.S. National Meteorological Center and Canadian Meteorological Centre grid spacing (381 km at 60°N; less at lower latitudes).

Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | AES | ASTRAP | CAPITA | ENAMAP-1 |
|---|---|---|---|---|
| f. Treatment of Emissions | emissions added to box every 3 h and dependent on location of box | puffs released at appropriate level at 6-h intervals | 3-h $SO_2$ emissions released in mixed layer in day, 450-750 m layer at night; 1% of S is $SO_4^{2-}$ | puffs containing 12-h emissions released from each source cell at 12-h increments |
| g. Analysis of Transport Wind (performed by a preprocessor) | objective analysis of 6-h horizontal wind components on 381 x 381 km grid at 1000, 850, 700, and 500 mb levels; vertical wind component computed at each level from temperature profile and interpolated to trajectory level | mean winds in the lowest 1.4 km (summer) and 1.0 km (winter) at upper-air sites are objectively analyzed using an inverse-distance-squared weighting scheme | surface winds, adjusted by a seasonal factor (1.7 to 2.2) and a 10° veering (day), are objectively analyzed for 3-h periods using inverse-distance-squared weighting scheme and the 127-km grid; upper winds in 4-layers (night) | mixed layer averages at rawinsonde sites are objectively analyzed using an inverse-distance-squared weighting scheme |
| h. Analysis of Precipitation (performed by a preprocessor) | objective analysis of daily precipitation amounts on a 127 x 127 km grid | hourly data are summed to produce 6-h totals across a grid of about a 76-km spacing* | no actual precipitation rates used; time averages of precipitation probabilities used for each 127 km grid square | hourly U.S. and 6-h Canadian data are summed to produce 3-h totals across 70-km grid squares* |
| i. Mixed Layer (m) | monthly climatological heights on a 127 x 127 km grid | diurnal pattern including nocturnal surface-based inversion; maximum: 1000 (w) and 1800 (s) | day: 800 (winter)<br>1200 (spring/fall)<br>1350 (summer)<br>night: 300 | 1150 (winter)<br>1300 (spring/fall)<br>1450 (summer) |
| j. Horizontal Dispersion | emissions evenly distributed across 127 x 127 km grid cells | computed from the distribution of plume centerlines at 6-h intervals downstream for a grid of virtual sources | 2000 $m^2\ s^{-1}$ (day)<br>100 $m^2\ s^{-1}$ (night),<br>but delineated by overnight shear and veer of the 4-layered winds | puff radius = $(r_o^2 + Kt)^{1/2}$, where $r_o$ is the initial puff radius (km), K is 36 $km^2\ h^{-1}$, and t is time (h) |

*If no precipitation monitoring sites exist in a grid cell, the value at the nearest site is adopted.

Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | MEP | MOE | RCDM-3 | UMACID |
|---|---|---|---|---|
| f. Treatment of Emissions | emissions allocated by height distribution to one of four levels (1% of S is $SO_4^{2-}$) | point sources with $SO_4^{2-}$ to $SO_2$ ratio assumed to be 0.02 | point sources at emission centroids of source areas | 6-h $SO_2$ and $SO_4^{2-}$ source emissions; 1 and 5% of S is $SO_4^{2-}$ for winter and summer, respectively |
| g. Analysis of Transport Wind (performed by a preprocessor) | 6-h surface pressure analysis generates modified geostrophic winds at 4 transport levels | long-term statistics; | monthly resultant wind vector for each emission cell by averaging rawinsonde wind data over North America | 3-h winds computed using all observed winds within 300 nautical miles of the trajectory segment end point and using an inverse-distance-squared weighting scheme |
| h. Analysis of Precipitation (performed by a preprocessor) | objective analysis of 3-h amounts | climatological lengths of Eulerian and Lagrangian wet and dry periods; rate of 1 mm $h^{-1}$ | spatially averaged precipitation amounts and the average durations of wet and dry periods | hourly data summed for 3-h periods for each 80 km grid square |
| i. Mixed Layer (m) | varies diurnally over model domain | 1000 | 600 (winter)<br>1200 (summer)<br>1000 (annual) | varies only with month |
| j. Horizontal Dispersion | Gaussian distribution about plume centerline (lateral only) | statistical dispersion coefficients<br>$\sigma_x = \sigma_u t$, $\sigma_y = \sigma_v t$<br>$\sigma_u = 10$ m $s^{-1}$<br>$\sigma_v = 6$ m $s^{-1}$ | $2 \times 10^6$ $m^2$ $s^{-1}$ | $\sigma_x = \sigma_y = 5.4t$, where t is travel time (h) |

Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | AES | ASTRAP | CAPITA | ENAMAP-1 |
|---|---|---|---|---|
| k. Vertical Dispersion | uniform distribution throughout mixing layer | dependent on diurnally varying eddy diffusivity profile | instantaneously mixed throughout mixed layer (day); none at night | instantaneously mixed throughout mixed layer |
| l. Transformation Rate (% $h^{-1}$) | 1.0 | varies diurnally:<br>0.2 - 5.5 (summer)*; avg. of 2.0<br>0.1 - 1.5 (winter)*; avg. of 0.5 | 0.6 (winter)<br>1.2 (summer) | 1.0 |
| m. Dry Deposition Velocity (cm $s^{-1}$) | | | | |
| 1. $SO_2$ | 1. 0.5 | (1) and (2) vary diurnally:<br>0.45 (summer avg.)<br>0.25 (winter avg.) | 1. 0.31 (winter)<br>1.20 (summer) | 1. 0.38 (winter)<br>0.48 (summer) |
| 2. $SO_4^{2-}$ | 2. 0.1 | ($SO_2$ and $SO_4^{2-}$ similar but not identical) | 2. 0.07 (winter)<br>0.15 (summer) | 2. 0.22 (winter)<br>0.28 (summer) |
| n. Wet Removal Rate** (% $h^{-1}$) | | | | |
| 1. $SO_2$ | 1. $3 \cdot 10^6\ P_{24}(t)/H$ | | 1. 0.6 PP (winter)<br>11.7 PP (summer) | 1. 28.0 $P_1(t)$ |
| 2. $SO_4^{2-}$ | 2. $85 \cdot 10^6\ P_{24}(t)/H$ | | 2. 5.0 PP (winter)<br>29.0 PP (summer) | 2. 7.0 $P_1(t)$ |
| 3. Bulk S | where H is the mixed layer (mm) | 3. minimum of $100(P_6(t)/10)^{1/2}$ and 80 | where PP = probability of precipitation (%) each 6-h period | |
| o. Sulfur Background Contribution | annual wet S deposition of 2 kg $ha^{-1}$ added | none considered | none considered | none considered |

*Rate is increased to 0.5 - 3.0% $h^{-1}$ when plume is less than 3 h old and located within the lowest 200 m.

**$P_x(t)$ represents the liquid precipitation rate in mm per x hours.

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Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | MEP | MOE | RCDM-3 | UMACID |
|---|---|---|---|---|

Table 7.2 Summary of Regional Model Attributes (continued)

| ATTRIBUTE | MEP | MOE | RCDM-3 | UMACID |
|---|---|---|---|---|
| k. Vertical Dispersion | uniform vertical distribution in mixed layer which varies diurnally | uniform mixing in boundary layer | uniform mixing in boundary layer | uniform mixing in boundary layer |
| l. Transformation Rate (% $h^{-1}$) | seasonal and diurnal variation: mean of 1.0 | 1.0 | chemical conversion time scale $2.4 \times 10^5$ s (1% $h^{-1}$) | winter: 1.4 (day)<br>0.1 (night)<br>summer: 2.8 (day)<br>0.2 (night) |
| m. Dry Deposition Velocity (cm $s^{-1}$) | seasonal and diurnal cycle: mean of | | weighted by the percent of dry time | varies acording to time after sunrise and land use: |
| 1. $SO_2$ | 1. 0.75 | 1. 0.5 | 1. 0.50 | 1. 0.10 - 0.55 (winter)<br>0.10 - 0.82 (summer) |
| 2. $SO_4{}^{2-}$ | 2. 0.25 | 2. 0.05 | 2. 0.05 | 2. 0.05 - 0.28 (winter)<br>0.03 - 0.43 (summer) |
| n. Wet Removal Rate* (% $h^{-1}$) | | | | |
| 1. $SO_2$ | 1. dependent on pH and temperature | 1. 10.8 | | 1. $5.0\cdot 10^4 P_1(t)/H$ |
| 2. $SO_4{}^{2-}$ | 2. precipitation rate dependent: mean of $30\ P_1(t)^{0.5}$ | 2. 36.0<br>(used in stochastic scavenging model with $\tau_d$ = 56h and $\tau_w$ = 7h (the avg. dry and wet period durations) | | 2. $2.32\cdot 10^5 P_1(t)^{-0.625}/H$<br>where H = mixing height (mm) |
| 3. Bulk S | | | 3. $\Lambda\ P_t\ \dfrac{T_d + T_w}{T_w}$<br>where $T_d$ and $T_w$ are the average duration of the dry and wet periods (h), respectively, and $\Lambda$ is the scavenging coefficient equal to 0.34 | |
| o. Sulfur Background Contribution | assumed background of wet sulfur deposition of 2 kg $ha^{-1}$ | 2 kg $ha^{-1}$ wet sulfur deposition and 2 μg $m^{-3}$ $SO_4{}^{2-}$ concentration | none considered | none considered |

*$P_x(t)$ represents the liquid precipitation rate in mm per x hours; $P_t$ represents the total precipitation (mm) over a grid cell for the entire simulation period.

$SO_4^{2-}/SO_2$ emission ratio of 0.02, while the CAPITA model assumes that 1% of the total sulfur emitted is sulfate. The UMACID model varies the percentage of sulfur emitted in the form of sulfate from 1% in the winter to 5% in the summer. The AES, ASTRAP, and ENAMAP-1 models require sulfate emissions input; if no emissions data are available, sulfate emissions are not considered.

Six of the models require objectively-analyzed meteorological observations, while the other two (MOE and RCDM-3) use the statistical characteristics of the climatological data. For example, the MOE model makes an assumption about long-term wind statistics and the RCDM-3 model uses monthly and seasonal resultant wind vectors at each source emission area to define the pollutant transport process. The MEP model uses 6-hourly surface pressure data to generate wind fields while the remaining models use analyses of actual wind data (either surface and/or upper air) observed at 3 to 24 hour intervals. Precipitation data input requirements range from 3 hour analyses to the average duration of wet versus dry periods over a seasonal or annual period. The analyses of the wind and precipitation data are performed by preprocessors and are not actually modules of these models.

### 7.2.2 Model Parameterization

The mixing heights parameterized in the AES, ENAMAP-1, RCDM-3, and UMACID models are treated as seasonally dependent constants. In these models, no diurnal fluctuation is considered. The heights reflect the estimated average mixing height over the simulation period. Only the AES model uses monthly gridded values of the mixing height based on seasonally stratified climatological data. The CAPITA model uses seasonally dependent mixing height values but also considers a nocturnal lowering of the mixing height to 300 meters thus allowing the nocturnal emissions to be released above the surface layer. The ASTRAP and MEP models consider a diurnally fluctuating mixing height as well as the occurrence of a nocturnal inversion. A user-specified, fixed mixing height of 1000 meters is used in the MOE model.

The MOE and RCDM-3 models use analytical functions to determine the distribution of mass in space and time after emission, while the other models treat the emissions as discrete puffs. The mass of sulfur in each puff is determined from the time increment used (3 to 12 hours) and the emission rate. The AES model allows input of pollutants into boxes which are transported across emission areas in 3 hour time steps, while the other five models simulate the transport of individual pollutant puffs.

Horizontal dispersion is simulated in different ways. The AES and ASTRAP models calculate long-term dispersion directly through the distribution of simulated trajectories. The MEP model assumes a Gaussian distribution about each simulated plume centerline. The CAPITA model uses constant daytime and nighttime horizontal dispersion rates . The RCDM-3 model uses a constant horizontal dispersion rate, while the ENAMAP-1, MOE, and UMACID models use a time-dependent dispersion parameter.

Vertical dispersion in all the models except ASTRAP occurs instantaneously within the specified mixed layer resulting in a homogeneous distribution of pollutant in the vertical. The MEP model also allows pollutant input above the mixed layer. The vertical dispersion in ASTRAP, which considers nine sublayers within the boundary layer, is dependent upon a diurnally varying stability profile.

The rate of transformation of sulfur dioxide to sulfate is defined to be 1% per hour in the AES, ENAMAP-1, MOE, and RCDM-3 models. The transformation rate varies seasonally in the remaining models. In addition to the seasonal variations, the ASTRAP, MEP, and UMACID models consider diurnal variations in the transformation rates.

Dry deposition of sulfur compounds is simulated using a constant deposition rate for sulfur dioxide and another for sulfate in the AES, MOE, and RCDM-3 models. The CAPITA and ENAMAP-1 models use seasonally dependent dry deposition rates, while the remaining models use diurnally and seasonally dependent rates. The RCDM-3 model also uses the total "dry time" (total time in a period minus the total precipitating time) to simulate dry deposition.

All but the CAPITA and MOE models simulate wet sulfur deposition based on the actual precipitation rate over a specific period, times a scavenging coefficient. The CAPITA model computes wet deposition using the hourly probability of the occurrence of various intensities of precipitation across each 127-kilometer grid square. The MOE model uses a constant wet deposition rate and wet and dry period statistics which are assumed to be constant over the region. Wet deposition in the RCDM-3 model is simulated by the product of the scavenging coefficient, the total precipitation for the simulation period, and the ratio of total to wet average durations of the dry and wet periods, respectively. The MEP model also considers the pH of the precipitation and the ambient temperature as factors determining the amount of wet sulfur deposition. The AES, MEP, and MOE models systematically add a constant background sulfur contribution to the annual wet sulfur deposition.

For several reasons, the approaches to the parameterization of physical processes in the eight models are quite different. For example, the MOE model, developed to simulate sulfur concentrations and depositions on a long-term basis, applies a statistical approach to the representation of the transport and dispersion. Other models, designed to simulate on a monthly (or less) basis, require time-consuming computations of trajectories generated from wind data. The best approach is difficult to select since each has advantages and disadvantages.

The model descriptions presented in this chapter relate to the general features of the models as they were applied by Work Group 2. However, as models are applied to other specific applications, some of these features may change. For example, the ASTRAP model, in its general form, considers pollutants emitted in multiple layers within the boundary layer. If the model was to be applied using an emission inventory with no stack height data, the aggregation of pollutant emissions within the multiple layers could not be considered, and the modeler would have to make an adjustment to the modeling procedure.

It should be noted that these models represent the various types of models available for simulating sulfur transport, transformation, and deposition. As the physical processes and relationships become better defined, these models will be modified to reflect the gains in knowledge.

## 7.3 Model Evaluation

A set of criteria for model evaluation has been formulated by the Regional Modeling Subgroup. The philosophy and mathematical details of these criteria appear in the Regional Modeling Subgroup Report No. 2F-M. This section will summarize the results of this evaluation of predicted against measured data using these criteria.

One criterion is based on the difference between observed ($C_o$) and model-predicted values ($C_p$) for (i) ambient sulfate concentrations, and (ii) wet sulfur deposition. This difference represents the error and is denoted by e which can have either positive or negative values for individual comparisons. If a model performs well, provided that the observations are of high quality, the arithmetic average of e denoted by $\bar{e}$ should be close to zero. Another useful indicator is the average scatter of e about its mean value ($\bar{e}$). This is denoted by the standard deviation, $\sigma_e$. Again, if the model performs well, $\sigma_e$ should be close to zero. Actual zero values of $\bar{e}$ and $\sigma_e$ would imply that predictions are identical with observations.

Another criteria is based on the ratio of $C_o$ and $C_p$. We define the average of $C_o/C_p$ as the n-th root of the product of its n values, where n is the number of observed points. We denote this average, which is the geometric mean, by $m_g$. One may compute $s_g$, the geometric standard deviation around $m_g$, just as $\sigma_e$ is the arithmetic standard deviation around $\bar{e}$. For an ideal model, both $m_g$ and $s_g$ should be close to unity which implies, on the average, that predicted closely approximate observed values.

The differences between model predictions and observations should be randomly distributed, that is, they should have no correlation with the predictions. Mathematically, this implies that the cross-correlation between e and $C_p$ should be small. These and other rigorous statistics were produced to evaluate the performance of the models. These tests and the results are described in detail in the Regional Modeling Subgroup Report. Although significant limitations exist in the input emissions and precipitation data as well as in the measurement data used for evaluation, some conclusions can be made regarding the overall performance of the models. These are:

1. that all models appear to predict the correct order of magnitude of the wet sulfur deposition for the 1978 data sets;

2. that, for the same data set, no models, with the possible exception of the MEP, predict well the ambient sulfate concentrations; and

3. that statistics $\bar{e}$, $\sigma_e$, $m_g$, and $s_g$ are more significant for larger numbers of observation points than were used in this evaluation. The evaluation data set for 1978 contained only eight points for annual wet sulfur deposition and nine points for annual sulfate concentrations. This does not constitute a sufficient data set from which to draw statistical conclusions on the relative performance of models. Therefore, although some models appear individually to perform better than others, no firm conclusion should be drawn without more extensive evaluations. Clearly, while a start has been made toward developing evaluation statistics, further testing must be done to provide reliable quantitative information about model performance.

## 7.4 Summary

The following conclusions are based on the review of the eight models and their evaluation statistics:

1. In the Regional Modeling Subgroup report, the input wind fields used by the models are displayed as mean trajectories and their standard deviations for one point in the U.S. and one point in Canada. Comparing the mean trajectories and their standard deviations, at various travel times from these two locations, shows that the models differ somewhat in their treatment of the "transport wind". For example, whereas the MOE model assumes that the mean flow and hence the mean trajectory should be from the west to the east, the AES, ASTRAP, ENAMAP-1, and UMACID models show that the mean trajectory may be from the west-southwest. The MEP model is significantly different from the other models both for

its mean trajectory location and direction. This may be caused by the fact that in the MEP model the transport wind is derived from the surface pressure data, while the trajectories for the other models are based upon upper level winds.

It is noted that, in principle, the mean upper level winds would flow in a westerly direction. However, the effective wind for transport is the mixed layer average wind which is affected by the surface conditions. Thus the true mean trajectory for the puffs, which are transported long distances, is expected to deviate somewhat from this westerly direction.

2. Extensive screening of the observed wet deposition and concentration data was necessary to correct for errors associated with catch efficiencies, evaporation and sample contamination. This screening is described in detail in the subgroup Report 2F-M.

3. Evaluations of the model predictions against observed data show that, collectively, most models predict the wet sulfur deposition better than the sulfate concentrations. It should be noted that sulfur dioxide was not used for this evaluation exercise due to unavoidable contamination of the data by local sources and errors in the measurements at very low concentrations.

   The model evaluation criteria used here are different from those generally used by air quality modelers. It is somewhat surprising that the predictions of wet sulfur deposition would be better than for sulfate. This is because wet deposition of sulfur is very 'episodic' in nature (most of the depositions occuring in a few precipitation events). It is, however, encouraging to note that simple linear models appear to be able to predict the correct order of magnitude of the wet sulfur deposition.

The uncertainties in the emissions data were not available at the time of the model evaluations. It is possible that these uncertainties are functions of the source regions, which could affect the model results significantly. A constant uncertainty factor, on the other hand, would only introduce a bias. To properly analyze the model predictions, one needs to know the magnitudes and spatial variabilities of the emission uncertainties. Furthermore, emissions are only available as annual totals, so that the monthly and seasonal predictions cannot be expected to simulate observed monthly and seasonal variations.

4. Only a few data points were found to be suitable for the evaluation of the models. Thus, it is difficult to make any definitive conclusions on the absolute performance of these models. This, together with the unknown uncertainties in the emissions, makes it difficult to assess whether some models are performing better than others.

5. The diversity of parameterizations in these operational models reflects the fact that they were independently developed. The variations in techniques and parameterizations reflect a breadth of scientific opinions and judgement amongst the modelers. It is not at all surprising that models show differences in detail when applied to a single data set.

6. A method is now available to properly evaluate model performance. However, more data (quality assured and available as a time series) is needed to quantitatively determine the uncertainties in the model predictions.

# MODEL APPLICATIONS

# 8. MODEL APPLICATIONS

## 8.1 Introduction

The Terms of Reference require Work Group 2 to recommend tools for preliminary assessment activities. This includes the explanation of observations and the estimation of emission reductions that would be needed to achieve proposed reductions in air pollutant concentrations and deposition rates to protect sensitive areas. The purpose of this chapter is to describe currently available tools, to explain how these tools may be used according to the circumstances of the application, and to review the limitations of the tools for these applications.

The principal tools available at present are air qualilty simulation models, including the long range transport models of the type evaluated in the previous chapter, local and mesoscale models as described in Chapter 10 and transfer matrices. The use of the transfer matrix approach is described in some detail in this chapter.

Transfer matrices should be viewed primarily as a convenient form for either representing the results of a model or for applying those results to the study of emission reductions. Their special limitations are described, in addition to some of the overall limitations present in the current generation of linear transport models.

The effect that emissions of pollutants from any source (or group of sources) will have in producing ambient concentrations and deposition of pollutants at some other location is known as the "source-receptor" relationship. As explained in Chapters 3 and 4, that relationship is determined by the directions in which pollutants are carried by the winds and also by the dispersal, chemical transformation and removal of pollutants along the way. The term, source-receptor relationship, is often used in this report to specify the question of the relative impact of different source locations on a given receptor. It should be understood, however, that non-linear processes and interactions among pollutants must be considered in determining the absolute source-receptor relationship. One cannot define an absolute relationship between a specific source and receptor because the effect that emissions have on any receptor depends on what and how much of several pollutants is emitted from other sources.

The determination of specific source-receptor relationships and of general relationships between pollutant emission levels and ambient effects clearly is important in the formulation of plans for emission reductions. Measurements of ambient pollutant concentrations and wet deposition rates can describe the current status of the problem, except for dry deposition. Measurements over a period of time could describe historical trends, but the past data are not reliable as described in Chapter 6. However, measurements cannot reveal directly the result of changes in emissions unless those changes can be isolated and distinguished clearly from other man-made and natural influences. Unfortunately, acid deposition is seldom an isolated or reproducible phenomenon. Variability in the meteorological factors of transport and changes in the levels of emissions of sulfur and interacting contaminants from a variety of sources tend to confound a simple cause-effect identification. With so many factors varying, it is necessary to formulate and test the validity of more complex relationships among the factors. While many different forms of relationships are conceivable, computer models that take account of physical transport relationships appear to provide the most reasonable basis today for a starting point to explain the observations.

Since models, or cause-effect relationships in some form, are necessary to estimate the impacts of future changes in emissions, the availability of observations to evaluate their performance is mandatory. In the previous chapter, observations of ambient sulfate and wet sulfur deposition during 1978 were used to assess performance. However, this type of observation does not reveal directly the impact of individual source regions, nor does it conclusively demonstrate that a change in ambient levels could result from gross changes in emissions of sulfur, nitrogen or other interacting pollutants.

To distinguish among these types of response in models, it would be useful to have a richer array of observations. If observations were available from time periods in which there were distinctly different sulfur emission patterns, or if some tracer were present that could identify source regions conclusively, then source-receptor relationships might be verified directly. Similarly, if data were available over a sufficient historical period to cover grossly different levels of sulfur and nitrogen in the atmosphere and to average over (or distinguish among) atmospheric fluctuations, then questions of non-linearity and co-pollutant interactions might be clarified. Unfortunately, one cannot rewrite the history of inadequate data collection, and natural or controlled tracer experiments have not been considered feasible in the past. However, further research efforts are warranted into the use of natural tracers and into the feasibility of controlled experiments. Controlled experiments might involve the release of tracer substances and/or planned changes in emissions on a substantial scale. Tracers might be found among the varying constituents of fly ash from coal and petroleum combustion.

## 8.2 Transfer Matrices

Transfer matrices are based on the principle of linear superposition of emissions of a pollutant from various sources. This means that one assumes that concentration and/or deposition at a receptor location are the sum of partial contributions. Each contribution is proportional to the emissions from a source or group of sources. Thus, the concentration C at receptor A would be of the form

$$C_A = T_{A1} \cdot E_1 + T_{A2} \cdot E_2 + \dots + T_{AJ} \cdot E_J + \dots + T_{AN} \cdot E_N$$

where $E_J$ is the emission rate in source region J and $T_{AJ}$ is a coefficient of proportionality connecting the source region with the receptor A. The array of these coefficients connecting all sources with all receptor locations of interest constitutes a transfer matrix. A separate matrix is calculated for each ambient concentration parameter (for example, sulfate) and each deposition parameter (wet, dry or total) for a given time period.

The meaning of and the values in a transfer matrix depend upon the pollutant, the particular type of concentration or deposition variable represented, the meteorology for the applicable time period, the manner in which sources are grouped, and how receptor locations are defined. The receptors might be at particular locations (points) or might represent an average over a broader "receptor" region. The new 40x9 matrices for this report pertain to 40 smaller source regions and to receptors in nine fairly small, "sensitive" receptor areas .

Transfer coefficients ($T_{AJ}$) are generated by models using meteorological data from specific periods of time. Typically the model estimates the incremental contributions (say, $\Delta C_{AJ}$) to the average ambient values of concentration and deposition at a receptor location from all sources in a specific group; that is, $\Delta C_{AJ}$ is the concentration in region A caused by sources in region J. Normalized matrix elements are computed by dividing the incremental contributions by the total emission rate from the group of sources; that is, $T_{AJ} = \Delta C_{AJ}/E_J$. Matrix elements are presented in units corresponding to an emission rate of 1 teragram (1,000 kilotonnes) of sulfur per year. An example of Transfer Matrix is shown in Table 8.1. This is selected arbitarily from the outputs of one of the models and should be treated only as an example. The 40 source regions were defined previously in Table 2.1 and 2.3 and the sensitive receptors are shown on Figure 2.3.

### 8.2.1 Applications of Matrices

The transfer matrix coefficient in the normalized matrix can be interpreted as a potential measure of the impact of the selected source region on the given receptor. A large value indicates that the source region has a potentially large impact on the receptor per unit of emission. The absolute impact depends upon the magnitude of the emissions. An illustration of transfer matrix calculations is shown in Figure 8.1 for a simple example of two source regions and two receptor areas.

The potential utility of the normalized matrix for emission reduction studies lies in its ability to identify the relative effectiveness of controlling the various source regions in an explicit, yet simplified manner. The matrix can serve as a tool for the selection of likely emission reduction configurations, and for the prediction of the long range impact of the selected configuration on the measured fields of concentration and deposition. When used as a tool for the formulation of emissions reduction, the way in which matrices are employed and the subsequent effect of errors in the matrix elements will depend upon how the objectives for control are expressed. If the objectives are expressed quantitatively in terms of control costs and an environmental damage function and/or constraints

Table 8.1 Example of a 40x9 transfer matrix

ANNUAL - 1978

WET DEPOSITION UNIT MATRIX IN KG.S/HA/TGS

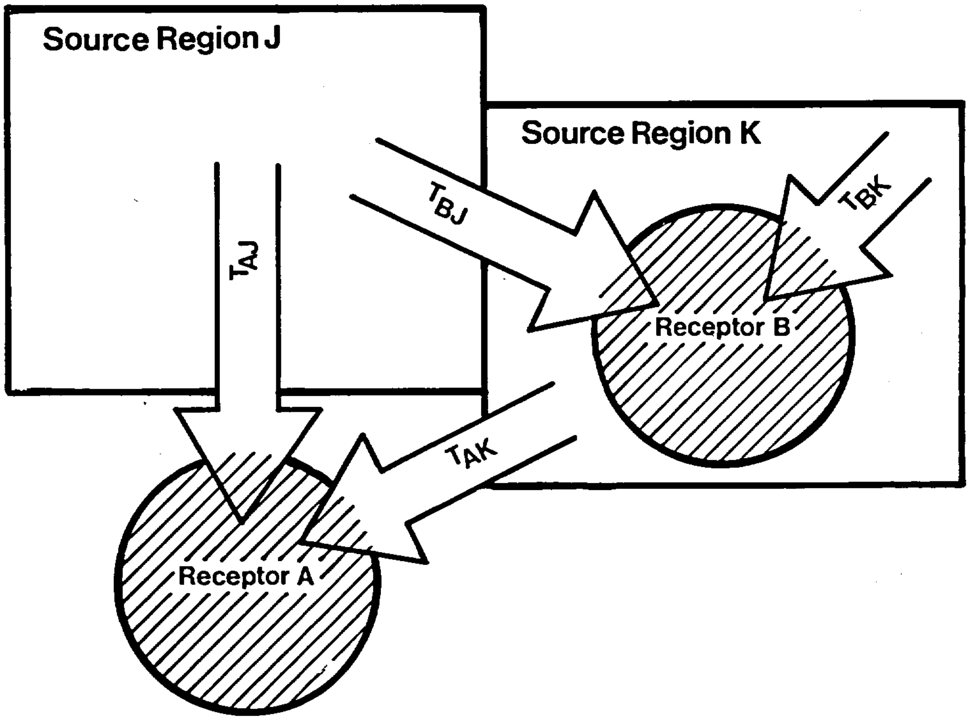
| REGION | BW | ALG | MUSK | QUEB | SNSC | VT | ADIR | PENN | SMOK |
|---|---|---|---|---|---|---|---|---|---|
| 10 NMN | 0.23 | 0.08 | 0.04 | 0.08 | 0.02 | 0.04 | 0.02 | 0.01 | 0.0 |
| 11 SMN | 4.43 | 0.71 | 0.28 | 0.14 | 0.03 | 0.11 | 0.11 | 0.08 | 0.01 |
| 12 NWO | 0.29 | 0.57 | 0.34 | 0.29 | 0.05 | 0.17 | 0.16 | 0.07 | 0.0 |
| 13 NEO | 0.01 | 3.22 | 1.34 | 1.14 | 0.23 | 0.78 | 0.74 | 0.28 | 0.01 |
| 14 SUD | 0.0 | 0.37 | 1.63 | 2.57 | 0.48 | 1.76 | 1.57 | 0.30 | 0.0 |
| 15 SWO | 0.01 | 0.31 | 4.57 | 1.55 | 0.57 | 1.91 | 2.77 | 3.19 | 0.01 |
| 16 SEO | 0.0 | 0.03 | 3.31 | 3.18 | 0.81 | 3.15 | 4.05 | 0.25 | 0.0 |
| 17 SLV | 0.0 | 0.0 | 0.0 | 7.70 | 1.04 | 3.27 | 0.61 | 0.01 | 0.0 |
| 18 NQU | 0.0 | 0.05 | 0.32 | 2.01 | 0.46 | 1.09 | 0.76 | 0.13 | 0.0 |
| 19 GBY | 0.0 | 0.0 | 0.0 | 0.05 | 0.35 | 0.04 | 0.01 | 0.0 | 0.0 |
| 20 NBK | 0.0 | 0.0 | 0.0 | 0.01 | 0.76 | 0.01 | 0.0 | 0.0 | 0.0 |
| 21 NSP | 0.0 | 0.0 | 0.0 | 0.01 | 0.29 | 0.01 | 0.0 | 0.0 | 0.0 |
| 22 NFL | 0.0 | 0.0 | 0.0 | 0.01 | 0.01 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23 ASK | 0.37 | 0.07 | 0.02 | 0.01 | 0.0 | 0.01 | 0.01 | 0.01 | 0.01 |
| 24 BCA | 0.01 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 50 OHO | 0.02 | 0.31 | 1.16 | 0.90 | 0.42 | 1.11 | 1.50 | 4.60 | 0.10 |
| 51 ILL | 0.14 | 1.49 | 1.81 | 0.64 | 0.14 | 0.64 | 0.88 | 1.30 | 0.32 |
| 52 PEN | 0.01 | 0.10 | 0.83 | 0.85 | 0.64 | 1.54 | 2.68 | 11.97 | 0.02 |
| 53 IND | 0.04 | 0.65 | 1.61 | 0.85 | 0.26 | 0.91 | 1.21 | 2.14 | 0.25 |
| 54 KEN | 0.01 | 0.31 | 0.79 | 0.55 | 0.26 | 0.68 | 0.87 | 1.96 | 0.52 |
| 55 MCH | 0.03 | 3.43 | 4.51 | 1.55 | 0.36 | 1.37 | 1.59 | 1.17 | 0.03 |
| 56 TEN | 0.01 | 0.07 | 0.35 | 0.11 | 0.07 | 0.25 | 0.46 | 1.22 | 7.95 |
| 57 MSU | 0.23 | 1.34 | 1.23 | 0.53 | 0.15 | 0.54 | 0.69 | 0.89 | 0.32 |
| 58 WVR | 0.0 | 0.12 | 0.51 | 0.54 | 0.47 | 0.76 | 0.98 | 3.44 | 0.13 |
| 59 NYK | 0.0 | 0.02 | 0.27 | 1.75 | 1.05 | 4.98 | 9.64 | 0.53 | 0.0 |
| 60 ALA | 0.0 | 0.10 | 0.20 | 0.02 | 0.01 | 0.03 | 0.08 | 0.36 | 7.60 |
| 61 WIO | 0.38 | 2.39 | 1.64 | 0.71 | 0.14 | 0.62 | 0.78 | 0.82 | 0.11 |
| 62 MIN | 2.90 | 1.42 | 0.71 | 0.35 | 0.05 | 0.28 | 0.34 | 0.31 | 0.05 |
| 63 VNC | 0.0 | 0.05 | 0.19 | 0.24 | 0.39 | 0.41 | 0.47 | 1.33 | 0.46 |
| 64 FLD | 0.0 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.08 | 2.36 |
| 65 GSC | 0.0 | 0.04 | 0.08 | 0.07 | 0.07 | 0.10 | 0.11 | 0.25 | 6.29 |
| 66 MDJ | 0.0 | 0.02 | 0.17 | 0.35 | 0.56 | 0.64 | 0.97 | 3.08 | 0.01 |
| 67 ALM | 0.02 | 0.23 | 0.26 | 0.03 | 0.01 | 0.04 | 0.10 | 0.48 | 2.12 |
| 68 MCR | 0.0 | 0.02 | 0.07 | 0.42 | 1.06 | 1.54 | 1.01 | 0.10 | 0.01 |
| 69 MAN | 0.0 | 0.0 | 0.0 | 0.29 | 2.69 | 0.79 | 0.06 | 0.0 | 0.0 |
| 70 VNH | 0.0 | 0.0 | 0.03 | 1.36 | 1.12 | 9.74 | 1.49 | 0.05 | 0.0 |
| 71 WNE | 0.79 | 0.37 | 0.16 | 0.03 | 0.0 | 0.03 | 0.04 | 0.05 | 0.02 |
| 72 WSE | 0.44 | 0.31 | 0.14 | 0.02 | 0.0 | 0.02 | 0.04 | 0.08 | 0.08 |
| 73 WNW | 0.07 | 0.01 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 74 WSW | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

THE OUTPUTS OF ALL ATMOSPHERIC SIMULATION MODELS ARE SUBJECT TO ERRORS AND UNCERTAINTIES OF VARYING DEGREE AND SIGNIFICANCE DEPENDING UPON THE VARIABLES BEING MODELLED AND THE SPECIFIC ANALYTICAL OR PREDICTIVE APPLICATIONS BEING CONSIDERED. TRANSFER MATRICES SHOULD NOT BE USED WITHOUT AN APPRECIATION OF THEIR LIMITATIONS AS OUTLINED IN THE ACCOMPANYING TEXT OF THIS REPORT.

# Illustration of the transfer matrix calculations

# Figure 8.1

### a) Schematic Map



### b) Transfer Matrix

| Source Region | Receptor Region A | Receptor Region B |
|---|---|---|
| J | $T_{AJ} = 4$ | $T_{BJ} = 2$ |
| K | $T_{AK} = 1$ | $T_{BK} = 3$ |

### c) Sample Calculations

Suppose Annual Emissions are:
$E_J = 2$ emission units
$E_K = 4$ emission units
The concentration (or deposition) is given by:
$C_A = T_{AJ} \cdot E_J + T_{AK} \cdot E_K = 4[2] + 1[4] = 12$ concentration units
$C_B = T_{BJ} \cdot E_J + T_{BK} \cdot E_K = 2[2] + 3[4] = 16$ concentration units

upon ambient concentrations or deposition rates, then matrices could be used in mathematical algorithms. For the case of absolute constraints on regional pollutant deposition or ambient concentrations, control solutions tend to be very sensitive to errors and uncertainties in the matrix elements. For benefit-cost objectives, sensitivity to matrix errors depend upon the form of the damage function. These procedures presume that linearity between emissions, concentrations and depositions hold over the range of emission changes considered, as discussed in the following subsection.

Tables of normalized transfer coefficients (matrices) for wet and dry sulfur deposition and ambient sulfate concentrations, calculated by eight long range transport models, are presented in the Regional Modeling Subgroup Report (Report No. 2F-M). These matrices show substantial variation in the absolute size of transfer coefficients from one model to another. Hence it is difficult to identify the actual values for the absolute size of source-receptor relationships.

If emission reductions are sought without regard for the absolute deposition or concentration levels, then the relative size of the matrix elements might be used as a partial basis for allocating total emission limits or emission reductions. For example, if there is a desire to reduce deposition levels in receptor region A, then the relative sizes of deposition matrix coefficients, $T_{A1}$, $T_{A2}$, ...., $T_{AN}$, might be used in principle to "weight" the effectiveness of emission reductions among the source regions, 1, 2, ...., N. The relative costs of emission reduction might also vary among the regions and might also be considered.

If emission reduction studies are not based on absolute values of source-receptor relationships, the demands upon the accuracy of the matrix elements are less critical. For example, if prescribed emission reductions were established for large regions, then matrix elements might be used only as qualitative indicators of the relative importance of different source regions to given receptor areas. For the purposes of qualitative assessment, such as the testing of institutional concepts, perhaps only the relative position or rank-orders* of source regions would be of concern. It is shown in the Regional Modeling Subgroup Report that the eight models produce matrices with reasonably consistent rank orderings. Preliminary analysis also indicates that the relative magnitudes of matrix elements correspond reasonably well among the eight models. Hence, the rank ordering or the relative magnitudes of matrix elements may be more reliable properties upon which to base decisions than the absolute magnitudes of the relationships. Table 8.2 gives an example of the model rankings for wet sulfur deposition at the Muskoka and Adirondacks sensitive areas. The eleven aggregated source regions are detailed in Chapter 2, Figure 2.3.

At the Muskoka receptor, all the models (except RCDM-3) indicate that, for 1978, the emissions from region 3 (Ontario) have the greatest impact (ranked 1) at the receptor and that region 10 (Michigan to Iowa) has the second greatest impact (ranked 2). The emissions from region 1 (Maritimes) have the least impact.

Similarly at the Adirondacks site, the models generally agree that region 5 (New York to Maine) has the greatest impact and that region 6 (Pennsylvania, Ohio, West Virginia) and region 3 (Ontario) are equally likely to have the second greatest impact at the site. The emissions from region 4 (Western Provinces) have the least impact.

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* Rank order means simply that the source regions are placed in order according to the value of the matrix elements pertaining to a given receptor. Thus, if the value for source region A exceeds that for B, it is ranked above B irrespective of the absolute size of the element.

## Table 8.2 Model Ranking for Wet Sulfur Deposition

### Muskoka (Ontario, Canada)

| Emission Regions | Model | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | AES | MEP | MOE | ASTRAP | ENAMAP | CAPITA | UMACID | RCDM |
| 1 | 11 | 8 | 10 | 11 | 11 | 11 | 11 | 11 |
| 2 | 6 | 5 | 3 | 10 | 5 | 4 | 8 | 9 |
| 3 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 |
| 4 | 8 | 9 | 7 | 9 | 10 | 10 | 10 | 10 |
| 5 | 5 | 4 | 5 | 6 | 8 | 6 | 5 | 6 |
| 6 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 2 |
| 7 | 7 | 7 | 8 | 5 | 6 | 7 | 6 | 7 |
| 8 | 9 | 10 | 11 | 7 | 7 | 8 | 7 | 5 |
| 9 | 4 | 6 | 6 | 3 | 4 | 5 | 4 | 1 |
| 10 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 4 |
| 11 | 10 | * | 9 | 8 | 9 | 9 | 9 | 8 |

### Adirondacks (New York, United States)

| Emission Regions | Model | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | AES | MEP | MOE | ASTRAP | ENAMAP | CAPITA | UMACID | RCDM |
| 1 | 8 | 6 | 9 | 11 | 11 | 10 | 8 | 11 |
| 2 | 4 | 2 | 3 | 7 | 5 | 5 | 7 | 8 |
| 3 | 2 | 3 | 1 | 2 | 3 | 3 | 3 | 4 |
| 4 | 10 | 10 | 8 | 9 | 10 | 11 | 11 | 10 |
| 5 | 1 | 1 | 2 | 1 | 2 | 1 | 1 | 3 |
| 6 | 3 | 5 | 5 | 3 | 1 | 2 | 2 | 1 |
| 7 | 5 | 4 | 7 | 6 | 4 | 4 | 5 | 6 |
| 8 | 9 | 9 | 11 | 8 | 8 | 8 | 9 | 7 |
| 9 | 7 | 8 | 6 | 5 | 6 | 7 | 4 | 2 |
| 10 | 6 | 7 | 4 | 4 | 7 | 6 | 6 | 5 |
| 11 | 11 | * | 10 | 10 | 9 | 9 | 10 | 9 |

* Western region element missing.

### 8.2.2 Limitations of the Matrix Method

Transfer matrices represent the results of model calculations and generally suffer from any limitations in the model and in the input data used to calculate them. Some additional limitations are inherent in the matrices as a result of definitions and approximations made in their calculation, which include the lumping of emission sources in each source region and the averaging of pollutant values over space and time in the receptor area. These specific matrix limitations are not at issue, but need to be accounted for in any application. For example, the lumping of emission sources means that additional emissions from a new source may not behave like the average value calculated for the source region.

More controversial questions about matrices relate to the interpretation of the significance of matrix elements and to their validity as predictive tools.* Normalized matrix elements explicitly

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*Only total concentration and total wet deposition are measured directly; not the individual contributions $\Delta C_{AJ}$. Information to validate the $\Delta C_{AJ}$ or $T_{AJ}$ values--the "source-receptor" relationships--might be obtained if a time series of values of $C_A$ were available during periods when the emission values $E_J$ vary appreciably (in comparison with the natural meteorological variations). Also, direct evidence for partial contributions might be obtained from tracer studies or methods for identifying the physical-chemical "signature" of pollutants. However, there are few observations available of any of these types with which to validate long range source-receptor relationships.

identify quantitative relationships between source regions and receptor regions and tend to imply a linear relationship between emissions and concentrations or deposition. While these relationships are imbedded in the parent model, if it is one of the linear types used in this work, the source-receptor relationship is not so obvious in aggregate model results. Predictions of absolute values of concentrations and depositions can be compared with observed data, but neither the linearity nor the partial contributions from each source region can be directly verified by comparison with currently available data. In the absence of such direct validation there is disagreement about the degree of confidence that can be placed in the linearity of prediction and in the inferred source-receptor relationships based upon any given level of agreement between model calculations and current observations.

### 8.2.3 Limitations of Work Group 2 Matrices

There are some general conclusions about the limitations of Work Group 2 matrices that can be made on the basis of the structure of the current LRTAP models, the resolution of meteorological input data, the variability of atmospheric processes, and the results of evaluation studies on the models. These are:

(1) that the matrices included in this final report are limited to sulfur compounds only;

(2) that transfer matrices were calculated for two individual months and/or one year of meteorological data and for only nine sensitive receptor areas common to all models. Applications that require a finer spatial resolution, a broader geographic coverage of receptors, or different meteorological conditions will require additional runs of the long range and local/mesoscale range models to estimate detailed impacts;

(3) that random ("stochastic") variations in atmospheric processes occur that are not reflected in model input data and invariably lead to differences between predicted and observed values of pollution. These differences are expected to be reduced when averages over longer periods of time are considered unless longer period trends (for example, droughts) are present;

(4) that greater variability in matrix elements calculated for different time periods (meteorological conditions) tends to occur as averages over shorter time intervals and smaller source and receptor regions are considered. Insufficient calculations have been made to establish the exact level of variability in seasonal and annual averages from year to year or over decades;

(5) that LRTAP models generally are not able to predict short-term conditions (averages over several days and changing frontal meteorology) and small scale variations (less than several hundred kilometers) as well as larger-scale averages, partly due to a lack of spatial detail in the meteorological input data and a lack of inclusion of certain processes. These limitations, in combination with conclusions (2) and (3) above suggest that matrix methods should be limited, at present, to the representation of long-term averages (say one month or more), and larger scale regions (of the order of 500 kilometers or so), as practiced in this report and the Subgroup Report 2F-M;

(6) that matrices, in their current form, do not represent the effects of varying other pollutants (for example, $NO_x$) that might alter the sulfur chemistry; and

(7) that a matrix representation is inherently linear and will not reflect non-linear responses to changing sulfur levels. Hence, using a matrix representation for predicting the consequences of

control strategies could be misleading if non-linear processes are found to be important for long-term averages.*

## 8.3 Use of Transport Models

As discussed above, transfer matrices are not well-suited for certain applications. Matrices are not suitable for assessing the impacts on receptors of changes in emissions at nearby sources, since such sources are not typical of the regional average source distribution. Matrices calculated for one meteorological period may not give a good approximation during another period of interest. For control strategy purposes, the limited number (nine) of receptor points treated in the matrices may not include all of the sensitive areas one wishes to protect. In all these situations, full model runs should be undertaken.

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*The term "non-linearity" may have several connotations. As used here, it refers to (1) the failure of the superposition principle to hold for the emitted pollutant, sulfur dioxide (that is, the concentration produced by a sum of emission values does not equal the sum of the concentrations produced by each emission value alone) and (2) the fact that concentration and deposition may also depend upon the values of emissions or atmospheric concentrations of other contaminants, such as nitrogen oxides and oxidants. (In this case, a matrix representation could still be used but the matrix elements would be functions of the other contaminant levels. We refer to these as "co-pollutant effects").

## 8.4 Summary

In an effort to provide the tools requested by the Terms of Reference for calculating the effects of selective emission reductions, the Regional Modeling Subgroup has evaluated eight models and produced transfer matrices for sulfur compounds. The matrix results are displayed in the Subgroup report (Report No. 2F-M).

The use of linear models has facilitated the construction of these matrices. As used in this application, transfer matrices avoid the questions of both non-linearity of the basic transformation and deposition processes, and co-pollutant effects. Scientists disagree at present about whether linearity is a good approximation even for long term averages. From the principle of conservation of mass, models are expected to be less sensitive to non-linear effects when they are used to predict long term, large scale total deposition (wet plus dry) of total sulfur (sulfur dioxide plus sulfate).

Owing to differences among the models used, there are variations among the absolute magnitudes of the transfer matrix elements produced by the various models. These variations could lead to substantial differences in the implications for emission reductions if applied to objectives expressed in terms of benefit-cost balance or absolute deposition levels. On the other hand, comparison of the models considered in this report indicates that all the models predict generally similar impacts on the receptors in terms of rank order of importance and relative magnitude. The matrices, therefore, are better suited for relative impact comparisons for sulfur oxides than for calculations of absolute concentration or deposition.

# OTHER POLLUTANTS

# 9. OTHER POLLUTANTS

Acid-forming sulfur and nitrogen compounds are not the only substances of environmental concern which are transported over long distances. Three other groups of substances have been identified for review: photochemical oxidants, primarily ozone; organics; and heavy metals. All three can cause environmental problems when transported over regional or hemispherical distances.

## 9.1 Ozone

In recent years there have been numerous studies of the generation, build up and dissipation of ozone concentrations across North America. While older studies emphasized human health effects, more recent ecological studies of the effects of ozone have increased the awareness of agricultural crop damage due to excessive ozone concentrations. Furthermore, ozone is an indicator for a variety of oxidants, many of which participate in the formation of acids from sulfur dioxide and nitrogen oxides (see Chapter 4). Ozone can originate from two different sources: (1) two natural ones, through the stratosphere or photooxidation of biogenic hydrocarbons and (2) an anthropogenic one, namely photochemical oxidation of hydrocarbons in the presence of nitrogen oxides. Meteorology plays a key role in how ozone is distributed, especially in the case of episodes of elevated concentrations.

There have been several studies of these episodes, which may occur when a high pressure system dominates the eastern part of North America during the summer. Under conditions of a stagnating air mass simultaneously with a high sun angle, large amounts of ozone will usually be formed and accumulate. However, the number of regional high ozone episodes can vary widely in frequency from year to year because of different meteorological conditions. In contrast, low ozone values occur on the arrival of cold frontal passages and such concentrations can be considered tropospheric background levels and a basis against which high ozone episodes can be compared.

Monitoring protocol for ozone measurements falls under 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 meteorological equipment into a compatible network, and; (3) a comprehensive quality assurance program involving maintenance of instrument calibration and comprehensive data evaluation. All of the above are considered in detail in MOI Report 2F-I.

## 9.2 Organics

Since World War II, the use, and hence the distribution in the environment of man-made organic compounds has increased dramatically. At present, over 40,000 different chemicals are being used in North America with several hundred new organic substances being produced every year. Most of these chemicals are produced in such small quantities that their effect, when they are released into the atmosphere, would only be on a very local area. However, many of the substances have chemical, biological and physical properties which are environmentally undesirable, for example, persistence, toxicity of trace levels to animals and other biota and teratogenic and carcinogenic effects on man. If released in sufficient quantities, the atmosphere, specifically the lower troposphere, acts as an important reservoir and vehicle for distribution and transport of some of these compounds for thousands of kilometers from their sources. These compounds have been identified in the atmospheric gaseous and particulate phases, and in precipitation. Volatile organic compounds (VOC) along with nitrogen oxides are precursors of ozone and other oxidants (see above and Chapter 4). However, this review is concerned with the potential effects of organics themselves rather than their participation in atmospheric reactions.

Only a limited number of organics were reviewed by the Work Group (MOI Report 2F-I). These included the following:

o Polynuclear Aromatic Hydrocarbons (PAH)

These substances are produced by common combustion sources such as coal, wood or oil burning and are also found in diesel exhausts. Ample evidence exists about the toxicity and the carcinogenic properties of PAH's. The low vapor pressures of most PAH's suggest that these compounds would be found principally in atmospheric aerosols. Increased combustion processes would produce aerosols containing PAH's which could be transported far from their sources (primarily in urban areas).

o Polychlorinated Biphenyls (PCB)

PCB's have been produced mainly for use as dielectric fluids in transformers and capacitors and other products requiring thermal stability. Although production was discontinued in North America during the 1970's, large quantities are still in commerical use. Over 80 million kilograms enter the environment annually. A large volume of evidence exists about the toxic and carcinogenic effects of these compounds.

- Pesticides and Herbicides

Pesticides and herbicides are a chemically diverse group of compounds widely used in agriculture, forestry and other activities which require pest and weed control; thus ensuring their wide distribution. DDT, for example, continues to show up in environmental samples even though is has not been manufactured for many years. The use of pesticides and herbicides is now more carefully controlled but their total use is bound to increase in the future. Atmospheric transport to distant regions is almost certain to occur. There is, therefore, a need to monitor and follow the trends of their atmospheric concentrations.

- Phthalate Esters

Large quantities of phthalate esters are produced in North America 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 poor sampling protocol or laboratory contamination. Because of their volatility, widespread use and potential health problems, some attention must be directed to understanding their distribution in the environment.

The organic compounds discussed above require special sampling and analysis techniques. Detailed information on our present capabilities for collecting and analyzing trace organics and the extent of our knowledge concerning their atmospheric behavior are presented in MOI Report No. 2F-I.

## 9.3 Heavy Metals

In recent years, heavy metals in the environment have been recognized as a significant potential hazard because of their ability to cause a broad spectrum of deleterious human health and ecological effects. Heavy metals which are commonly measured in the environment include antimony (Sb), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), tin (Sn), vanadium (V), and zinc (Zn), but not all of these metals are of equal potential hazard. Such parameters as toxicity, susceptibility to bioaccumulation, widespread commercial use, and likelihood of entry into the environment in harmful quantities vary from metal to metal. Unfortunately at the present time, there is no objective procedure for setting priorities or ranking heavy metals in terms of their harmfulness in the natural environment.

Heavy metals are introduced into the atmosphere by various natural and anthropogenic sources. 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.

Methods for monitoring heavy metals released into the atmosphere can be divided into two broad categories. These are: monitoring of ambient air concentrations and monitoring of deposition. In turn, deposition measurements for airborne heavy metals may be divided into two classes -- wet and dry. Problems in monitoring specific heavy metals both for ambient air concentrations and deposition is outlined in more detail in MOI Report 2F-I.

## Conclusions

The major thrust of this report is acidic deposition and emissions which contribute to such deposition. Oxidants (for which ozone is the principal measured indicator) participate in acid forming atmospheric reactions, and organics are precursors to oxidant formation. But ozone and some organics, can cause adverse effects by themselves, and may be transported along with heavy metals long distances across national and international boundaries. Of the three categories of materials discussed here (ozone, organics and metals), ozone has been the one most studied. The transport and environmental effects of the other two are less clear, but must be carefully monitored and evaluated.

# LOCAL/MESOSCALE CONSIDERATIONS

# 10. LOCAL AND MESOSCALE CONSIDERATIONS

## 10.1 Concentrations and Deposition on a Local Scale

Although the emphasis in the Work Group 2 transboundary pollution studies have been for travel distances of the order of 1000 kilometers or more, the understanding and prediction of atmospheric processes occurring in the local to mesoscale range (up to several hundred kilometers from the source) are also important. There are many instances of transboundary transport of air pollution which occur over local and mesoscale distances, such as those occurring in the Detroit, Michigan - Windsor, Ontario region and in the vicinity of the power plant at Poplar River, Saskatchewan. There are also sensitive areas including publicly owned land at or near the international border which could be adversely affected by local or mesoscale transport. Concentrations and deposition from sources within local and mesoscale distances may augment or even dominate those from long range transport and may be a factor that has to be taken into account if we are to develop accurate regional sulfur and nitrogen budgets. Finally, apart from the aspect of mesoscale transboundary transport, improved knowledge and modeling of mesoscale effects may improve the predictions of the models that are used for long range transboundary transport.

The literature describes many field studies that attempt to evaluate the contribution of sulfur sources to concentrations and depositions within the local and mesoscale. For a more detailed summary of the literature, the reader is referred to the Local/Mesoscale Analysis Subgroup Report 2F-L.

### 10.1.1 Sulfur compounds

There is a wide range of estimates in the literature of the importance of nearby sources to the concentration and deposition of sulfur compounds at a given point. Some studies of both point and urban sources indicate that as little as a few per cent of the sulfur emitted from a source is converted to sulfate and deposited within 50 or 100 kilometers of its source. If this is the case, then most of the emitted sulfur is available for long range transport. Other studies indicate that under certain circumstances most of the emitted sulfur is converted and deposited within 100 kilometers, leaving little pollutant available for long range transport. Some investigators have found that 10 to 20% of deposited sulfur is accounted for by nearby sources, while in other studies the local contribution may account for most of the total deposition.

These apparently contradictory results may be due to several factors including strength, composition and emission height of the local sources, the degree of pollution in the incoming air mass interacting with the local emissions and meteorological factors, not the least of which is whether or not dry and wet deposition is occurring. If precipitation is not occurring, the rate of dry deposition by diffusion to the surface will depend upon the nature and roughness of the surface, the height at which polutants are emitted into the atmosphere, the height to which they are mixed into the atmosphere, and the form (species) of the sulfur. The last point is important because the rate of dry deposition of sulfur dioxide is greater than that for sulfate. The more quickly the sulfur dioxide is converted to sulfate, the lesser is the fraction of emitted sulfur that will be deposited locally in the absence of precipitation. The processes which control the rate of conversion to sulfate have been described in detail in Chapter 4.

When cloud and rain water are present, the rate of conversion and deposition of emitted sulfur dioxide may be much more rapid than under dry conditions and, therefore, the influence of local emissions may be important. The conversion of $SO_2$ to sulfate will depend upon the chemical makeup of the cloud and rain water including the concentration of oxidants and catalysts, and the fraction of time that the polluted air parcel spends in a cloud. The rate of removal of sulfur by precipitation will, in addition, depend upon the frequency and intensity of the precipitation.

Despite the possible variability in the relative influence of local sources, enough evidence now exists of the rapid conversion and deposition of local $SO_2$ emissions to warrant further research and analysis into the important factors governing deposition close to a source. Furthermore, models capable of accounting for local deposition should be applied, tested and further improved.

### 10.1.2 Nitrogen Compounds

Nitrogen oxides are transformed to nitrate more quickly than sulfur dioxide is transformed to sulfate. Furthermore, a large fraction of these nitrogen oxides are emitted close to the ground (from vehicles) greatly enhancing the potential for near-source deposition. One might expect therefore, that the local deposition of nitrogen oxides will be more pronounced than that for sulfur dioxides. However, less information exists about the local deposition of nitrogen compounds than about sulfur although some investigators have estimated that the deposition of nitrate in the vicinity of St. Louis is comparable in magnitude to the emissions from that city.

### 10.1.3 Oxidants

Transboundary flow of oxidants and precursor pollutants has been observed in southwestern Ontario for many years. The high ozone concentrations are believed to be associated with warm humid air moving into the area from the south and southwest directions. There is some evidence that local emissions cause increased concentrations of ozone downwind of the sources. Researchers have reported vegetation damage in the areas north of Lake Erie with high ozone concentrations.

### 10.1.4 Organics

The Joint Air Pollution Study of the St. Clair-Detroit River areas by the International Joint Commission reported benzo(a)pyrene concentrations in samples of suspended particulate matter collected in the Port Huron, Windsor and Detroit areas during 1967 and 1968. The results showed elevated levels of this carcinogen in parts of Windsor and Detroit. The Windsor concentrations were similar to those reported in cities which have steel mills. Since there are no steel mills in Windsor, the suspected cause of the elevated organics concentrations is local transboundary flow from the steel mills in Wayne County, Michigan.

### 10.4.5 Suspended Particulate Matter

Much of Detroit, Michigan and Windsor, Ontario experience unacceptably high concentrations of suspended particulate matter. The International Michigan-Ontario Air Board report for 1980 indicates, that for most of the Detroit-Windsor area, the air quality objectives for particulate matter were exceeded in spite of the fact that there have been significant decreases in annual ambient values from 1971 to 1974 and again in 1980 (from 1975 to 1979, there was no significant decrease in annual values of suspended particulate matter).

The Ontario Ministry of the Environment Annual Reports on Ambient Air Quality in Windsor, Ontario show a high correlation between elevated concentrations of suspended particulate matter and winds from the direction of Wayne County, Michigan. It would appear, therefore, that local and mesoscale transboundary flow of suspended particulate matter occurs from Wayne County to Windsor; 90% of the emissions of particulate matter in that area come from the Wayne County area.

Alkaline particulate material introduced into the atmosphere from wind blown dust and fugitive dust from industrial or mining activities may neutralize acidic particles and may modify the chemical conversion processes even on the local to mesoscale. There is evidence, for example, of emissions of alkaline dust from cement plants in the vicinity of Syracuse, New York raising the pH of precipitation sampled in their vicinity.

### 10.1.6 Fluorides

There has been documented evidence of the transport of fluorides emitted by aluminum smelters located near Massena, New York into the neighbouring area of Cornwall Island, Ontario.

## 10.2 Survey of Local and Mesoscale Models

The Regional Modeling Subgroup Report (2F-M) includes a detailed description of eight long range transport models and their computational results. These models produce transfer matrices for the purpose of determining source-receptor relationships over eastern North America. The long range transport models can be used to indicate the fraction of both wet and dry sulfur deposited on the mesoscale or available for long range transport. The models generally suggest that a larger fraction of the dry deposition occurs within the mesoscale than does wet deposition. The models also indicate substantial, but variable, deposition amounts on both scales. Possible reasons for the variability between these two ranges are: (1) the inadequate spatial resolution to accommodate near-source region contributions to air pollution concentrations; (2) the variations in the distributions of the emissions used in the models; (3) the variations in the vertical resolution and treatment of vertical diffusion among the long range transport models; (4) lack of detailed chemistry in the models especially close to sources; and (5) the variations in the way that the models treat the deposition processes. Therefore, consideration should be given to using local and mesoscale models for estimates at distances smaller than 300 kilometers.

Recent modeling survey papers, which are referenced in the Local/Mesoscale Subgroup Report, indicate that there are many models presently in use for predicting local/mesoscale air pollution concentration distributions.

Included in this chapter is a brief discussion of local and mesoscale models which have been applied to distances as great as 300 kilometers. Since there has been more extensive use and evaluation of models on the local scale (less than 50 kilometers) than on the mesoscale (50 - 300 kilometers), the modeling survey is broken into two parts: local and mesoscale.

### 10.2.1 Local Models (transport of less than 50 kilometers)

The dilution of pollutants emitted from sources and transported on the local scale is strongly dependent upon transport and diffusion processes, and less dependent upon chemical transformation, dry deposition, and wet deposition. Therefore, the majority of the models included in the survey do not include these latter processes as they have until recently been used primarily for assessing ambient concentration rather than deposition.

The local models may be classified into three main categories: 1) analytical; 2) Eulerian; and 3) Lagrangian. Presently, the analytical models are the most commonly used and most widely accepted for regulatory use, although they are the least versatile for incorporating the deposition processes. The Eulerian models are the most versatile but they are more expensive and complicated to use, and have not been applied as extensively on the local scale. Few decision makers are familiar with these models and able to interpret the results effectively. Also, a very small number of evaluation studies have been carried out on these models. Lagrangian models have not been used as extensively as the analytical models but they have been applied more than Eulerian models. These models are rather versatile and can include, with some simplifications, parameterizations of the deposition processes. While more evaluation studies on these models have been conducted than on Eulerian models, the need for more extensive evaluations is apparent.

Application of all three types of models in regions with complex topography can be expected to provide results which have a greater uncertainty than those applied in flat terrain. Research is needed to determine the performance of models which incorporate deposition processes, in various regions (shoreline, plain, mountain valley, etc.).

### 10.2.2 Mesoscale Models (transport of 50 to 300 kilometers)

The survey of dispersion models, applicable for this intermediate range, indicates the availability of more than 50 models. The survey includes the following categories of models: 1) analytical; 2) Eulerian; 3) Lagrangian; and 4) hybrid (a combination of Eulerian and Lagrangian). In addition to the more common attributes of long range transport models, that is, transport and diffusion, physical and chemical transformation, and wet and dry deposition, other features important for intermediate-range transport are considered in the survey. These other significant features include the models capability to: (1) resolve vertical pollutant distributions, (2) accommodate urban emissions, and (3) simulate detailed atmospheric chemistry. A discussion and tabulation of these attributes for the models surveyed is included in the Local/Mesoscale Subgroup Report.

A mesoscale model validation workshop was recently conducted at the Savannah River Laboratory. A report indicated that model predictions were reasonably accurate for annual averages, but that the accuracy decreased with decreasing averaging times. A general conclusion from this workshop was that the overriding meteorological factor in improving computational accuracy was the accurate description of the wind field. The model evaluations were performed using a non-reactive pollutant, $Kr^{85}$. Of course, for reactive pollutants such as sulfur oxides, improvements will have to be made in the chemistry modules.

### 10.3 Recommendations for Future Work

(1) Detailed field studies should be carried out to learn more about the concentration and deposition fields within 100-200 kilometers of a major source of sulfur and nitrogen for an extended period to determine

how much of the emitted sulfur and nitrogen is being deposited locally. Results should be averaged over both extended and shorter periods during specified meteorological conditions. These studies would include the measurement of concentrations in the ambient air and in precipitation, not only of sulfur and nitrogen compounds but if possible other substances which may effect the sulfur and nitrogen chemistry, such as oxidants and catalysts such as trace metals. These measurements should be carried out with sufficient spatial extent and resolution to shed insight into the transformation rates of the various chemical species and their budgets.

(2) A careful examination should be made of the existing data on local and mesoscale deposition that can be found in the literature in order that maximum use be made of them.

(3) Existing, less complex, analytical models may be appropriate for use out to distances of a few kilometers. Existing, more complex, Lagrangian, Eulerian or hybrid models, may also be appropriate for distance scales of the order of a few tens to a few hundred kilometers. The local models need to be improved to better account for chemical transformation and wet and dry deposition processes.

(4) Mesoscale models which are used for large spatial scales with corresponding time scales of the order of a few hours to a few days must include the chemical transformation, wet and dry deposition processes, as well as transport and diffusion processes with suitable vertical resolution.

(5) As indicated in the survey, there are numerous models in all of

the above categories. It is difficult, however, to select a model, or combination of models for use in a particular application. With so many models available, which appear to have been developed on sound theoretical principles, the Work Group recommends that research and development of new models be given a lower priority than evaluating the performance of existing models.

The models which the Work Group feels are most likely to be suitable for application in the local/mesoscale range, which include the important physical and chemical processes and complement the long range transport models, are the hybrid models.

# CONCLUSIONS AND PROPOSALS

# 11. CONCLUSIONS AND PROPOSALS

## 11.1 Introduction

As specified by the U.S./Canada Memorandum of Intent (MOI) of 1980, the major objective of the Atmospheric Sciences and Analysis Work Group (Work Group 2) has been to provide technical advice for the development of a bilateral agreement on transboundary air pollution. Specifically, the Work Group has developed information on the application of current long range transport models and acidic deposition monitoring data for this purpose.

This Final Report is a summary of more detailed technical information provided in four sub-group reports to be published separately. The report discusses these technical matters using terms defined in a glossary.

Acid rain occurs in eastern North America within and downwind of the major source regions of oxides of sulfur and nitrogen. This geographical association between the region of the largest North American emissions of sulfur and nitrogen oxides and the region of the largest wet deposition of sulfur and nitrogen acids constitutes the strongest evidence of an anthropogenic origin for much, if not most, of the acidic deposition in the northeastern U.S. and eastern Canada. Furthermore, there is no doubt that polluted air can readily cross the Canada-United States border in either direction.

The modeling effort by Work Group 2 has tried to quantify the origin of the sulfur falling on various parts of eastern North America. The adequacy of available models to predict the results of alternative emission patterns (i.e., the change in deposition that would result from a change in emissions) is uncertain.

The modeling effort has been directed toward sulfur and its compounds because relatively more information is available about sulfur oxides than for other chemical species. Further Work Group 2 has focused its efforts on emissions and depositions encompassing large time and space scales over eastern North America. With regard to other species, atmospheric models have not yet reached a stage of development suitable for application to formulating, or understanding the impact of, control strategies for reducing the long range transport of nitrogen oxides, ozone, toxic organics and heavy metals. Progress in modeling long range transport has been encouraging, in part due to stimulus from the Memorandum of Intent process, but many significant modeling unknowns persist. Vigorous research to overcome these unknowns continues in both countries.

## 11.2 Conclusions

The main conclusions of the Work Group are summarized below:

### 11.2.1 Observations of Deposition

- Monitoring data in North America show a strong geographical correspondence between a large contiguous region of precipitation having low pH (that is, below 4.5) and the region of the most intense emissions of sulfur and nitrogen oxides. The region with low pH also corresponds closely with the region having the highest concentrations and depositions of sulfates and nitrates in precipitation and in both cases the maxima are over and immediately downwind of the major source regions. Maps of sensitive ecosystems produced by Work Group 1 make it apparent that this region of high deposition covers extensive sensitive areas in both eastern Canada and the eastern United States. There is another extensive region of low pH precipitation which can also be geographically associated with a major source of anthropogenic emissions; namely, the highly populated, industrial region of Europe.

- On a global basis, the presence of occasional, very acidic (low pH) rains in extremely remote areas suggest that there are possible natural and/or very distant anthropogenic sources of sulfur and other compounds that are capable of contributing to the acidity of precipitation. The sources of such substances producing acidity in these remote locations has not yet been determined but may be due to the relative absence of buffering substances (such as calcium) and the presence of organic acids in the precipitation. The role which such natural or very distant anthropogenic sources of acidity play in eastern North America, although likely to be small, remains to be clarified in order to determine what "background" deposition to use in constructing atmospheric models of source-receptor relationships.

o Monitoring data at individual stations have been classified according to the trajectory that the air mass appeared to have taken during the preceding time period. Observations at monitoring sites, such as those in Ontario, New York State, Illinois and Bermuda generally indicate higher sulfate and nitrate concentrations in the air and in precipitation when the air mass has passed over areas of higher emissions. While such back air trajectory analyses reinforce the conclusion that man-made emissions have a major influence on acidic deposition, this method is unable to distinguish between near and more distant sources within the same directional sector and cannot be used to trace an air mass trajectory during periods of weak, variable air flows or over very long distances.

o Although the historical data are of poor quality and limited quantity, one may note that in the eastern U.S.: a) the lack of a noticeable trend in wet sulfate deposition during approximately the past 5 years is consistent with the small changes in sulfur dioxide emissions; and b) an upward trend in the wet nitrate deposition agrees with a similar upward trend in nitrogen oxide emissions.

o Acidic deposition can occur via precipitation (rain, snow, etc.) or through dry deposition involving gaseous or particulate species. Wet deposition measurements are available for a large number of chemical species. Experimental techniques to monitor dry deposition levels are under development and currently available estimates of dry deposition levels have not been verified by direct observations.

### 11.2.2 Mass Budget Studies and Man-Made versus Natural Sources

- Gross budget studies over large regions have examined the major input (including natural) and output quantities of sulfur compounds in the atmosphere. Studies for North America indicate that man-made sulfur oxide emissions exceed natural emissions by a factor of 10 to 20. Results derived from simple climatological analyses indicate that about three to five times more sulfur flows north, from the U.S.A. to Canada, than south. The ratio of the U.S.A. to the Canadian emissions of sulfur is almost six to one.

- Budget studies also suggest that in eastern North America the three removal terms, wet deposition, dry deposition and outflow (into the Atlantic) are roughly equal. Further work is underway to determine the validity of this estimated apportionment.

- Mass budget studies are in progress for nitrogen oxides and other species.

### 11.2.3 Local Versus Long Range Transport

- Deposition values at the more remote pristine locations in eastern Canada and in other remote areas worldwide clearly cannot be attributed to local sources, which are negligible, and demonstrate the reality of a long range transport component.

- While this report concentrates primarily on the long range transport aspects of transboundary pollution, it is recognized that near-source (less than 50 kilometers) and mesoscale (50-300 kilometers) phenomena are important.

- Areas in eastern North America experiencing high wet deposition are generally situated in the vicinity (less than 300 kilometers) of non-negligible sources of emissions, while, at greater distances, lesser wet deposition rates occur over wider areas. In the context of the acid rain issue both scales must be considered.

- The proportion of emitted material deposited in the first 50-100 kilometers is highly variable.

### 11.2.4 Atmospheric Transformations and Depositions of Sulfur Compounds

- Sulfur compounds can be transported and transformed by a variety of chemical and physical processes. As a result of these processes, a number of different sulfur compounds are deposited. Our understanding of these processes varies depending upon the compound under consideration and the manner in which it is deposited.

- The transformation of sulfur dioxide to sulfate aerosol and/or sulfuric acid in the atmosphere is a key aspect of the acid deposition problem.

- Over the shorter time and space scales, all of the important sulfur dioxide chemical conversion processes are non-linear. Current long range transport model studies by the Work Group make linear approximation of these various chemical processes and may be subject to error in the prediction of the depositions of individual sulfur species (e.g., sulfates). Such modeling errors would also apply to predictions of the change in deposition of individual sulfur species that would result from a change in emissions. Because of the lack of scientific information on some of the conversion reactions, an estimate of the magnitude of errors due to non-linear processes is unavailable.

- Applications of present models to the prediction of total sulfur, rather than individual species, deposition may reduce the importance of non-linear chemistry. Likewise, the effects of non-linear processes may diminish as larger space and time scales are used. The magnitude of the reduction in error, if any, resulting from such aggregation is not known at this time.

### 11.2.5 Long Range Transport Models as Assessment Tools

- Concentrations and depositions (both dry and wet) of sulfur compounds are predicted by long range transport models using simplified formulations. These simplifications result from (1) an incomplete understanding of some of the physical and chemical processes; (2) limitations in the data available for model input; (3) the paucity of data for testing deposition simulations and (4) the difference between the model and process scales.

- Using available wet deposition measurements, current models are able to reproduce the correct order of magnitude of the large time and space scale features of measured wet sulfur deposition fields.

- Model evaluation, that is, the statistical comparison between model predictions and observed values, is not yet considered to be complete. For the 1978 data set, most models appear to perform relatively better in predicting the deposition of sulfate in precipitation than in predicting sulfur concentrations in ground level air.

- The eight long range transport models have been used to produce tables (that is, transfer matrices) which relate sulfur emissions from specific regions to the deposition of sulfate in precipitation and ambient sulfur concentrations in specific regions. The transfer matrices of the different models exhibit variations among the magnitudes of the transfer matrix elements. This variability could lead to substantial differences in the selection of optimum emission reduction scenarios depending upon the particular model applied and the level of detail required. The long range transport models examined by the Work Group predict generally similar relative impacts on receptor regions in terms of ranked order of importance. It has not been possible to date to choose a "best model" among the eight or to produce with confidence a "best estimate" single transfer matrix for each variable based upon a valid statistical analysis of all model results.

### 11.2.6 Terms of Reference

With reference to the terms of Reference of the Work Group (Appendix 1):

1. Work Group 2 has identified source regions and their applicable sulfur emissions (supplied by Work Group 3B) and has attempted, through the use of the 8 atmospheric transport models, to relate these regions to loadings in the identified sensitive areas.

2. Work Group 2 has evaluated available field measurements and has employed them to assess model performance. Trends of emissions, concentrations and depositions have also been examined to gain further insights into source-receptor relationships. It is up to others to determine what degree of success the Work Group has achieved.

3. Work Group 2 has provided the kind of "operational tools" required for calculating emission reductions required to achieve concentrations and deposition rates necessary to protect sensitive areas; however, the Work Group has not been able to provide definitive guidance concerning a preferred model or the quantitative degree of confidence that can be placed in any of the individual models.

## 11.3 Proposals for Research, Modeling and Monitoring in the Agreement

### 11.3.1 Introduction

An initial transboundary air pollution agreement between the United States and Canada that reflects our scientific understanding may not be sufficient to resolve completely all aspects of the problem. Therefore, it is important to provide a mechanism whereby new knowledge can be acquired and assimilated by those responsible for managing the environmental protection programs of the two countries. Additionally, recognizing our limitations to predict with certainty the full consequences of controlling emissions, it is important to determine, by observations of concentrations and deposition rates, the effectiveness of the initial agreement in resolving transboundary impact issues.

In making the following proposals the Work Group has taken into consideration current U.S. and Canadian planning information as embodied in the U.S. National Acid Precipitation Assessment Plan and the Canadian LRTAP Plan. The Work Group supports the initial steps already being taken to coordinate further planning and implementation of joint programs. The Work Group recommends that a specific bilateral group be formed as soon as possible to assist in the coordinated implementation of air and precipitation chemistry research and related monitoring and modeling activities.

### 11.3.2 Proposals

The Work Group recommends that the following items be considered for inclusion in an Agreement:

1. The United States and Canada agree to give high priority to research and widespread routine monitoring of dry deposition. We also agree to include the known temporal and spatial details of dry deposition velocity in the current LRT Models.

2. Canada and the United States agree to develop methods for monitoring, and to begin routine measurements of, the important chemical species and other pollutants (such as ozone, toxic organics and heavy metals) to elucidate the important gas and aqueous-phase atmospheric pathways.

3. The United States and Canada agree to put more research effort into modeling and monitoring acid deposition occurrences during episodes, including the associated meteorological phenomena.

4. Canada and the United States agree to include atmospheric chemistry modules in current LRT models so that the issues of non-linearity and atmospheric saturation can be studied.

5. The United States and Canada make a strong commitment to continue routine ground-based monitoring networks for air and precipitation chemistry, and to establish a joint monitoring, quality control, archiving and publishing protocol.

6. Canada and the United States agree to joint studies for the quantification of uncertainties in LRT models and their input data.

7. The United States and Canada give high priority to the prediction of meteorological conditions associated with transboundary transport.

8. Canada and the United States agree that LRT models should be developed jointly for nitrogen oxides, oxidants, heavy metals and toxic organics.

9. The United States and Canada agree to give high priority to the evaluation and development of hybrid local/mesoscale models which will provide more detailed and reliable estimates of deposition in the near source zone.

10. Canada and the United States agree to jointly conduct studies, through the use of tracers, that increase the understanding of source-receptor relationship.

11. The United States and Canada agree to design appropriate monitoring strategies to assess the effectiveness of any controls which might result from an agreement.

12. Canada and the United States agree to set up a mechanism for the continued development, application and evaluation of models for control strategy development.

13. The United States and Canada agree to provide a joint mechanism for evaluating, giving priority and communicating to the appropriate agencies, the many specific recommendations to be found in this and the subgroup reports.

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Lou Shenfeld
Eva C. Voldner

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Washington and carried a particularly heavy workload with great patience and perseverence. Nels Laulainen of the Environmental Protection Agency took on this responsibility as U.S. Coordinator in Phase 3. Doug Whelpdale of Environment Canada was the Canadian Coordinator for Phase 1 ensuring that the work continued and built upon previous work of the Bilateral Research Consultation Committee. Jim Young of Environment Canada was the Canadian Coordinator for Phases 2 and 3 of the Work Group activity and provided a highly-effective continuity to Work Group logistics and working arrangements as well as assuming the responsibility for the completion of this final report.

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This report was prepared by the members of Work Group 2 listed below. The first two authors listed carried the primary responsibility for the chapters. Reviewers provided comments on final draft sections. In all cases U.S. and Canadian Work Group members worked closely on the preparation of individual chapters and on the final integration of the complete report. Drs. James W.S. Young and Nels Laulainen were responsible for co-ordinating the preparation of this report.

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| 9. | Other Pollutants | 1. J. Miller<br>2. P.W. Summers | 1. M. Barad<br>2. R.W. Shaw<br>3. G. Van Volkenburgh |
| 10. | Local/Mesoscale Considerations | 1. R.W. Shaw<br>2. D. Henderson | 1. L. Shenfeld<br>2. N. Laulainen |
| 11. | Conclusions and Proposals | 1. L. Machta<br>2. H.L. Ferguson | 1. G. Van Volkenburgh<br>2. K. Demerjian<br>3. J.W.S. Young |

# APPENDIX 1

## Terms of Reference
## for
## Work Group 2
## of the
## Memorandum of Intent

# APPENDIX 1

## A1.1 Terms of Reference for Work Group 2 of the MOI

The Group will provide information based on cooperative atmospheric modeling activities leading to an understanding of the transport of air pollutants between source regions and sensitive areas, and prepare proposals for the "Research, Modeling and Monitoring" element of an agreement. As a first priority the Group will by October 1, 1980 provide initial guidance on suitable atmospheric transport models to be used in preliminary assessment activities.

In carrying out its work, the Group will:

- identify source regions and applicable emission data bases;
- evaluate and select atmospheric transport models and data bases to be used;
- relate emissions from the source regions to loadings in each identified sensitive area;
- calculate emission reductions required from source regions to achieve proposed reductions in air pollutant concentration and deposition rates which would be necessary in order to protect sensitive areas;
- evaluate and employ available field measurements, monitoring data and other information;
- assess historic trends of emissions, ambient concentrations and atmospheric deposition to gain further insights into source-receptor relationships for air quality, including deposition; and
- prepare proposals for the "Research, Modeling and Monitoring" elements of an agreement.

## A1.2 Additional Guidance from Work Group 3A

Each Work Group will be responsible individually for the following:

a. Developing data needs and analysis methods for their Work Group and identifying required inputs from other Work Groups.

b. The technical review (including peer review as necessary) of their work products.

c. Coordination with their counterparts from the other country in conducting full cooperative analyses in order to fulfill the Terms of Reference.

d. Being prepared to draft language for that portion of the agreement that pertains to their tasks as directed by the Coordinating Committee.

# APPENDIX 2

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# APPENDIX 3

## Glossary of Terms

## GLOSSARY OF TERMS

Absorption: The taking up or assimilation of one substance by another.

Accumulation mode: Particles formed principally by coagulation or growth through vapor condensation of short-lived particles in the 0.1 to 1.0 micrometer diameter size range.

Acid (or acidic) compounds: One of a class of substances that neutralize and are neutralized by alkalis and are compounds made up of hydrogen and another element or elements. A chemical compound which upon dissolution in water can add hydrogen ions to the solution.

Acid Deposition: Collectively, the processes by which acidic and acidifying materials are removed from the atmosphere and deposited at the surface of the earth. Also, the amount of material so deposited. (Units: $ML^{-2}T^{-1}$.)

Acid Precipitation: Usually refers to all types of precipitation with a pH of less than 5.6; a more precise term than acid rain.

Acid Rain: A popular term used to describe precipitation that is more acidic than "clean" rain.

Acidification: The process of increasing the acid content of a system.

Acidity: The quantity of hydrogen ions in solution.

Adsorption: Solid, liquid, or gas molecules, atoms, or ions retained on the surface of a solid or liquid, as opposed to absorption, the penetration of a substance into the bulk of the solid or liquid.

Aerosol: A suspension of liquid or solid particles in a gas.

Aitken nuclei: Those particles and ions measured by means of an instrument in which water vapor is made to condense on particles by supersaturating the vapor; the term "condensation nuclei" is often used synonymously.

Air mass: A widespread body of air, the properties of which can be identified as (a) having been established while that air was situated over a particular region of the earth's surface and (b) undergoing specific modifications while in transit away from the source region. An air mass is often defined as a widespread body of air that is approximately homogeneous in its horizontal extent, particularly with reference to temperature and moisture distribution; in addition, the vertical temperature and moisture variations are approximately the same over its horizontal extent.

Alkaline: The opposite of acidic. An alkaline compound can upon dissolution in water decrease the amount of hydrogen ions ($H^+$). This process is due to the fact that alkaline compounds can add hydroxy ions ($OH^-$), which will neutralize the hydrogen ions.

Alkalinity: The quantity of hydroxide ions in solution.

Ammonia ($NH_3$): Colorless, toxic, corrosive, alkaline gas with a very pungent odor, highly soluble in water, in which it forms the ammonium ion ($NH_4^+$); also soluble in alcohol, chloroform and ether. It is one of the primary substances that neutralizes acid particles and droplets.

Ammonium ion: See ammonia.

Anion: A negatively charged ion.

Anthropogenic: Produced by man's activity.

Anthropogenic emissions: Emissions resulting from the impact of human activities on the natural world.

Atmospheric aerosols: A suspension in the atmosphere of microscopic particles of a liquid or solid.

Atmospheric loading: The concentration or mass of a substance in a given part of the atmosphere.

Background: The atmospheric loading that is the result of natural emissions or pollutants transported into an area from sources far upwind.

Below-cloud scavenging: Collectively, the mechanisms by which atmospheric constituents are incorporated into falling hydrometeors.

Benzene: Clear, colorless, highly flammable liquid, highly poisonous and carcinogenic, boiling point 80°C. Used widely as organic solvent in industrial processes; scarcely mixes with water, but mixes with most organic solvents, as well as oils.

B(a)P [benzo-(a)-pyrene]: Yellowish crystalline material, suspected to be highly carcinogenic. Melting point 179°C. Occurs mainly in cool tar. Soluble in benzene, toluene, xylene and sparingly in alcohol.

Biogenic: Produced by actions of living organisms.

Bioindicator: Any species of plant or animal that is particularly sensitive to a specific pollutant.

Biological uptake: The assimilation by living species (usually plants) of atmospheric constituents.

Biosphere: The portion of the earth in which living systems are encountered.

Biota: The living animals, plants, and microorganisms of the environment.

Brownian diffusion: The diffusion of the dispersed particles in a colloidal system (aerosol), resulting from random collisions between the molecules of the dispersing medium (air) and the particles of the dispersed phase.

Budget: A complete balance of amounts and flows of a substance (e.g. sulfur) or property (e.g. heat flux) within a set of specified boundaries.

Bulk Deposition: The term applied to atmospheric deposition collected in a collector which is open at all times. Bulk deposition consists of wet deposition, plus an unknown fraction of the dry particulate deposition, plus an unknown and probably very small fraction of the dry gaseous deposition.

Carcinogenic: A producer of cancer.

Carcinogenesis: The production of cancer.

Cation: A positively charged ion.

Cloud: A system of particles, such as water droplets, having a definite form.

Cloud condensation nucleus: (see condensation nucleus).

Cloud nucleus: (see condensation nucleus).

C(0): Elemental carbon in the form of soot (see Chapter 4).

Coefficient: A number placed before and multiplying another quantity known or unknown.

Co-pollutant: (see text page 8-14).

Coarse particles: Airborne particles larger than 2 to 3 micrometers (μm) in diameter.

Column mass: The mass of a specified atmosphere constituent in a column of unit cross-section extending vertically through the atmosphere.

Condensation nucleus: A particle, either liquid or solid, upon which condensation of water vapour begins in the atmosphere.

Convective storm: A storm which owes its vertical development, and possibly its origin, to circulating warm air. A precipitation event usually characterized by showers, sometimes violent (thunderstorms) and scattered precipitation cells and usually associated with cold fronts or warm unstable air masses.

Deposition velocity: A parameter which provides a measure of the rate of deposition of a substance to the earth's surface, defined as the ratio of flux to the surface to near-surface concentration of the substance (Units: $LT^{-1}$).

Dichotomous sampler: A device used to separate and collect fine and coarse particles.

Dissolution: The process of dissolving.

Dry Deposition: Collectively, the processes, excluding precipitation processes, by which materials are removed from the atmosphere and deposited at the surface of the earth. Processes include sedimentation of large particles, the turbulent transfer to the surface of small particles and gases, followed, respectively, by impaction and sorption or reaction. Also, the amount of material so deposited. (Units: $ML^{-2}T^{-1}$.)

Dust: Solid materials suspended in the atmosphere in the form of small, often irregular particles many of which are microscopic in size.

Ecosystem: A functional unit of the environment that includes all organisms and physical features within a given area. Derived from ecological system.

Aquatic --- An ecosystem functioning in a marine environment.

Terrestrial --- An ecosystem functioning on the surface of the earth.

Ensemble: Things viewed as a whole or all parts considered as a whole.

Ensemble Mean: The average over a number of individual events (e.g. model runs) in which only one or a few adjustable parameters are allowed to change.

Episodic: Events or phenomena which occur periodically or at infrequent intervals such as during precipitation events; intermittent; occurring in episodes.

Eulerian Model: A mathematical model in which computations are made successively at fixed points in space (as opposed to Lagrangian models where computations are made following an air parcel). Computation points are usually arranged in a fixed grid, and the model is also known as a grid model.

Fe(III): Ferric ion, the triply positively charged ionic form of iron ($Fe^{3+}$).

Fine particles: Airborne particles smaller than 2 to 3 micrometers in diameter.

First order: A kinetic process (e.g. chemical reaction) in which the rate of change of a species is linearly related to its concentration or content.

Fluorides: A binary compound of fluorine, normally in the form of a fluoride salt. The positively charged ion is then a metal ion, while the negatively charged ion is the fluoride ion ($F^-$).

Flux: A physical quantity, the amount (mass) of material passing through a unit area in a unit of time. (Units: $ML^{-2}T^{-1}$.)

Fogs: Suspension of liquid droplets formed by condensation of vapor or atomization; the concentration of particles is sufficiently high to obscure visibility.

Fugitive emissions: Air pollutants arising from human activities, such as roadway and industrial dust, that do not emanate from a particular point, such as an exhaust pipe or stack, and are not readily amenable to control.

Geostrophic wind: That horizontal wind velocity for which the coriolis acceleration exactly balances the horizontal pressure force; the wind that blows parallel to weather map isobars and whose speed is related to the isobaric spacing.

Grid (gridded): A frame of spaced parallel lines; system of numbered squares printed on a map and forming the basis of map references (used as a method of quantifying the spatial distribution of some element or parameter.

$H^+$: See hydrogen ion.

Heavy metals: Metallic elements with high atomic weights, generally toxic in low concentrations to plant and animal life. Such metals are often residual in the environment and exhibit biological accummulation. Examples include mercury, chromium, cadmium, arsenic and lead.

High volume (hi-vol) sampler: A high flow-rate device used to collect particles from the atmosphere.

$HNO_2$: Nitrous acid. A weak acid, rather unstable in solution. In the atmosphere present in low concentrations as a colorless gas, which rapidly is decomposed in sunlight, giving rise to the formation of nitric oxide (NO) and a hydroxyl radical (HO).

HO: a) HO, the hydroxyl radical. An ubiquitous species, present in low levels in the atmosphere, where it is formed through photochemical reactions (due to sunlight), ozone ($O_3$) or nitrous acid ($HNO_2$). The hydroxyl radical is extremely reactive, being the primary agent in the gas phase oxidation, of such species as $SO_2$ and $NO_2$, leading to the formation of $H_2SO_4$ and $HNO_3$ respectively.

b) $HO^-$, the hydroxy ion (see $OH^-$).

$H_2O_2$: Hydrogen peroxide, colorless, rather unstable liquid, melting point 1.7°C, boiling point 152°C. Miscible with water, soluble in ether. Caustic to the skin. May decompose violently in the presence of impurities. In the atmosphere gaseous hydrogen perioxide is formed in low levels as a result of photochemically initiated reactions between oxides of nitrogen and reactive hydrocarbons. The $H_2O_2$, thus formed is believed to be the main oxidizing species of $SO_2$ to form $H_2SO_4$, once $H_2O_2$ and $SO_2$ are dissolved in cloud water.

Homogeneity: Turbulent flow field is homogeneous when flow characteristics remain unchanged to a linear translation of the coordinate axes.

$H_2SO_4$: Sulfuric acid, oil of vitriol. Clear, colorless, odorless, oily liquid, very corrosive, boiling point 200°C. Miscible with water and alcohol with the generation of much heat and with contraction in volume. Used for the manufacture of fertilizers, explosives, dye stuffs, other acids, glue, purification of petroleum and pickling of metal.

Hydrogen Ion: $H^+$ the positive ion of acids, consisting of a hydrogen atom whose electron has been transferred to the anion of the acid. The concentration of hydrogen ions in a solution determines the acidity.

Hydrometeor: Any product of condensation or sublimation of atmospheric water vapor, whether formed in the free atmosphere or at the earth's surface; also, any water particles blown into the air by the wind from the earth's surface.

Hydroxyl Radical: See HO.

Impaction: The process of an aerosol particle colliding with a falling hydrometeor or any other obstacle.

In-cloud Scavenging: Collectively, the mechanisms by which atmospheric constituents are incorporated into cloud elements.

Individual Realization: The result from a single model run with a given set of input parameters.

Input Fields: Ordered sets of data which are used to initiate computer model runs.

Inventory: A listing of emission source strengths of a particular pollutant for a specified time period. Inventories and parameters used in models are normally organized on a point-source basis, an area-source basis, or a combination of the two. Area sources may be represented on a grid, urban-area, county, state, province, or national basis.

Ion: One of the electrically charged particles into which the atoms or molecules of certain chemicals are dissociated by solution in water.

Isopleth: (1) A line of equal or constant value of a given quantity with respect to either space or time. Also known as an isogram; (2) A line drawn through points on a graph at which a given quantity has the same numerical value as a function of the two coordinate variables.

Lagrangian Model: A mathematical model in which computations are made successively for the same air parcel as it moves along a trajectory. Because this type of model is based on following an air parcel, it is also known as a trajectory model.

Laminar Flow: A flow in which the fluid moves smoothly in streamlines in parallel layers or sheets; a non-turbulent flow.

Linear Model: A model where all the interrelationships among the quantities involved are expressed by linear equations which may be algebraic, differential, or integral.

Loading (atmospheric): See atmospheric loading.

Local: An arbitrary length scale to describe events in the immediate locality of a source usually of the order of 0-100 kilometers.

LRT: Long Range Transport (see LRTAP).

LRTAP: The Long Range Transport of Air Pollutants refers to the processes, collectively, by which pollutants are transported, transformed and deposited, on a regional scale (of the order of hundreds to thousands of kilometers).

Mesoscale: An arbitrary length scale between the local scale and the synoptic scale of the order of 100-500 kilometers.

μm: Micrometer ($10^{-6}$ meters).

mb (Millibar) Level: A surface of constant pressure in the atmosphere, identified by the pressure expressed in millibars. (Common pressure levels used in air quality modeling are 925 and 850 mb levels.)

Mixing Height: The height above the earth's surface of a boundary layer inversion which is usually the upper limit of turbulent mixing activity, and which inhibits upward flux of pollutant.

Mn(II): Manganese ion, the doubly positively charged ionic form of manganese ($Mn^{++}$).

Model: A quantitative simulation of the behaviour of a portion of any system.

Model Evaluation: A procedure by which the validity and sensitivity of a model is assessed. Usually the validity is ascertained by comparing model outputs with measurements, and the sensitivity assessed through a series of model runs in which input parameter values are altered in sequence, and the results intercompared.

Model Intercomparison: A procedure of comparing the results of several models which have been run using the same data bases and with (usually) specified values of model parameters.

Model Resolution: The ability of a model to distinguish (utilize) small spatial or temporal changes in input variables.

Model Sensitivity: A model characteristic which is described by the response of an output parameter to a unit change in an input variable or a model parameter.

Molecular Diffusion: In meteorology, the exchange of fluid parcels (and hence the transport of conservative properties) between regions in space, because of the apparently random motions on a molecular scale.

Monte Carlo Technique: A technique which obtains probabilistic type approximations to a solution of a problem by using statistical sampling methods.

N: Elemental nitrogen; nitrogen molecule.

$NH_3$: See ammonia.

$NH_4^+$: See ammonium ion.

Nitric Acid ($HNO_3$): Colorless liquid, forming in moist air, characteristic choking odor. In the presence of traces of oxides it attacks virtually all base metals (except Al and Cr). Boiling point 83°C. Miscible with water, reacts violently with alcohol, turpentine, charcoal and organic refuse. Used for the manufacture of nitrates and nitro compounds for fertilizers, dye intermediates, explosives, and many organic chemicals.

Nitric Oxide (NO): Colorless gas, rapidly forms $NO_2$ when in contact with air at high concentration, which is highly poisonous (see $NO_2$). Boiling point -152°C. Used in the manufacture of nitric acid, bleaching of rayon, and as a stabilizer for propylene, methyl ether, etc.

Nitrogen Dioxide ($NO_2$): Reddish-brown gas, with irritating odor. Deadly poison. Actually at high concentration in equilibrium with its colorless dimer $N_2O_4$ (nitrogen tetroxide) and liquid below 21.3°C. Used as intermediate in nitric and sulfuric acid production.

$HNO_3$: See nitric acid.

NO: See nitric oxide.

$NO_2$: See nitrogen dioxide.

$NO_3^-$: See nitrate ion.

Non-Linear Model: A model in which processes are not simulated by first-order relationships.

Nucleation: In meteorology, the initiation of either of the phase changes from water vapor to liquid water, or from liquid water to ice.

$OH^-$: The hydroxyl ion; the negative ion of bases. The concentration of hydroxyl ions in solution determines the alkalinity.

Organics: This term is usually used to denote the grand total of all chemical species that contain carbon atoms in their chemical formula.

Oxidant: An oxidizing species. An oxidizing chemical provides an oxygen atom upon reacting with another chemical.

Oxidation (various types): A chemical reaction which increases the oxygen content of a compound or in which a compound or radical loses electrons, that is in which the positive valence is increased.

Oxides of Nitrogen: This term usually denotes the sum of nitric oxide (NO) and nitrogen dioxide ($NO_2$). Other forms are nitrate ($NO_3^-$), nitrous oxide ($N_2O$), and dinitrogen pentoxide ($N_2O_5$).

Ozone: Bluish, explosive gas, boiling point -112°C. Pleasant, characteristic odor at concentration of less than 2 ppm, irritating and injurious at higher concentration. Unstable, rapidly photolyzed in sunlight, strong oxidant. Used as disinfectant for air and water, for bleaching of waxes, textiles, oils and organic synthesis. It is an important component of atmospheric chemical reactions.

PAN: see peroxyacetal nitrate.

Parameterization: The representation of a physical, chemical or other process by a convenient mathematical expression containing quantities (parameters) for which measurements or estimates are usually available.

Particle: Any object, solid or liquid, having definite physical boundaries in all directions; in air pollution, practical interest is concentrated on particles less than 1 millimeter in diameter.

Particle size distribution: A frequency distribution of particle sizes (radii or diameters).

Particulate matter: Matter in the form of small airborne liquid or solid particles.

Pathway: Conceptually, a route or series of processes by which atmospheric constituents proceed from emission source to sink.

Peroxyacetyl Nitrate: A family of unstable, highly oxidized organic nitrogen compounds that are formed in polluted air by the photochemical action of sunlight on hydrocarbons and nitrogen oxides. They are extremely toxic to vegetation and are powerful eye irritants.

pH: A quantity to describe the acidity of a solution, pH is defined as the negative logarithm (base 10) of the $H^+$ concentration.

$$pH = -\log [H^+]$$

Phoretic effects: Molecular scale processes in which a gradient of some scalar property causes motion of a particle.

Photochemical reaction: A chemical reaction that takes place as the result of the absorption of light by the reactant(s).

Photochemistry: The study of the effects of light on chemical reactions.

Photooxidation: An oxidation reaction that occurs after one of the reactants has been activated by the absorption of light.

Physical damage function: The mathematical expression linking exposure to damage, expressed in terms appropriate to the interaction of the pollutant and material.

Planetary boundary layer: First layer of the atmosphere extending up to several kilometers above the earth's surface. Above this layer lies the free atmosphere.

Precipitation element: A falling liquid or solid water particle for example, raindrop, snowflake, hail stone, etc.

Precipitation regime: Precipitation of a certain relatively uniform type such as steady precipitation along a front or showery precipitation in the summer.

Precursor: In atmospheric chemistry, a species which is the forerunner of another in a chemical transformation.

Primary particles (or primary aerosols): Dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere.

Radicals (free): Chemical species that are characterized by an excess electron, normally therefore highly unstable and reactive.

Reactive hydrocarbons: Usually used to denote all hydrocarbons in the atmosphere that play a role in the $NO_x$ - oxidant chemistry. Therefore, almost any hydrocarbon except methane.

Receptor: An organism, ecosystem or object which is the direct or indirect recipient of atmospheric deposition.

Receptor Sensitivity: The degree to which a receptor (or receptors) exhibit damage in response to a (pollution-imposed) stress.

Removal Processes: Collectively, those mechanisms by which atmospheric constituents are removed from the atmosphere.

Removal Rate: The rate at which species are removed from the atmosphere.

Residence Time: A term used to characterize the length of time that a substance remains in a particular environmental reservoir.

Resolution: See model resolution.

RH (Relative Humidity): The dimensionless ratio of the actual vapor pressure of water in the air to the saturation vapor pressure at the current temperature of the air.

S: Sulfur.

Saturation: A moist air sample is said to be saturated, with respect to water or to ice, if it can coexist in neutral equilibrium with a plane surface of pure condensed phase, water or ice, at the same temperature and pressure as the sample.

Scale: The magnitude of the time period or geographical area of interest.

Sample (sampling): A specimen.

Scavenging: The processes by which materials are incorporated into precipitation elements and (usually) brought to the earth's surface.

Scavenging Ratio: Ratio of the concentration of a species in precipitation to its concentration in air.

Scenario: In the modeling context, a set of specified conditions (usually an emission inventory) for input to a model which reflects some anticipated future situation (e.g., energy use).

Secondary particles (or secondary aerosols): Dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases.

Sedimentation: The deposition of atmospheric constituents (coarse particles) by the force of gravity.

Sensitive Area: A geographical area in which a receptor (or receptors) can exhibit damage in response to a (pollution-imposed) stress.

Simulate: Pretend to have the same attributes as something else.

Simulation: The process of simulating.

$SO_2$: See sulfur dioxide.

$SO_4^{2-}$: See sulfate ion.

Source-Receptor Relationship: An expression of how a pollution-source area and a receptor region are quantitatively linked.

Spatial Resolution: The minimum distance in space over which meaningful differences in results can be determined (using a particular model). For example, a model based on a 381-km grid will provide no significantly different information for two receptor points separated by less than approximately 381 kilometers.

Stability: A measure of the ability of a system to resist change or to remain in a given state.

Stable: Something not easily changed or destroyed. In the atmosphere, conditions that suppress turbulence.

Stationarity: A turbulent flow field is stationary when the flow characteristics remain constant in time.

Statistical Model: A mathematical model which uses statistical values or parameters as inputs for the computations.

Stochastic: In statistical analysis, a synonym for random.

Stratosphere: The portion of the atmosphere between the troposphere and a height of about 50 kilometers above the earth's surface.

Sulfate: (1) A compound containing the [$SO_4^{2-}$] group, as in sodium sulfate ($Na_2SO_4$); (2) A salt of sulfuric acid.

Sulfate ion ($SO_4^{2-}$): The doubly negative ion of sulfuric acid (see $H_2SO_4$).

Sulfur Dioxide ($SO_2$): A toxic, irritating, colorless gas; soluble in water, alcohol, and ether; boils at -10°C; used as a chemical intermediate in paper pulping, a solvent, a disinfectant, and a preservative; emitted by the combustion of sulfur-bearing fuels. Also known as sulfurous acid anhydride. In the atmosphere it is one of the major acidifying agents.

Sulfur oxides: Oxides of sulfur, such as sulfur dioxide ($SO_2$) and sulfur trioxide ($SO_3$).

Surface element: A physical feature of a surface.

Surface resistance: The resistance to the uptake of atmospheric constituents exhibited by a surface.

Surrogate: The term applied to a parameter which is used to represent another. For example, modeling hydrogen ion behavior in the atmosphere is difficult, so that sulfate ion is often used as a substitute.

Susceptibility: A receptor or receptor area is said to be susceptible if it is both sensitive and receiving a pollutant loading or stress of sufficient magnitude.

Synoptic Scale: In meteorological terms, the scale of motion of the order of 500-5000 kilometers (continental scale).

Temporal Resolution: The minimum time during which meaningful differences in results can be determined (using a particular model). For example, models using upper air data which are only available every six hours are limited in their temporal resolution to about 6 hours.

Teratogenic: Compounds which can produce birth defects in lower forms of life.

Thermal reaction (chemical): A thermal reaction between chemical species occurs due to the internal energy of the reacting species (vibrational, translational, etc.). The reaction occurs without the need for an external source of energy (e.g., light) and the efficiency is usually a function of the temperature.

Time-step: The interval of time at which computations are made in a computer model.

Trajectory: The path or track of an air parcel through the atmosphere. It can be calculated from observed or gridded wind data either forward or backward from a point.

Transfer Matrix: A series of numbers relating the deposition or concentration of a pollutant in one region to the emissions of the pollutant or its precursors from another region.

Transformation (chemical): The processes by which chemical species are converted into other chemical species (in the atmosphere).

Trend: Have a specified general direction in space or time.

Troposphere: The portion of the atmosphere from the earth's surface to the tropopause; that is, the lowest 8 to 16 kilometers of the atmosphere.

Turbulent Diffusion: The spread or dispersion of a conservative property by eddies in a turbulent flow.

Turbulent Mixing: The exchange of air parcels in different regions of the atmosphere as a result of turbulent air motions.

Validation: The process of comparing results of a computer model with observations.

Vapor Pressure: The pressure exerted by molecules of a given vapor.

Variability: Changes or oscillations of a quantity in space or time.

Variance: A measure of variability. It is denoted by $\sigma^2$ and defined as the mean-square deviation from the mean, that is, the mean of the squares of the differences between individual values of x and the mean value $\bar{x}$.

VOC: Volatile organic compounds. Used usually interchangeably with "reactive hydrocarbon".

Wet Deposition: Collectively, the processes by which materials are removed from the atmosphere and deposited at the surface of the earth by precipitation elements. The processes include in-cloud and below-cloud scavenging of both gaseous and particulate materials. Also, the amount of material so deposited. (Units: $ML^{-2}T^{-1}$.)

# APPENDIX 4

## List of Acronyms

# LIST OF ACRONYMS

| | | |
|---|---|---|
| AES (Model) | - | Atmospheric Environment Service Long Range Transport Model |
| ASTRAP (Model) | - | Advanced Statistical Trajectory Regional Air Pollution Model |
| CAD | - | Critical Assessment Document |
| CAPITA (Model) | - | Center for Air Pollution Impact and Trends Analysis Monte Carlo Model |
| ENAMAP-1 (Model) | - | Eastern North American Model of Air Pollution |
| EPA | - | Environmental Protection Agency |
| LRT | - | Long Range Transport |
| LRTAP | - | Long Range Transport of Air Pollutants |
| MEP (Model) | - | Meteorological and Environmental Planning Limited Transport of Regional Anthropogenic Nitrogen and Sulfur (TRANS) Model |
| MOI | - | Memorandum of Intent |
| $NO_x$ | - | oxides of nitrogen |

MOE (Model) - Ontario Ministry of Environment Long Range Transport Model

ppb - parts per billion

ppm - parts per million

RCDM (Model) - University of Illinois Regional Climatological Dispersion Model

$SO_2$ - sulfur dioxide

$SO_4^{2-}$ - sulfate ion

UMACID (Model) - University of Michigan Atmospheric Contributions to Interregional Deposition Model

VOC - volatile organic compounds