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# Florida Acid Deposition Study

## FINAL REPORT: A Synthesis of the Florida Acid Deposition Study

FLORIDA ELECTRIC POWER
COORDINATING GROUP, INC.
402 Reo Street, Suite 214
Tampa, Florida 33609

CONDUCTED BY:
ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.

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Final Report-Synthesis of the Study

**ABSTRACT:**

In 1980, the Florida Electric Power Coordinating Group, Inc. (FCG) approved the Florida Acid Deposition Study, with the overall objective of assessing and/or developing information on the magnitude, variability, sources, effects, and control options of acidic deposition in Florida.

The study was implemented in four major phases, each phase investigating three major areas of research: acid deposition monitoring, source attribution, and ecological effects.

In this report, the information developed in all phases of the Study is analyzed within and across the three research areas to provide answers to key study questions.

Acid Deposition Monitoring: To provide precipitation and air chemistry data for the source attribution and ecological effects research areas.

Source Attribution: To assess the contribution of the Florida electric utilities to current levels of acidity within Florida and in surrounding states using long-range transport (LRT) and mass-balance models.

Ecological Effects: To assess the response and potential sensitivity of aquatic and terrestrial resources within Florida to acid deposition and the potential for effects on man-made material. A series of literature, process-oriented, direct-response experimental, and modeling studies was performed from January, 1981 through June, 1985.

Recommendations for further research are indicated.

# Florida Acid Deposition Study

## FINAL REPORT:
## A Synthesis of the Florida Acid Deposition Study

FLORIDA ELECTRIC POWER
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March 1986

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# FCG PERSPECTIVE

The following represents the perspective of the Florida Electric Power Coordinating Group, Inc. (FCG) regarding the study and this Final Report: A Synthesis of the Florida Acid Deposition Study.

## PROJECT BACKGROUND AND OBJECTIVES

In the early 1970s acid rain began to be recognized as an environmental problem by scientists and became an issue of international significance in Europe. By the late 1970s and early 1980s, the issue had become one of national significance in the United States. Claims of damages throughout the northeastern United States from acid rain were being made that cited adverse effects on everything from lakes and fish to human health. Sulfur dioxide ($SO_2$) emissions from the Ohio River Valley states and some other states were being pointed to as the source of the acid rain. Supporting evidence was largely correlative and hypothetical. Federal legislative solutions were being proposed that spanned the range of political positions at the time. Research bills were proposed by those who felt more information was needed before cost-effective control decisions could be made. Emissions control bills were proposed by those who felt that enough was known and that the damages were large enough to justify reductions in $SO_2$ emissions of up to 50 percent.

Also in the late 1970s and early 1980s relatively simple measures of sensitivity developed in Europe and the Northeast were used to identify sensitive areas outside the northeastern United States, including Florida. Limited studies in Florida also suggested increased acidity in precipitation as well as in a small number of lakes in Florida. These results prompted the Florida Department of Environmental Regulation in 1980 to recognize the potential for an acid rain problem in Florida. At that time, it was also generally recognized that there was no evidence of demonstrated effects due to acid rain in Florida and that the Florida environment had and continues to have significant differences from the Northeast which must be taken into consideration.

Therefore, against this backdrop of 1) assertions that Florida ecosystems were sensitive to acid rain, 2) these assertions being an extrapolation of findings and claims in the Northeast, 3) the potential uniqueness of the Florida environment as compared with that of the northeastern United States, 4) the limited amount of Florida-specific research, 5) the lack of any demonstrated effects of acid rain in Florida, and 6) the possibility of emissions control legislation, the FCG selected Environmental Science and Engineering in November 1980 to conduct the Florida Acid Deposition Study. The overall objective was to assess and/or develop the information needed on acid deposition concerning its magnitude, variability, sources, effects, and control options in Florida. Therefore, the goal of the study has been to better define the significance of acid deposition and its effects for Florida -- to take it from an issue characterized largely by speculation to one that is defined by facts and to realistically describe the magnitude of its potential effects. It is hoped that if this goal is achieved, decision-makers will have credible information with which to address such questions as how big or small potential effects may be, how long before possible effects manifest themselves, whether they are reversible, what research is necessary to resolve effects questions definitively, how long will this resolution take, and are controls necessary at this time.

## PROJECT DESCRIPTION

The study was divided into three areas of investigation: acid deposition monitoring, source attribution, and effects research. Each area had its specific objectives and specific research questions to be addressed. Criteria for selecting research areas were: importance for meeting objectives, necessity for understanding the potential uniqueness of the Florida environment, and feasibility with respect to available time and resources. The study was performed in four phases, which allowed the program to be adjusted to meet changing needs and respond to the results of earlier phases of the study. For example, in the monitoring program the network design was modified in the latter phases to meet the needs of the source attribution program (i.e., the sampling frequency was increased from weekly to daily); and, based on results of the earlier phases that showed the redundancy of certain stations, the number of stations was reduced. The study did not conduct research in all possible areas. The study relied heavily on the literature and national research programs in those research areas where results could legitimately be applied to the Florida environment.

A final facet of the study was an assessment and integration of study results. This was necessary to meet the objective of better characterizing the issue for Florida. Whether research was actually conducted under this study or not, all pertinent issues related to acid deposition in Florida were assessed using available information. In this way, each important aspect of the acid deposition issue was addressed and evaluated, and the status of knowledge described relative to Florida.

## PROJECT RESULTS

Substantial information was developed and/or assessed that has succeeded in characterizing the acid deposition issue as it relates to the State of Florida. Although there are not yet definitive answers to all of the questions evaluated by the study, considerable progress has been made toward that goal. By far the most progress has been made in describing the temporal and spatial variability of acid deposition within Florida. Where data of disparate and unknown quality existed prior to the study, there is now a quality assured 3-1/2 year database on wet deposition from which trends can be assessed in the future. Where previously no credible dry deposition data existed, 2 years of ambient air concentration data have been collected from which the variability of dry deposition can be reasonably inferred. The combined wet deposition and air chemistry data base is a first of its kind in the United States on a state-wide, multi-year scale. Also, rigorous evaluation of historical data, using what is now known of the variability of existing data, shows that the long-term historical data are not sufficient to draw definitive conclusions regarding trends. However, data from the mid-1970s suggests the acidity has remained steady over the last 10 years. Without the knowledge gained in this study, such conclusions would not have been possible.

Prior to the study, the sensitivity of Florida lakes to acid deposition was suspected based on a limited survey of 20 lakes in Florida and the extrapolation of relatively simple sensitivity criteria developed elsewhere. At that time, claims were being made that Florida lakes were on the verge of disaster. As a result of the study, the following is now known about this issue:

1) rigorous evaluation of historical data, considering the uncertainties related to sampling and analytical techniques and natural variability, shows that the data base is not sufficient to draw definitive conclusions regarding trends;

2) simple titration models such as proposed by Henriksen are inappropriate to Florida lakes and exaggerate the potential for acid deposition to harm any lake;

3) lakes potentially sensitive to changes in acid deposition are lakes

    a) with hydrologic budgets dominated by precipitation directly to the lake surface (i.e., seepage lakes),

b) with dilute lakewater chemistry, low acid neutralizing capacity, and low dissolved organic carbon (DOC is an important lake buffering system and reduces toxicity of metals to lake biota),

c) with watersheds dominated by acidic soils with low cation exchange capacity, low base saturation, and minimal ability to adsorb sulfate, and

d) isolated from cultural development within their watersheds;

4) an upper-limit estimate of seepage lakes is 2,000 out of approximately 7,600 lakes in Florida. However, not all of these lakes have the characteristics which make them sensitive (e.g., approximately 50 percent of these seepage lakes have relatively high dissolved organic carbon levels). Therefore, the actual number of potentially sensitive lakes is less than 2,000 and may be much less;

5) the relative response time of these potentially sensitive seepage lakes to sustained changes in acid deposition is approximately from 10 to 50 years and is a direct function of lake hydrology or residence time;

6) these seepage lakes are located in the highlands and ridge regions of Florida; and

7) the seepage lakes in northern Florida have the potential to respond to a sustained change in rainfall acidity 50 percent faster on average than the lakes in southern Florida.

These findings apply generally to the lakes in these regions. Any single lake may or may not fit these general findings. Significant progress has been made in identifying the key in-lake processes (i.e., biogeochemical processes which result in the removal of hydrogen, sulfate, nitrate, and ammonium) and hydrologic processes (i.e., evaporation/precipitation and inseepage/outseepage budgets) that are likely to control how acidic and how fast a lake will respond to a sustained change in rainfall acidity. Focused research on these processes can result in an appropriate sensitivity index which could be used to define the distribution of sensitive lake systems in Florida. Therefore, the improved understanding of lake acidification processes is a prime example of the progress made by the study.

Progress has also been made in the areas of vegetation (i.e., crops and forests) effects and materials damage. In a finding consistent with the apparent national consensus, it is clear that effects on crops in Florida are not of concern at current levels of acid deposition. In 1980, the evidence on the effects of acid deposition to forests was theoretical. Although preliminary evidence of growth rate reduction in the commercial forests of the Southeast now exists, no such evidence exists for Florida. The cause of the reduction in Southeastern forests is not known and may include drought, pests, disease, management practices, and air pollution. However, if air pollution is involved, many scientists are beginning to suggest that the cause is not likely to be related to the sulfur component of acid deposition but to air pollutants such as ozone. Acid deposition, however, cannot be ruled out at this time. Although no research per se was done on materials damage, the study was still able to assess state-of-the-art understanding of the issue and show that the risk of significant damage in Florida under current conditions is very small.

The progress made in the source attribution area includes Florida-specific modifications and applications of two complementary techniques that can be used to develop future regional air quality models. Also, an excellent data base has been developed that will help to validate future models. Due to the limitations of existing source attribution tools, their use in this report to attribute Florida deposition to source regions in and out of Florida can only be viewed as illustrative of how improved tools can be applied in the future.

The report has been reviewed, the comments carefully considered, and are reflected in this report. The FCG feels that this report represents a balanced view of the current state of knowledge on the issue for Florida. The reader is cautioned to realize that the study was never designed to, nor could it hope to, totally resolve the multitude of complexities making up the acid deposition issue. Therefore, it would be inappropriate to overinterpret or extrapolate the results and conclusions stated in this report.

In summary, the FCG believes that the Florida Acid Deposition Study has met its objectives. Substantial progress has been made. The study has developed and assessed a substantial amount of data and knowledge about acid deposition and its effects in Florida and placed bounds on the issue. Speculation can now be replaced with a sound database upon which to proceed with future research, assessments, and informed decision-making.

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The following people were involved in the technical preparation of this Final Report: A Synthesis of the Florida Acid Deposition Study.

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## ACKNOWLEDGEMENTS

### REVIEWERS

Several distinguished scientists assisted in the preparation of this report by reviewing and commenting on the initial draft. Their comments were carefully considered, and, where appropriate, the final draft reflects those comments. The final report was strengthened substantially via this peer review process, and both FCG and ESE appreciate the input of these reviewers:

Dr. Norbert S. Baer--New York University
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### STUDY SUBCONTRACTORS

In addition to the major study contractor, certain studies and consultations were performed in previous phases by university researchers.
Drs. P. Brezonik and L. Baker (formally with University of Florida, currently with University of Minnesota) either performed or assisted in the following ecological effects studies during Phases III and IV: buffering capacity of lake sediments; nutrient and pH relationships in softwater lakes, sulfate reduction/adsorption in lake sediments, and diagnostic model development for lake acidification in Florida.
Dr. R. Volk of University of Florida performed the Phase III study investigating sulfate adsorption in surficial soils. The study investigating the effects of simulated acidic deposition on certain terrestrial plants was performed in part by Drs. H. Biggs and P. Webb of

the University of Florida. Continuation of the Lake McCloud soil studies was performed by Drs. D. Graetz and G. Bitton of the University of Florida. A study of the biogenic emissions of selected Florida wetland systems was undertaken during Phase IV by a team of researchers from Florida International University and the University of Miami. Mr. W. Cooper of Florida International University lead the biogenic emissions research with Drs. R. Zika, L. Gidel, and J. Prospero from University of Miami.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued, Page 2 of 8)

TABLE OF CONTENTS
(Continued, Page 3 of 8)

TABLE OF CONTENTS
(Continued, Page 4 of 8)

TABLE OF CONTENTS
(Continued, Page 5 of 8)

TABLE OF CONTENTS
(Continued, Page 6 of 8)

TABLE OF CONTENTS
(Continued, Page 7 of 8)

## TABLE OF CONTENTS
(Continued, Page 8 of 8)

# LIST OF TABLES

LIST OF TABLES
(Continued, Page 2 of 8)

LIST OF TABLES
(Continued, Page 3 of 8)

# LIST OF TABLES
(Continued, Page 4 of 8)

## LIST OF TABLES
(Continued, Page 5 of 8)

LIST OF TABLES
(Continued, Page 6 of 8)

LIST OF TABLES
(Continued, Page 7 of 8)

# LIST OF TABLES
(Continued, Page 8 of 8)

## LIST OF FIGURES

## LIST OF FIGURES
(Continued, Page 2 of 6)

## LIST OF FIGURES
(Continued, Page 3 of 6)

LIST OF FIGURES
(Continued, Page 4 of 6)

## LIST OF FIGURES
(Continued, Page 5 of 6)

# LIST OF FIGURES
(Continued, Page 6 of 6)

## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| AA | flameless atomic absorption |
| AAS | atomic absorption spectrophotometer |
| AC | asbestos-cement |
| ACS | American Chemical Society |
| AI | Aggressiveness Index |
| $Al^{+3}$ | aluminum cation |
| $Al(OH)_3$ | gibbsite |
| ANC | acid-neutralizing capacity |
| ANOVA | analysis of variance |
| APCA | Air Pollution Control Association |
| APHA | American Public Health Association |
| APIS | Air Permit Inventory System |
| ARL | Air Resources Laboratory |
| ASACCCRT | American Statistical Association Coordinating Committee Crops Review Team |
| $As_2O_3$ | arsenic trioxide |
| ASTM | American Society for Testing and Materials |
| ATAD | Atmospheric Transport and Deposition |
| ATOLL | Atlantic Tropical Oceanic Lower Layer |
| ATP | adenosine triphosphate |
| AWWA | American Water Works Association |
| | |
| BNC | base neutralizing capacity |
| | |
| °C | degrees Celsius |
| $Ca^{+2}$ | calcium cation |
| $CaCO_3$ | calcium carbonate |
| CDC | Control Data Corporation |
| CEC | cation exchange capacity |

| | |
|---|---|
| CENRP | Center for Environmental and Natural Research Programs |
| $CHCl_3$ | chloroform |
| $CH_3COOH$ | acidic acid |
| CHOOH | formic acid |
| $C_3H_8O_3$ | glycerol |
| $Cl^-$ | chloride anion |
| cm | centimeter |
| cm/event | centimeters per event |
| cm/hr | centimeters per hour |
| cm/sec | centimeters per second |
| cm/week | centimeters per week |
| cm/yr | centimeters per year |
| $CO_2$ | carbon dioxide |
| COS | carbonyl sulfide |
| $CS_2$ | carbon disulfide |
| CSI | calcite saturation index |
| CV | coefficient of variation |
| | |
| ° | degrees |
| °N | degrees north |
| °W | degrees west |
| D/D | daily versus daily |
| D/W | daily versus weekly |
| DEM | Department of Environmental Management |
| DER | Florida Department of Environmental Regulation |
| DNR | Department of Natural Resources |
| DOC | dissolved organic carbon |
| DOE | U.S. Department of Energy |
| DOT | Department of Transportation |
| | |
| EF | enrichment factor |
| EIPR | external-internal proton ratio |

| | |
|---|---|
| ELA | Experimental Lakes Area |
| ENAMAP | Eastern North American Model of Air Pollution |
| EPA | U.S. Environmental Protection Agency |
| EPD | Environmental Protection Division |
| EPRI | Electric Power Research Institute |
| eq/ha | equivalents per hectare |
| eq/ha-yr | equivalents per hectare per year |
| eq/hr/event | equivalents per hour per event |
| eq/L | equivalents per liter |
| ERT | Environmental Research and Technology, Inc. |
| ESE | Environmental Science and Engineering, Inc. |
| EST | Eastern Standard Time |
| EURMAP | European Regional Model of Air Pollution |
| $F^-$ | fluoride anion |
| FCG | Florida Electric Power Coordinating Group |
| FeOOH | goethite |
| FERC | Federal Energy Regulatory Commission |
| FIU | Florida International University |
| FLADAB | Florida Lakes Data Base |
| ft | foot |
| $ft^3$ | cubic feet |
| g | gram |
| $g/cm^3$ | grams per cubic centimeter |
| $H^+$ | hydrogen cation |
| ha | hectares |
| HCl | hydrochloric acid |
| HCOOH | formic acid |
| $H_2CO_3$ | carbonic acid |
| $H_2O$ | water |
| $HNO_3$ | nitric acid |

| | |
|---|---|
| $HNO_3$-N | nitric acid as nitrogen |
| hr | hour |
| $H_2S$ | hydrogen sulfide |
| $H_2SO_4$ | sulfuric acid |
| ICAAS | Interdisciplinary Center for Aeronomy and (Other) Atmospheric Sciences |
| ICAP | inductively coupled argon plasma |
| ILWAS | Integrated Lake-Watershed Acidification Study |
| $K^+$ | potassium cation |
| KCl | potassium chloride |
| keq | kiloequivalents |
| keq/ha | kiloequivalents per hectare |
| keq/ha/yr | kiloequivalents per hectare per year |
| keq/yr | kiloequivalents per year |
| kg | kilogram |
| kg/hr | kilograms per hour |
| $kg/m^2$ | kilograms per square meter |
| kg-S/ha | kilograms of sulfur per hectare |
| km | kilometer |
| km/hr | kilometers per hour |
| $km^2$ | square kilometers |
| $km^3$ | cubic kilometers |
| KOH | potassium hydroxide |
| kPa | kilopascals |
| LFM | limited fine mesh |
| LIS | low ionic strength |
| LRT | long-range transport |
| m | meter |
| m/sec | meters per second |

| | |
|---|---|
| m/yr | meters per year |
| $m^2$ | square meters |
| $m^3$ | cubic meters |
| $m^3/yr$ | cubic meters per year |
| MAGIC | Model of Acidification of Groundwater in Catchments |
| MAP3S | Multistate Atmospheric Power Production Pollution Study |
| mb | millibar |
| meq/100 g | milliequivalents per 100 grams |
| $meq/m^2$ | milliequivalents per square meter |
| $meq/m^2/yr$ | milliequivalents per square meter per year |
| $meq/m^3$ | milliequivalents per cubic meter |
| meq/yr | milliequivalents per year |
| mg | milligram |
| mg/L | milligrams per liter |
| $mg/m^2$ | milligrams per square meter |
| $mg\text{-}S/m^2$ | milligrams of sulfur per square meter |
| $Mg^{+2}$ | magnesium cation |
| mL | milliliter |
| mL/min | milliliters per minute |
| $Mn^{+2}$ | manganese cation |
| mm/hr | millimeters per hour |
| mm/month | millimeters per month |
| MOI | Memorandum of Intent |
| moles/L | moles per liter |
| mph | miles per hour |
| msl | mean sea level |
| MT | metric tons |
| $MT/km^2$ | metric tons per square kilometer |
| MT/yr | metric tons per year |
| MTB | methylthymol blue |
| n | number of observations |
| N | nitrogen |

| | |
|---|---|
| $Na^+$ | sodium cation |
| NADB | National Air Data Branch |
| NADP | National Acid Deposition Program |
| NaOH | sodium hydroxide |
| NAPAP | National Acid Precipitation Assessment Program |
| NAS | National Academy of Sciences |
| NASA | National Aeronautics and Space Administration |
| NATO | North Atlantic Treaty Organization |
| NBS | National Bureau of Standards |
| NC | neutralizing capacities |
| NCAR | National Center for Atmospheric Research |
| NCC | National Climatic Center |
| NCSU | North Carolina State University |
| NEDS | National Emission Data System |
| NERDC | Northeast Regional Data Center |
| $NH_3$ | ammonia |
| $NH_4^+$ | ammonium cation |
| $NH_4^+$-N | ammonium cation as nitrogen |
| NHC | National Hurricane Center |
| NLS | National Lakes Survey |
| NMC | National Meteorological Center |
| NO | nitric oxide |
| $NO_2$ | nitrogen dioxide |
| $NO_2$-N | nitrogen dioxide as nitrogen |
| $NO_3^-$ | nitrate anion |
| $NO_3^-$-N | nitrate anion as nitrogen |
| $NO_x$ | nitrogen oxides |
| $NO_x$-N | nitrogen oxide as nitrogen |
| NOAA | National Oceanic and Atmospheric Administration |
| NRC | Nuclear Regulatory Commission |
| NSEPB | National Swedish Environment Protection Board |
| NTIS | National Technical Information Service |
| NWS | National Weather Service |

| | |
|---|---|
| $O_2$ | dioxide |
| ORD | Office of Research and Development |
| P | phosphorus |
| PAN | peroxyacetylnitrate |
| PCU | platinum-cobalt units |
| PMA | phenylmercuric acetate |
| $PO_4^{-3}$ | organophosphate anion |
| PSC | Florida Public Service Commission |
| PVC | polyvinyl chloride |
| QA | quality assurance |
| QA/QC | quality assurance/quality control |
| QC | quality control |
| $R^2$ | coefficient of determination |
| RHS | relative height of sigma |
| S | sulfur |
| SAS | Statistical Analysis System |
| SFGLTF | Southeastern Forest Growth Loss Task Force |
| $SO_2$ | sulfur dioxide |
| $SO_2$-S | sulfur dioxide as sulfur |
| $SO_4^{-2}$ | sulfate anion |
| $SO_4^{-2}$-S | sulfate anion as sulfur |
| $SO_x$ | sulfur oxides |
| $SO_x$-S | sulfur oxides as sulfur |
| SRI | Stanford Research Institute |
| SSSA | Soil Science Society of America |
| STP | standard temperature and pressure |
| SURE | Sulfate Regional Experiment |

| | |
|---|---|
| TDS | total dissolved solids |
| tons/yr | tons per year |
| TP | total phosphorus |
| | |
| UAPSP | Utility Acid Precipitation Study Program |
| μeq | microequivalents |
| μeq/g | microequivalents per gram |
| μeq/L | microequivalents per liter |
| UF | University of Florida |
| μg/L | micrograms per liter |
| $\mu g/m^3$ | micrograms per cubic meter |
| μm | micrometer |
| μm/yr | micrometers per year |
| UM | University of Michigan |
| μmho/cm | micromhos per centimeter |
| μN | micro-normal (1 μN = 1 μeq/L) |
| UNAMAP | User's Network of Applied Models of Air Pollution |
| UPS | United Parcel Service |
| μS/cm | microsiemens per centimeter |
| USAF | United States Air Force |
| USDA | United States Department of Agriculture |
| USGS | United States Geological Survey |
| | |
| V | vanadium |
| $V^{+4}$ | vanadium cation |
| v/v | volume-to-volume |
| VWM | volume-weighted mean |
| | |
| W/W | weekly versus weekly |
| | |
| yr | year |
| YSI | Yellow Springs Instruments |
| | |
| $Zn^{+2}$ | zinc cation |

# EXECUTIVE SUMMARY

## INTRODUCTION

In 1980, the Florida Electric Power Coordinating Group, Inc. (FCG) approved the initiation of the Florida Acid Deposition Study, which had as its overall objective the assessment and/or development of information on the magnitude, variability, sources, effects, and control options of acidic deposition in Florida. This study was deemed necessary since the climate, meteorology, soil conditions, and terrestrial and aquatic resources of the Florida peninsula are different from most of the rest of the eastern United States. In addition, since the majority of research on acidic deposition had been conducted in the northeastern United States, the transferability of results to Florida was questionable. Therefore, having Florida-specific data would directly assist in drawing conclusions related to acidic deposition in Florida.

Beginning in the last quarter of 1980, the study was planned and implemented in four major phases:

Phase I--Began on January 1981 with four reports issued in September 1981 and one issued in January 1982;
Phase II--Began in September 1981 with reports issued in January 1983 and November 1983;
Phase III--Began in September 1982 with a report issued in August 1984; and
Phase IV--Began in September 1983 with a report issued in June 1985.

Within each phase, three major areas of research were investigated: acid deposition monitoring, source attribution, and ecological effects.

In developing the plans of study to meet this research objective, the study focused on providing information from which certain key research questions could be addressed. The extent to which each research area was investigated was based upon the ability to obtain definitive Florida-specific results, the complexity of the acid-deposition-related phenomena that were to be addressed, and the desire to draw from national, regional, state, and university research efforts, as well as available time and funding.

The data and analyses developed within the study demonstrated that the current knowledge about the acidic deposition phenomenon in Florida (see Table 1) was significantly increased. In this report, the information developed in all phases of the Florida Acid Deposition Study is analyzed within and across the three major research areas to provide answers to key study questions. All research areas were not investigated to the same degree; however, each key question was addressed based on available information.

## ACID DEPOSITION MONITORING

At the study inception, the primary objective of the monitoring effort was to provide information necessary to:

1. Quantify the current levels of acidity and related chemical species in wet deposition at regionally representative sites in the State of Florida;
2. Identify the spatial and temporal variabilities of these species over a 3-year period;
3. Provide a limited set of data complementary to the Utility Acid Precipitation Study Program (UAPSP); and
4. Establish the accuracy, precision, and overall uncertainty of the data obtained.

In addition to this objective, a major purpose of monitoring was to provide a body of useful precipitation and air chemistry data for the source attribution and ecological effects research areas.

Table 1. Accomplishments of the Florida Acid Deposition Study

| Research Area | Direct Evidence Developed | Limited Direct Evidence Developed | Indirect Evidence Developed | Literature Review Only |
|---|---|---|---|---|
| Acidic Deposition | | | | |
| 1. Wet—magnitude | X | | | |
| 2. Dry—magnitude | | | X | |
| 3. Spatial variability | X | | | |
| 4. Temporal variability | | | | |
| a. Short term | X | | | |
| b. Long term | | X | | |
| 5. Chemical relationships | X | | | |
| 6. Organic acids | | X | | |
| Ecological Effects | | | | |
| 1. Lakes | | | | |
| a. Chemistry | | X | | |
| b. Biology | | | X | |
| 2. Terrestrial | | | | |
| a. Soils | | X | | |
| b. Forests | | X | | |
| c. Crops | | X | | |
| 3. Materials | | | | X |
| Source Attribution | | | | |
| 1. Florida anthropogenic emissions | X | | | |
| 2. Biogenic emissions | | X | | |
| 3. Source contributions | | | X | |

Source: Environmental Science and Engineering, Inc. (ESE), 1986.

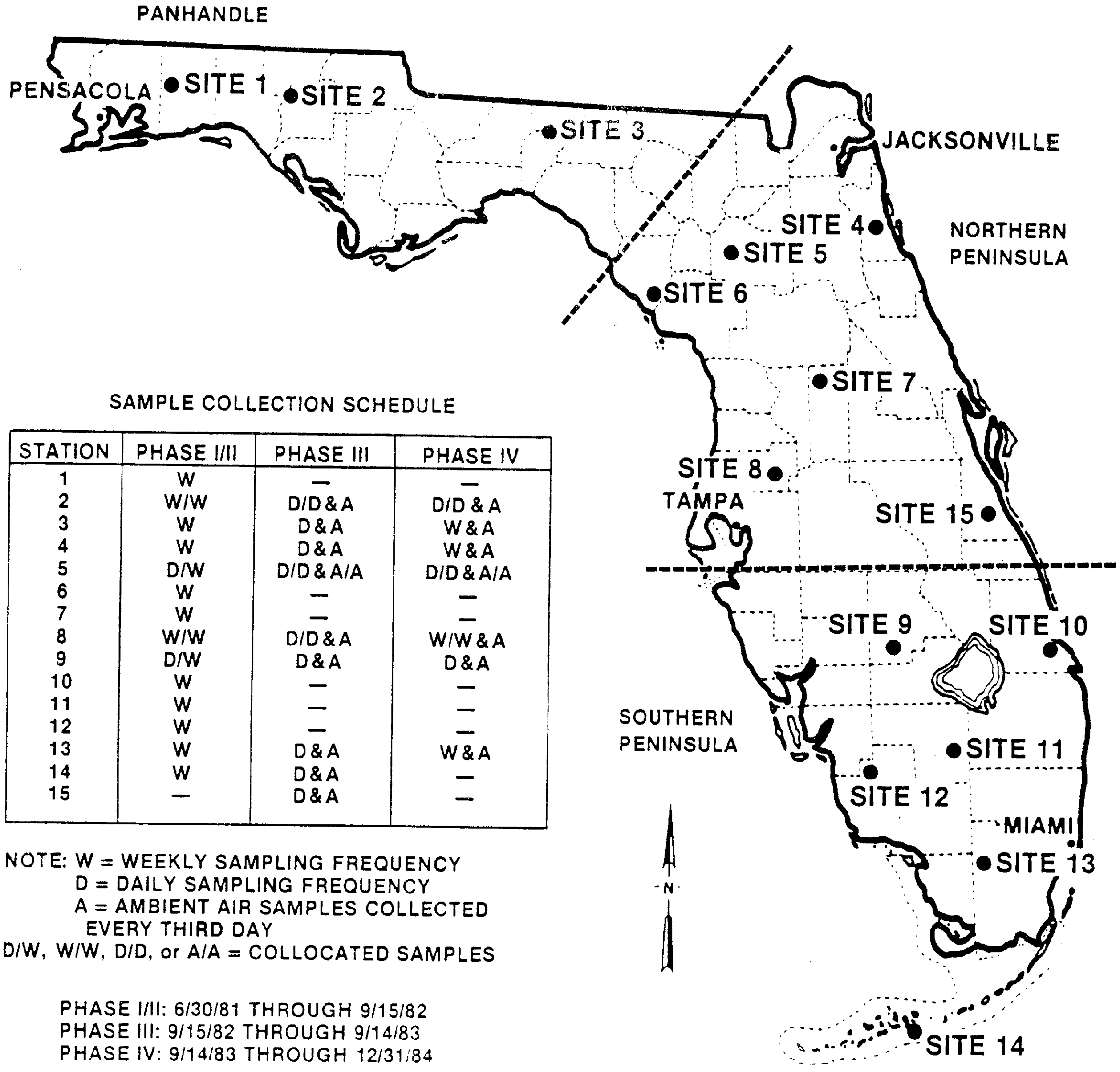
During the course of the study, the monitoring program scope was adjusted to satisfy the study's objectives by modifying the network number, frequency, and type of monitoring without sacrificing the specific research needs (see Figure 1 and Table 2). Quality assurance standards were maintained throughout the monitoring program to ensure that results from different years would be comparable.

The precipitation and ambient air chemistry measured over the 3½-year period (i.e., July 1, 1981, through December 31, 1984) were analyzed in order to address key research questions. From this analysis, major findings were obtained in three monitoring related areas: spatial patterns, temporal trends, and chemical/physical relationships.

SPATIAL PATTERNS

- The Florida acidic deposition monitoring network results over a 3-year period, when compared with data from the eastern United States, show that pH in Florida averaged approximately 4.6 while precipitation pH in the northeastern and midwestern United States averaged about 4.3 for the same period (see Figure 2). These differences in pH indicate that Florida's precipitation is roughly half as acidic as that of the northeastern and midwestern United States. Sulfate ($SO_4^{-2}$) deposition in Florida precipitation was about 14 kilograms per hectare per year (kg/ha-yr) as opposed to about 24 kg/ha-yr in the northeastern and midwestern United States. Similarly, nitrate ($NO_3^-$) deposition in Florida precipitation was about 8 kg/ha-yr compared to about 14 kg/ha-yr observed in the northeastern and midwestern United States. In a broad sense, these data demonstrate a decrease in acidity and related parameters (i.e., $SO_4^{-2}$ and $NO_3^-$) from north to south. This gradient was also observed in Florida's precipitation chemistry.

- Over the 3-year period evaluated, the data and analyses indicate a north-south gradient in observed concentration and deposition



SAMPLE COLLECTION SCHEDULE

| STATION | PHASE I/II | PHASE III | PHASE IV |
|---|---|---|---|
| 1 | W | — | — |
| 2 | W/W | D/D&A | D/D & A |
| 3 | W | D&A | W&A |
| 4 | W | D&A | W&A |
| 5 | D/W | D/D&A/A | D/D&A/A |
| 6 | W | — | — |
| 7 | W | — | — |
| 8 | W/W | D/D&A | W/W&A |
| 9 | D/W | D&A | D&A |
| 10 | W | — | — |
| 11 | W | — | — |
| 12 | W | — | — |
| 13 | W | D&A | W&A |
| 14 | W | D&A | — |
| 15 | — | D&A | — |

NOTE: W = WEEKLY SAMPLING FREQUENCY
D = DAILY SAMPLING FREQUENCY
A = AMBIENT AIR SAMPLES COLLECTED EVERY THIRD DAY
D/W, W/W, D/D, or A/A = COLLOCATED SAMPLES

PHASE I/II: 6/30/81 THROUGH 9/15/82
PHASE III: 9/15/82 THROUGH 9/14/83
PHASE IV: 9/14/83 THROUGH 12/31/84

● FLORIDA ACID DEPOSITION STUDY MONITORING SITE

Figure 1
LOCATION OF MONITORING STATIONS AND SAMPLE COLLECTION SCHEDULE, 6/30/81-12/31/84

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Table 2. Chemical and Physical Parameters Analyzed in Precipitation and Ambient Air

| Type of Monitoring | Parameters Analyzed |
|---|---|
| Precipitation* | Field laboratory: hydrogen ion ($H^+$), measured as pH; conductivity, volume, and precipitation amount.<br>Central laboratory: $H^+$; calcium ($Ca^{+2}$); ammonium ($NH_4^+$); sodium ($Na^+$); potassium ($K^+$); magnesium ($Mg^{+2}$); $NO_3^-$; chloride ($Cl^-$); and $SO_4^{-2}$. During the periods September 15, 1982, through September 14, 1983, concentrations of orthophosphate ($PO_4^{-3}$), fluoride ($F^-$), vanadium ($V^{+4}$), aluminum ($Al^{+3}$), total/strong acidity, alkalinity, and dissolved organic carbon (DOC) were analyzed (see ESE, 1983). Formic acid (CHOOH) and acetic acid ($CH_3COOH$) were analyzed in precipitation at one site from September 15, 1982, through September 14, 1983. |
| Ambient Air† | Central laboratory: particulate $SO_4^{-2}$, gaseous sulfur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), and nitric acid ($HNO_3$). |

*Measured using Aerochem Metrics Model 301 Wet/Dry Collector.

†Measured from a 10-meter (m) tower using a high-volume filter pack for particulate $SO_4^{-2}$, $SO_2$, and $HNO_3$. Gas bubbler used for $NO_2$.

Source: ESE, 1986.

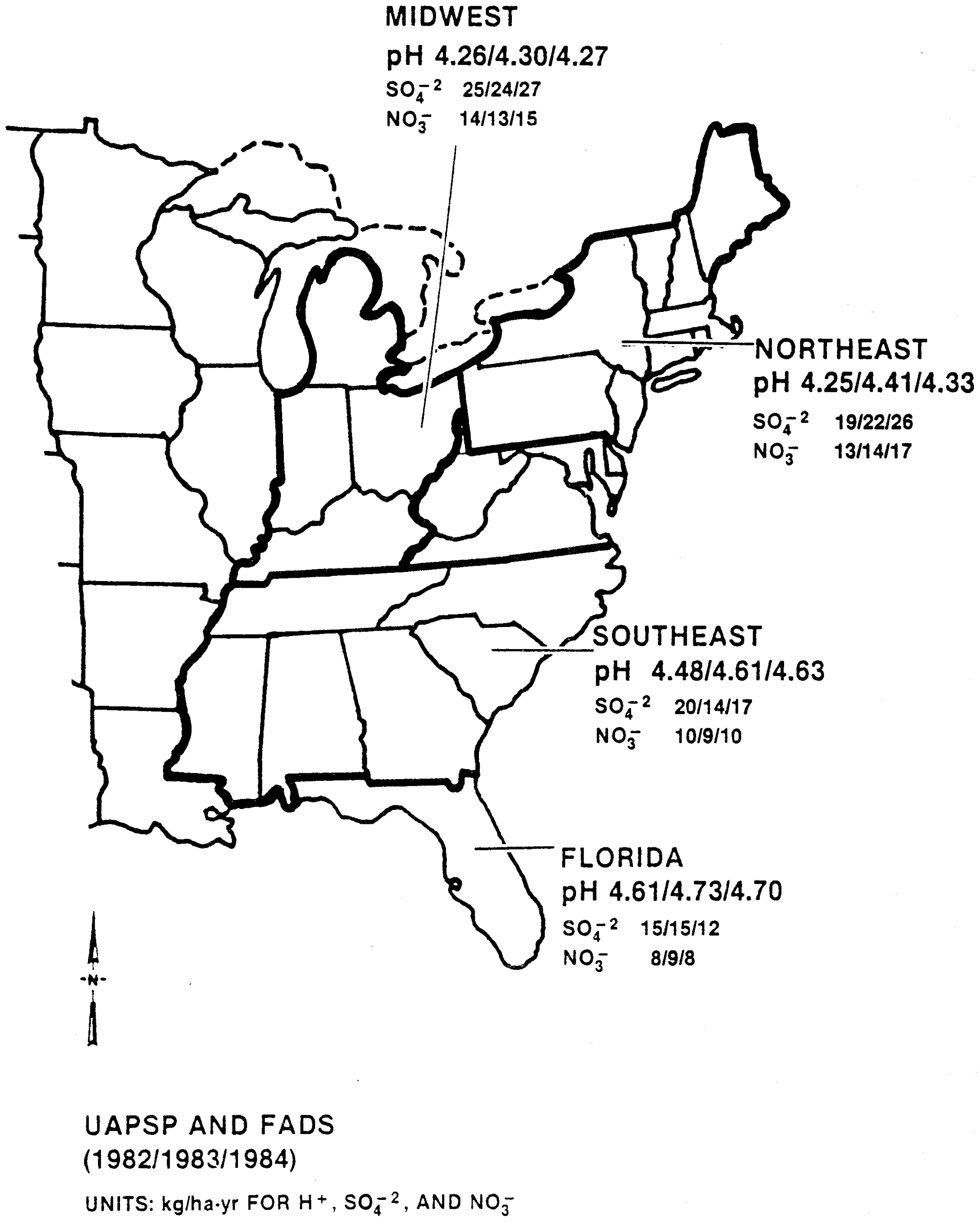

Figure 2
COMPARISON OF pH AND DEPOSITION DATA COLLECTED FROM THE FLORIDA ACID DEPOSITION STUDY WITH AVAILABLE DATA FROM THE UAPSP NETWORK

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patterns of acidity and related parameters in Florida (see Figure 3 and Figure 4). However, this gradient is not uniform, especially throughout the panhandle and northern peninsula of Florida. Statistically significant differences were found among sites, with the highest concentrations and depositions of $H^+$ and $NO_3^-$ observed at Sites 2, 5, and 8. For $SO_4^{-2}$, the highest significantly different concentrations were observed at Sites 5 and 8, and the highest significantly different depositions were observed at Sites 2, 5, and 8. The lowest concentrations and depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$ were observed at Sites 9 and 13 located in the southern peninsula of Florida. The observed pattern appears to be somewhat influenced by meteorology and site location.

- Ambient air concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ observed over a 2-year period suggest distinct, and statistically different, spatial patterns (see Figure 5). A statistically significant pattern in concentrations of particulate $SO_4^{-2}$ and $HNO_3$ was observed and indicated a north-south gradient in these acid precursors of $SO_4^{-2}$ and $NO_3^-$ in precipitation. Ambient $SO_2$ and $NO_2$ concentrations were not uniform, suggesting influences from local sources superimposed on a north-south gradient.

## TEMPORAL TRENDS

- Differences in seasonal concentrations and depositions were observed over the 3-year period. Summer (April through September) was generally significantly (about a factor of 2) higher than winter (October through March) in both concentrations and depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$. These differences were greater for sites located in the panhandle and northern peninsula than for sites located in the southern peninsula. Rainfall amount, which is higher in the summer, appears to influence this seasonal variability.

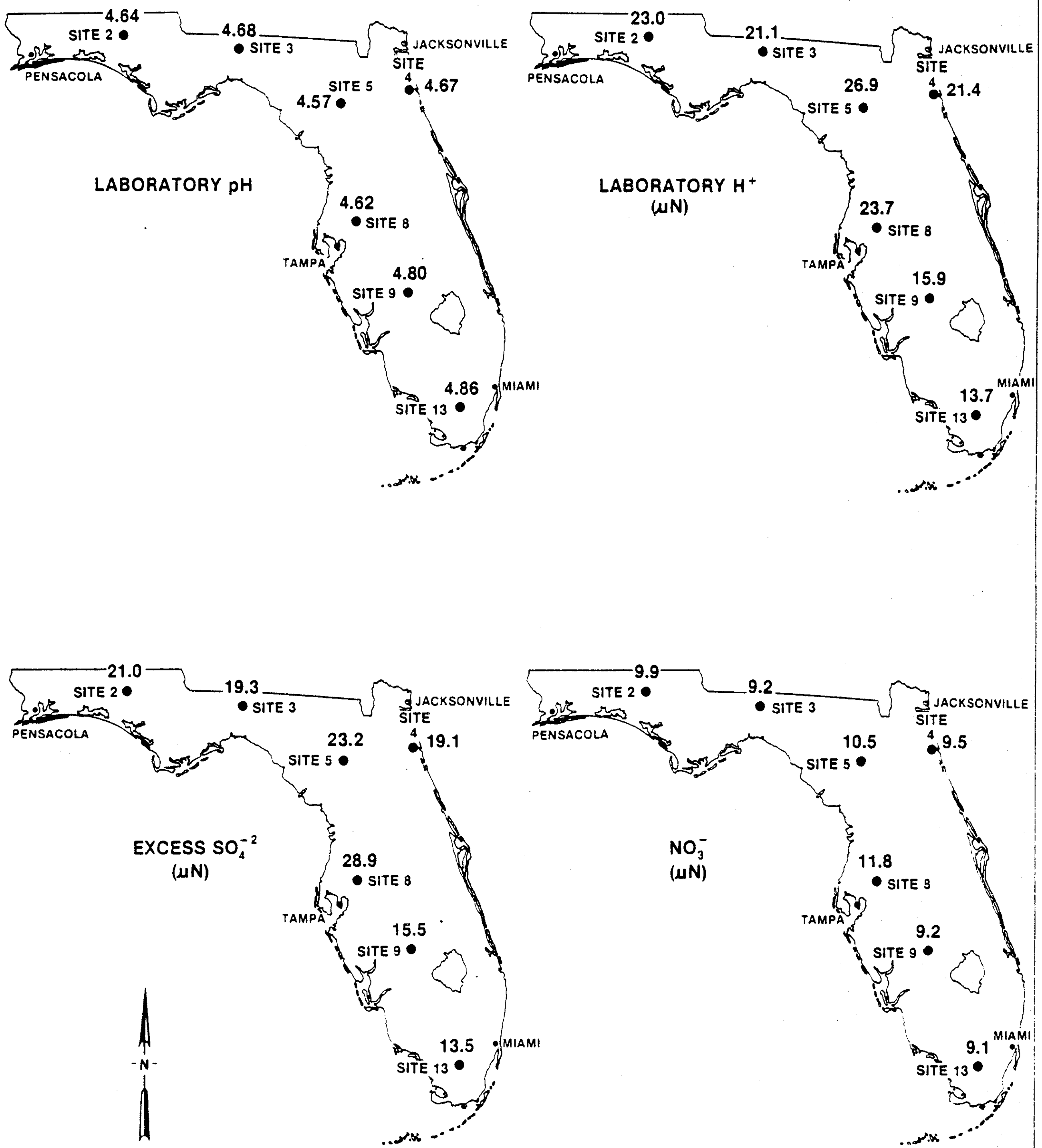

Figure 3
3-YEAR VOLUME-WEIGHTED MEAN (VWM) CONCENTRATIONS

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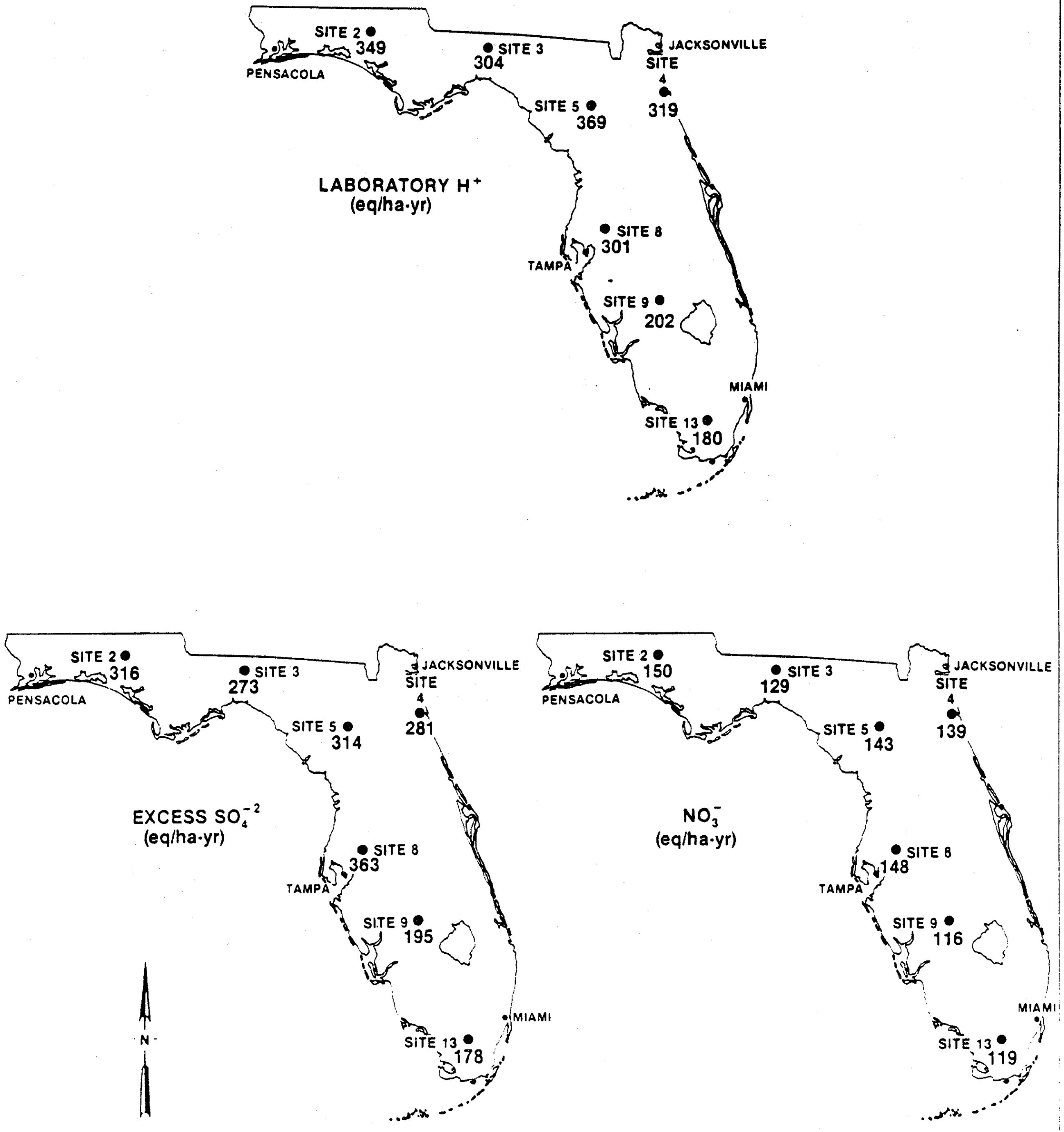

NOTES:

For excess $SO_4^{-2}$, 1 equivalent per hectare per year (eq/ha·yr) = 0.048 kg/ha·yr

For $NO_3^-$, 1 eq/ha·yr = 0.062 kg/ha·yr

Figure 4
3-YEAR VWM DEPOSITIONS

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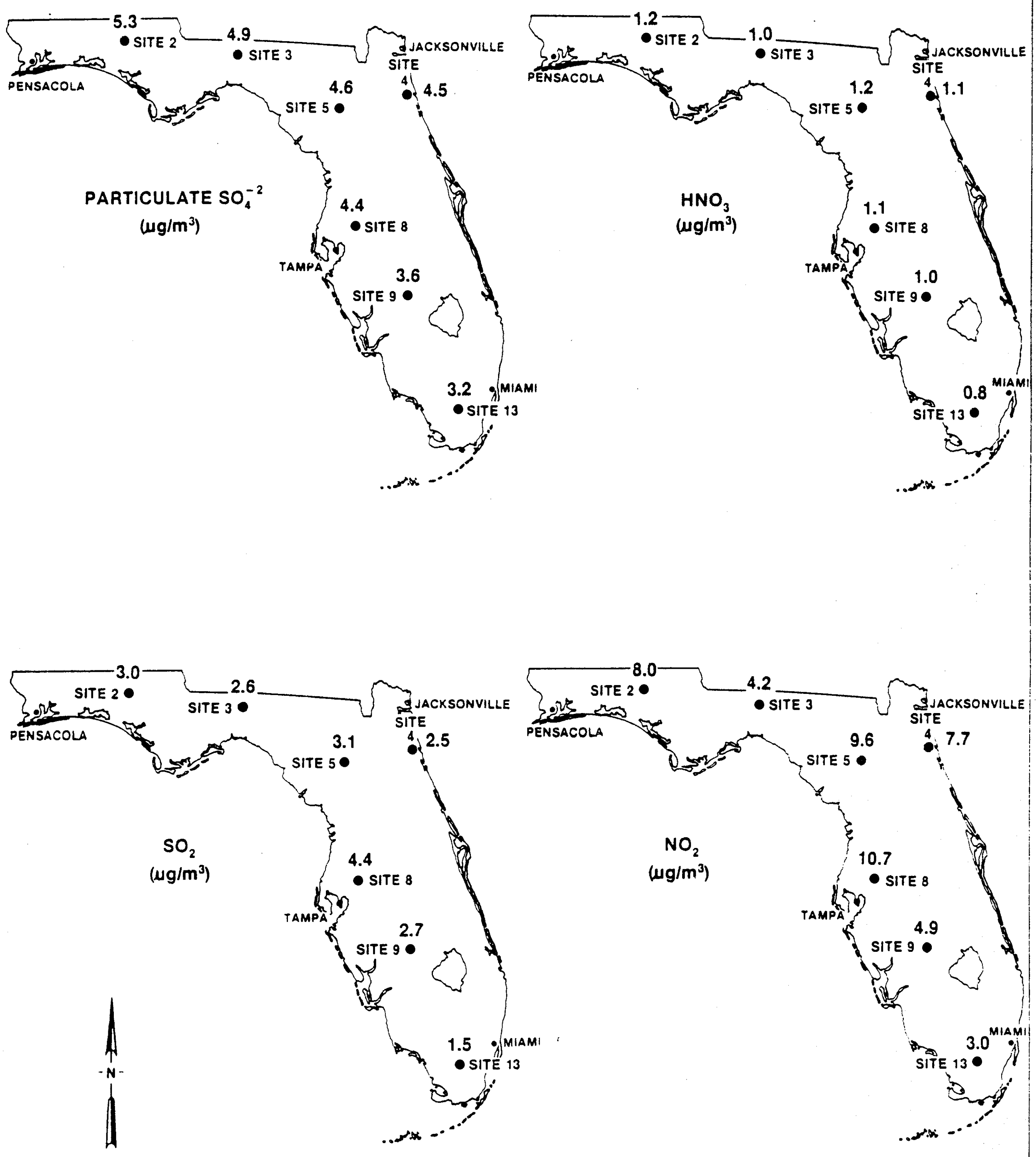

NOTE: mg/m³ = micrograms per cubic meter.

Figure 5
2-YEAR AVERAGE AMBIENT AIR CONCENTRATIONS

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- Data from the mid-1970s suggest that acidity in Florida has not increased during the last 10 years. Data on acidic deposition in Florida prior to the mid-1970s are not sufficient to draw definitive conclusions regarding trends.

- During the 3 years analyzed, concentration and deposition of laboratory $H^+$ and excess $SO_4^{-2}$ decreased in the panhandle and northern peninsula of Florida by 30 percent and 20 percent, respectively. This decrease was statistically significant between the first and third years. For sites located in the southern peninsula, the decrease in laboratory $H^+$ and excess $SO_4^{-2}$ was less than that observed for the more northern sites. Concentrations and depositions of $NO_3^-$ remained relatively constant over the 3-year period with no statistically significant differences observed.

CHEMICAL/PHYSICAL RELATIONSHIPS

- The variability in Florida's rainfall acidity is closely related to the concentrations of excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$. Excess $SO_4^{-2}$ was found to be the most important rainfall parameter in accounting for the variability in acidity, and excess $Ca^{+2}$ or $NH_4^+$ was the second most important. $NO_3^-$ was typically the least important parameter. These relationships were found to be site-specific.

- Statistically significant relationships were obtained between rainfall amount and laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, and excess $Ca^{+2}$. Concentrations of these parameters were found to decay rapidly with increasing precipitation amount.

- The potential acids and bases contributing to net rainfall acidity were found to vary as a function of parameter and site location. Excess $SO_4^{-2}$ as sulfuric acid ($H_2SO_4$) and $NO_3^-$ (as

$HNO_3$) were found to contribute about 2/3 and 1/3 of the total potential acidity, respectively. Excess $SO_4^{-2}$ became a decreasingly important contributor to acidity from north to south, whereas the reverse was observed for $NO_3^-$. The importance of $NH_4^+$ and excess $Ca^{+2}$ as potential bases increased from north to south. $NH_4^+$ was slighly higher in importance as a base than excess $Ca^{+2}$ for north Florida, whereas excess $Ca^{+2}$ was more important than $NH_4^+$ for south Florida. The period of study was September 15, 1982, through September 15, 1983.

- Precipitation and ambient air chemistry was found to vary as a function of synopotic meteorological conditions. The observations were not uniform across the state, suggesting that different meteorological conditions influence precipitation and air chemistry differently across the state.

## SOURCE ATTRIBUTION

The overall objective of the source attribution program was to assess the contribution of the Florida electric utilities to current levels of acidity within Florida and in surrounding states. To meet this objective, two distinct but related atmospheric transport techniques were performed: long-range transport (LRT) modeling and mass-balance modeling. In support of these modeling analyses, an emissions inventory of acid precursors was prepared for Florida sources. For out-of-state regions, the analyses relied on pre-existing databases. The period of study was from September 15, 1982, through September 15, 1983.

In this study, an existing LRT model was modified for Florida-specific conditions to evaluate temporal and spatial estimates of sulfur oxide ($SO_x$) concentration/deposition fields against observed data in order to improve model estimates, and assist in the interpretation of monitoring data.

After extensive literature reviews, the Eastern North American Model of Air Pollution (ENAMAP) developed for the U.S. Environmental Protection

Agency (EPA) was selected as the LRT model that would provide the necessary components that could be modified and adapted to the southeastern United States. Extensive technical, logical, and editorial modifications were made to ENAMAP and its meteorological preprocessor program WNDFLD to adapt the model to Florida. In addition, programs were also developed to process the necessary emission, terrain, and atmospheric stability data into a format acceptable to ENAMAP.

The development, diagnostic applications, and evaluations of LRT models are necessary to determine their limitations and assist in the interpretation of observational data. However, the state of the art in LRT modeling has not progressed sufficiently to accurately predict concentration and deposition fields over the model domains, i.e., eastern United States. Inherent limitations in simulating the complex physical and chemical processes in the atmosphere exist in LRT models and have not been overcome through rigorous verification and validation studies. As a result, any estimates of concentration and deposition fields using LRT modeling should be considered preliminary and should not be used as the basis for the development of emission strategies. Indeed, the process of modifying and correcting ENAMAP and associated input data reinforced this observation. Currently, major efforts are being implemented and planned by national research groups [e.g., Electric Power Research Institute (EPRI), EPA] to validate certain LRT model results.

The mass-balance technique, as used in this study, is to assess the relative contribution of in-state and out-of-state sources of acid precursors to the observed precipitation acidity in Florida. In this technique, estimates of sources, sinks, import, and export of $SO_x$ and nitrogen oxides ($NO_x$) are combined to form the basis of a mass balance model for Florida. Sources and sinks of $SO_x$ and $NO_x$ were estimated using the emissions inventory developed for the LRT modeling effort and acid deposition monitoring data, respectively. Air mass trajectory calculations coupled with ambient air monitoring data were then used to estimate import and export of $SO_x$ and $NO_x$. The National Oceanic and Atmospheric Administration (NOAA)-Atmospheric Transport and Deposition (AT^D) model was selected to perform the trajectories and was modified to use meteorological database available to estimate transport over the Gulf of Mexico and Atlantic Ocean. In addition, coding errors were corrected. From this analysis, the mass-balance model was constructed.

The results of the mass-balance modeling are limited by the accuracy of trajectory analyses as well as estimates of dry depositon across the state. Such limitations make the interpretation of mass-balance model results only an inferential estimate of source contributions.

The results of the data analysis and modeling efforts indicate the following findings for the study period:

- The total anthropogenic statewide $SO_2$ and $NO_x$ emissions, including point and area sources, are approximately 937,000 and 810,000 tons per year (tons/year), respectively. For $SO_2$ emissions, the emissions from point sources contributed 91 percent to the total, with the contribution from utilities accounting for 68 percent of the total emissions. The quantity of $NO_x$ emissions from point sources was 52 percent of total emissions which was similar to the quantity from area sources (48 percent of total $NO_x$ emissions). Utility sources accounted for 32 percent of total $NO_x$ emissions.

- Preliminary results from field monitoring indicate that biogenic sulfur emissions are from approximately 1 to 5 percent of total emissions.

- From ENAMAP modeling, Florida anthropogenic sources were estimated to account for 66 percent of sulfur deposition in Florida, and out-of-state sources were estimated to account for

34 percent. Florida utilities were estimated to account for 44 percent of the sulfur deposition in Florida. Florida sources are not an important contributor to sulfur deposition in any out-of-state region, contributing at most 7 percent of all sulfur deposited in any state, about 2 percent to the southern Appalachians, and less than 1 percent to the Adirondacks.

- Mass-balance modeling indicated that anthropogenic sources located in Florida contribute 50 percent of the $SO_x$ deposition. Utility sources in Florida contribute 35 percent of the $SO_x$ deposition. For $NO_x$, anthropogenic sources in Florida were estimated to contribute 53 percent of $NO_x$ deposition; utility sources in Florida were estimated to contribute 17 percent of total $NO_x$ deposition. There are, however, inherent errors which would directly translate to uncertainties in the calculated contributions. The exact magnitude of individual errors is not known, and their cumulative effect may be quite large.

- Taken together, the LRT and mass-balance modeling suggest that a major portion of Florida's acidity is attributable to out-of-state sources (about 40 percent). The estimated contribution of Florida utilities to total acidic deposition in Florida is about 30 percent. Area (vehicular) sources and other point sources were estimated to contribute about 15 percent each.

## ECOLOGICAL EFFECTS

The objective of the ecological effects research was to assess the response and potential sensitivity of aquatic and terrestrial resources within Florida to acid deposition and to assess the potential for effects on manmade material. In order to accomplish this objective, a series of literature, process-oriented, direct-response experimental, and modeling studies was performed. From January 1981 through June 1985, the research included:

1. Review of literature on the ecological and material effects of acidic deposition;
2. Assessment of the geophysical distribution of soils and lakes with equivalent buffering characteristics;
3. Performance of sulfate adsorption experiments in selected soils;
4. Evaluation, through available data, of the geographical distribution of fish and pH;
5. Performance of experiments on buffering characteristics of selected lake sediments;
6. Performing aluminum solubilization experiments with selected lake sediments in response to pH;
7. Determination of the effects of foliar applications of simulated acidic precipitation on slash pine, citrus, and tomato;
8. Performance of a 1-year study of the effects of simulated acid precipitation on the soil chemistry and microbiology of the Lake McCloud watershed;
9. Examination of productivity and pH relationships in selected Florida softwater lakes;
10. Analysis of the role of sulfate dynamics in alkalinity production; and
11. Development of a diagnostic model for lake acidification in Florida.

Through an integration of the results from these studies, the following major conclusions were derived:

- Significant biological effects are not likely to occur in Florida lakes unless lakewater pH levels are depressed below approximately pH 4.0. As a general class, lakes with the greatest likelihood for becoming acidified to these levels or below are seepage lakes which, by definition, have hydrologic budgets dominated by precipitation directly to the lake surface. Seepage lakes potentially sensitive to acidic deposition may be further defined as those with (1) extremely dilute lakewaters with low acid-neutralizing capacity (ANC) and dissolved organic carbon (DOC), and (2) watershed soils dominated by low cation exchange capacity (CEC), low base saturation, and minimal ability to adsorb sulfate. Current estimates indicate an upper-limit estimate of approximately 2,000 out of Florida's 7,600 lakes are seepage lakes.

- The National Lake Survey (NLS) conducted by EPA estimates that approximately 50 percent of the seepage lakes located in Florida and southeast Georgia are relatively colored. Organic acids (which impart the yellow-brown color characteristic of colored waters) can contribute measurably to the pH and ANC regime of softwater lakes and, if present in sufficient quantities, will constitute the predominant buffering system. The magnitude of the effect of organic acids on lakewater pH depends on (1) the amount of DOC derived from decaying vegatation in the watershed exported to the lake, and (2) the degree of neutralization of DOC inputs as a result of ion exchange and weathering reactions with watershed soils and lake sediments. In addition, organic acids can modify lake sensitivity to acidic deposition by forming stable complexes with aluminum and reducing its toxicity to aquatic organisms. The magnitude of these effects in Florida lakes, however, is virtually unknown and requires further analysis.

- Watershed influences (via ground water or seepage inputs) are important contributors to the ion balance and chemistry of seepage lakes although the hydrologic influence is generally small (approximately 10 percent). The amount of seepage to seepage lakes in general is governed by the difference between evaporation and precipitation. Lakes characterized by greater differences in evaporation and precipitation generally receive more inseepage and thus more ANC from the watershed compared to lakes which receive greater amount of precipitation.

- Internal or biogeochemical processes resulting in the removal of $H^+$, $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ also appear to contribute significantly to the ANC and pH dynamics of seepage lakes. The extent and rate at which seepage lakes may be influenced by rainfall pH thus integrates in-lake processes, hydrologic, and watershed factors as well as deposition.

- The seepage lakes likely to be most susceptible to acidic deposition are located in the western highlands of the panhandle and the highlands of north-central Florida (see Figure 6). This perceived differential in sensitivity reflects several factors:

  1. Total (wet) deposition of $H^+$ and the potentially acid specie $NH_4^+$ in the panhandle and north-central Florida exceeds total deposition in south-central Florida by 60 percent or more.

  2. Atmospheric deposition of fine calcareous particles is hypothesized to be a relatively more significant source of acid neutralization in south-central Florida compared to more northern portions of the state.

  3. Regional gradients in precipitation and evaporation suggest that ground water inputs constitute a less significant fraction of the hydrologic budget of seepage lakes in the panhandle compared to south-central Florida. This implies comparatively lower ANC contributions from the watershed in panhandle lakes.

  4. Preliminary survey results indicate that DOC (or organic acid) and ANC concentrations are lower in panhandle seepage lakes compared to south-central Florida seepage lakes.

- Limited historical data suggest that changes symptomatic of progressive lake acidification may have occurred in several clear and relatively undisturbed seepage lakes in north-central

Florida. Apparent declines in ANC and pH accompanied by concommitant increases in nonmarine sulfate have been noted. However, the actual significance of these apparent historical trends is uncertain for several reasons. For each of these parameters, the magnitude of the change is rather small and approximates the limits of analytical uncertainty. Differences in analytical techniques for sulfate and ANC that have evolved with time are biased toward overestimation of any apparent historical change in concentration of these constituents. The influence of changes in lake levels due to normal variations in precipitation is also unclear.

- Several surveys of a limited number of Florida lakes indicate that the diversity (or numbers of species) of phytoplankton, zooplankton, and macrophytes is correlated with pH; i.e., lakes with higher pH tend to have greater diversity of these organisms compared to more acidic lakes. These correlations infer that, for a particular lake, some reduction in diversity is likely to occur with a reduction in lakewater pH. Based on similar evidence, minor declines in the numbers of species of Florida fish are probable with reductions in surface water pH to approximately 4.0. Limited acute toxicity studies indicate significant biological effects are not likely occur in Florida lakes unless lakewater pH levels are depressed below approximately pH 4.0. However, the limited availability of appropriate data necessitates further research before the biotic response to incipient changes in Florida seepage lakewater chemistry attributable to acidic deposition can be conclusively established.

- Certain soils in Florida have limited ability to neutralize acidic inputs. These soils, which predominate in the highlands and ridge physiographic regions of the state (see Figure 6), are

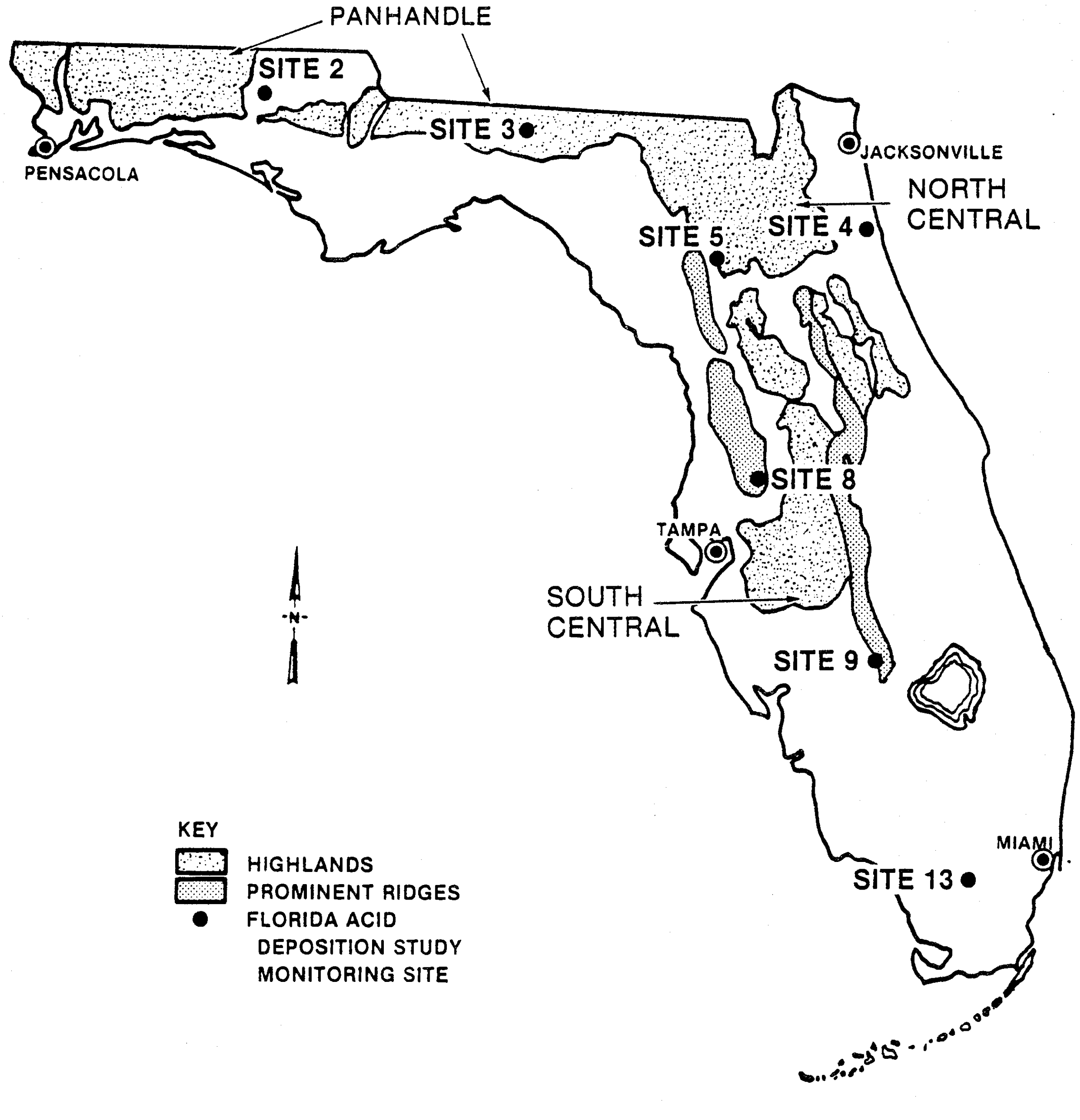

**Figure 6**
**HIGHLANDS AND PROMINENT RIDGE REGIONS IN FLORIDA**

SOURCES: Florida State University, 1981; ESE, 1986.

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inherently acidic in nature, resulting from extensive weathering over thousands of years. Thus, at current levels of acidic deposition, increases in acidification of these soils over the next several decades is not likely to be measurable.

- Preliminary evidence has documented declines in growth rates of pine forests in the southeast. Causes have not been conclusively established and may include drought, pests, disease, management practices, and air pollution including ozone as well as acidic deposition.

- Within Florida over the past decade, net annual growth of pine has increased in contrast with the general decline observed in other regions of the southeast. Coincident with increases in growth in Florida has been an observed increase in pine mortality rates which may be attributed to diseases such as fusiform rust. It is not possible to predict the potentail effect of acidic deposition on forests in Florida until the reasons for the forest declines in other regions are better understood.

- Current levels of acidity are not likely to have a significant effect on crop yields in Florida.

- Overall, acidic deposition can potentially increase metal corrosion and materials damage rates; however, the magnitude of these incremental effects might be immeasurably low when the influence of a variety of environmental factors (e.g., humidity, sunlight, sea spray) is taken into account.

- There is little information available to support an estimate of the effects of acidic deposition on exposed cultural materials.

The available studies indicate that, under Florida's climatic conditions, current levels of acidic deposition probably cause small, and perhaps unobservable, effects.

## RECOMMENDATIONS FOR FUTURE RESEARCH

Significant progress was made in the research efforts on the magnitude, variability, effects, and sources of the acidic deposition phenomenon in Florida. Because of its complexity, however, uncertainies exist in the current knowledge which suggest areas of additional research to those interested parties who may wish to extend the efforts made by this study (see Subsection 5.5).

# 1.0 INTRODUCTION

This report is a synthesis of information developed in all phases of the Florida Acid Deposition Study. Rather than merely recapitulate the findings made in previous study reports, this effort first merges databases across phases and then across disciplines to provide answers to key study questions (see Subsection 1.2). This section presents a brief history on how the study began, the objectives of the major program areas, and the general scope, organization, and schedule for the study. Sections 2.0, 3.0, and 4.0 present the methods and results of each of the three study program areas: acid deposition monitoring, source attribution, and ecological effects. The final two sections (Sections 5.0 and 6.0) present an integrated assessment of the acidic deposition phenomenon in Florida and the final study conclusions.

## 1.1 STUDY BEGINNINGS

The "acid rain" issue has evolved in North America since the mid-1970s. Initially, the greatest concern over the potential impacts of acidic deposition was for aquatic systems, especially in the northeastern United States and Canada. As the research on its potential effects broadened, it became evident that acidic deposition may be one of many factors that can act singularly or synergistically to cause deleterious effects. In addition, issues such as the impact to forests and materials have eclipsed, or at least equaled, the concern over aquatic systems. Although some researchers have attempted to address these issues, their efforts have not been successful in clearly providing the information necessary to support policy decisions regarding "acid rain."

Recognizing the urgency of the "acid rain" issue and the need to address research, the United States Congress began a comprehensive study of acidic deposition, the National Acid Precipitation Assessment Program (NAPAP). Under the auspices of the Interagency Task Force on Acid

Precipitation, a national research effort has been launched into the sources, deposition mechanisms, effects, and control options of acid deposition in North America. The NAPAP agenda also calls for a preliminary damage assessment in 1985 and a series of integrated assessments in 1987 and 1989 to guide both research and policy initiatives. Overall funding for NAPAP was \$11 million during fiscal year 1980 and was expected to exceed \$75 million for fiscal year 1989 (NAPAP, 1984). In addition, a memorandum of intent (MOI) has been signed with Canada that may lead to further control of sulfur oxides ($SO_x$) and nitrogen oxides ($NO_x$), the main precursors to acidic deposition (Carter, 1979). The MOI agreement also resulted in an attempted assessment of transboundary pollution transport and effects. The findings of this evaluation, based on available data through 1982, showed that much additional research was necessary, especially in the areas of ecological effects and source-receptor modeling.

The electrical utility industry, through its research arm, the Electric Power Research Institute (EPRI), initiated a comprehensive research program in the late 1970s to provide scientific data in many key research areas such as atmospheric chemistry, transport, and deposition; aquatic processes; crop and forest production; materials and crop damage assessments; and tools for policy decision processes. Through 1984, EPRI's research efforts expended \$84 million and was budgeted for \$77 million from 1984 through 1989. The research is designed to closely coordinate with the utility industry and federal government while not duplicating current studies.

Acidic precipitation research was initiated in Florida by Brezonik and co-workers under U.S. Environmental Protection Agency (EPA) sponsorship (Brezonik, 1983). Their studies, which collected data from a network of 25 monitoring stations throughout Florida, suggested that the acidity of rainfall has increased markedly since 1956. In addition, a study of 20 softwater lakes (13 lakes in northern peninsular Florida and 7 lakes in south-central peninsular Florida) suggested that pH decreased by up to 0.5 unit in some of the northern softwater lakes, whereas no trend was observed in the more southern lakes (Brezonik, 1983). However, their results indicated that acidic conditions in the lakes do not have major impacts on community structure.

The results from these Florida studies prompted Florida Department of Environmental Regulation (DER) recognition of the potential for environmental effects from acidic deposition in Florida. Notwithstanding the work performed by Brezonik _et al_. (1983), sufficient information was not available to assess the impact of acidic precipitation in Florida.

To address this information gap, the Florida Electric Power Coordinating Group, Inc. (FCG) Executive Committee approved the initiation of the Florida Acid Deposition Study in November 1980. The overall objective of the study was to assess and/or develop the information needed on acidic deposition concerning its magnitude, variability, sources, effects, and control options in Florida. A study was deemed necessary since the climate, meteorology, soil conditions, and terrestrial and aquatic resources of the Florida peninsula are different from most of the rest of the eastern United States. The bulk of research on acidic deposition had been, and is continuing to be, performed in the northeastern United States; therefore, the transferability of results from such studies may be questioned if their results are applied to Florida. Therefore, having site-specific data would directly assist in drawing conclusions related to acidic deposition in Florida.

Beginning in January 1981, the study was planned in four major phases. Phase I of this four-phased study was initiated in January 1981; Phase II was initiated in September 1981; Phases III and IV were initiated in September 1982 and September 1983, respectively. Phase IV was completed in June 1985.

The study was designed with three major research areas:

1. Acid Deposition Monitoring Program,
2. Source Attribution Program, and
3. Ecological Effects Program.

## 1.2 STUDY AND PROGRAM OBJECTIVES

The overall objective of the Florida Acid Deposition Study was:

> To assess and/or develop the information needed on acid deposition concerning its magnitude, variability, sources, effects, and control options in Florida.

To accomplish this overall objective, three major program areas were established. For each of these major program areas (i.e., acid deposition monitoring, source attribution, and ecological effects), separate objectives were developed and pursued throughout the course of the study. These objectives were:

1. Acid Deposition Monitoring:
    - a. Quantify the current levels of acidity and related chemical species in wet deposition at regionally representative sites in Florida;
    - b. Identify the spatial and temporal variability of these species over a 3-year period;
    - c. Provide a limited set of complementary data to the electric utility industry's Utility Acid Precipitation Study Program (UAPSP) study; and
    - d. Establish the accuracy, precision, and overall uncertainty of the data obtained.
2. Source Attribution:
    - a. To determine the relative contribution of Florida's electric utility industry to atmospheric deposition of acidity and related chemical species in Florida and neighboring states.
3. Ecological Effects:
    - a. To assess the response and potential sensitivity of aquatic and terrestrial resources within Florida to acid deposition, and
    - b. To assess the potential for material effects.

For each of the program areas, key research questions evolved and were refined to focus on meeting the study's overall objective. In addition, it was desired to address concerns expressed by DER. The objective of this Final Report, which integrates the findings of the study, is to answer the key research questions presented in Table 1.2-1.

At the study inception, a fourth program, alternate emission reduction scenarios, was planned. The objective of this program was to assess the Florida-specific costs and benefits of various federal, state, and local regulations aimed at reducing acidic deposition. During the course of the study, a joint effort undertaken by DER and the Florida Public Service Commission (PSC), with input from Florida electric utilities, addressed the costs of several potential federal regulations. The results of this combined effort can be found in Acid Deposition Issues (DER, 1984). This DER report serves as a framework from which generic costs can be estimated for certain emission reduction scenarios that were proposed for national legislation. Because of this effort, further work in this program area was not performed and is not discussed in this report.

## 1.3 STUDY SCOPE, PROGRESSION, ORGANIZATION, AND PEER REVIEW

The planning for the Florida Acid Deposition Study was initiated in mid-1980 by developing an overall scope with assistance of EPRI, EPA, and other research groups. Assistance was sought in the early design of the study in order to:

1. Use recognized sampling, analytical quality control, and quality assurance procedures;
2. Perform research that was compatable with other existing and planned research efforts;
3. Focus individual studies on Florida-specific information needs; and
4. Develop databases that would be accepted by the research community.

Table 1.2-1. Key Research Questions for Florida Acid Deposition Study Program Areas

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Acid Deposition Monitoring Program (Acidic Deposition in Florida)

1. How do the field collection and analytical methods influence the observed wet-only acid deposition levels and related chemical species in Florida?
    a. What is the overall quality of field measurements?
    b. What is the accuracy of laboratory data?
    c. What is the precision of laboratory data?
    d. What are the effects of contamination from buckets, filters, and overall sample handling?
    e. What is the variability in, and differences between, the following:
        1) Precipitation amounts collected in collocated rain gages and wet-fall buckets,
        2) Precipitation amounts collected in collocated rain gages versus wet-fall buckets,
        3) Weekly versus weekly (W/W) collocated monitoring,
        4) Daily versus weekly (D/W) collocated monitoring, and
        5) Daily versus daily (D/D) collocated monitoring?
    f. What are the differences between field and laboratory pH?
    g. What is the overall uncertainty in the data?

2. What are the current spatial patterns of wet-only acidic deposition and major chemical species in Florida?
    a. What are the statistically significant patterns in concentration fields?
    b. What are the statistically significant patterns in deposition fields?
    c. What are the spatial patterns in air chemistry?

3. What are the likely current values of total acidic deposition in Florida?

4. What are the monthly, seasonal, and near-term trends of wet-only acidic deposition and major chemical species in Florida?
    a. What are the statistically different temporal relationships in precipitation chemistry by site, by group, and by season?

5. What are the chemical and physical relationships between acidity of Florida's rainfall and (1) the major cations and anions in rainfall, (2) rainfall amount, and (3) ambient air concentrations?
    a. What are the chemical and physical relationships between laboratory hydrogen cation ($H^+$) and the major cations and anions found in precipitation?
    b. What are the relationshps between precipitation chemistry and rainfall amount?

Table 1.2-1. Key Research Questions for Florida Acid Deposition Study Program Areas (Continued, Page 2 of 3)

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   c. What are the potential acids and bases in Florida's precipitation?
   d. What are the interrelationships in air chemistry?
   e. What are the relationships between precipitation and air chemistry?

6. What are the relationships between observed precipitation and air chemistry and meteorological conditions in Florida?
   a. How does precipitation chemistry vary as a function of synoptic meteorological conditions?
   b. How does ambient air chemistry vary as a function of synoptic meteorological conditions?

Source Attribution Program (Relationships of Source to Acidic Deposition in Florida)

1. What are the current anthropogenic and biogenic sources of acid precursors found in Florida's atmosphere?
   a. From Florida utilities?
   b. From nonutilities in Florida?
   c. From sources located outside of Florida?
   d. From biogenic sources?

2. What is the uncertainty in estimating the predicted impact of Florida anthropogenic emission sources on current levels of acidic deposition?
   a. How do initial model results compare to observational data?
   b. What changes were evaluated to improve model comparisons with observational data?
   c. What is the sensitivity of such changes to model results?
   d. Can such changes be supported?
   e. How did the adjusted model compare with observational data?
   f. Can further adjustments of the model be supported?

3. How do Florida's current anthropogenic emission sources contribute to current levels of acidic deposition in Florida and neighboring states?

Ecological Effects Program (Effects of Acidic Deposition on Ecological Resources in Florida)

1. What are the chemical/physical relationships between acidic deposition and lake sensitivity and which lakes are potentially sensitive to current levels of acidic deposition?
2. What are the chemical/physical relationships between acidic deposition and soil sensitivity and which soils are potentially sensitive to current levels of acidic deposition?

Table 1.2-1. Key Research Questions for Florida Acid Deposition Study Program Areas (Continued, Page 3 of 3)

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3. How are lakes likely to respond to current levels or changes in current levels of acid deposition?
4. How are soils likely to respond to current levels or changes in current levels of acid deposition.
5. What are the long-term trends in soil chemistry in Florida?
6. What are the long-term trends in lake chemistry in Florida?
7. What are the potential effects of current levels of acidic deposition to agricultural crops and terrestrial systems? In addition, what are the responses of agricultural crops and terrestrial systems to changes in deposition?
8. What are the potential effects of acidic deposition and precursor emissions to manmade materials in Florida?
9. How are changes in acidic deposition levels and precursor emissions likely to influence manmade materials?

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Source: Environmental Science and Engineering, Inc. (ESE), 1986.

As previously discussed, the overall study was performed in four major phases. A phased approach was considered necessary because it provided the flexibility to modify plans to meet the study objectives and allowed interim progress reports to be issued. The general scope and progression of the study during each phase are presented in Table 1.3-1 and Figure 1.3-1. Initially, efforts focused on developing a regionally representative monitoring network and performing comprehensive literature searches. As the study progressed, monitoring and studies were performed on an annual basis, with data analysis and report preparation generally taking an additional 10 months after the monitoring period ended.

The study plans for each phase were sent to DER, EPA (Region IV and Research Triangle Park), and EPRI for review and comments to ensure the study's consistency with existing state, federal, and other research programs. Beginning with Phase III, draft study reports were submitted for peer review by recognized experts in the field of acidic deposition research (see Authors and Contributors) and provided to DER for review. All comments received from these reviews were considered carefully and incorporated into final reports. Sixteen major documents were issued during the course of the study (see Table 1.3-2).

In February 1985, a peer review panel was brought together by DER to evaluate the study and recommend potential future studies the state could undertake. The findings of that panel can be found in the DER report titled "Report of the Florida Acid Research Peer Review Panel" (DER, 1985).

Table 1.3-1. General Scope of the Florida Acid Deposition Study

| Program | Phase I | Phase II | Phase III | Phase IV | Final Report |
|---|---|---|---|---|---|
| Acid Deposition Monitoring | 14-station weekly acid deposition monitoring network operated from July 1, 1981 to mid-Sept. 1981 | 14-station weekly network operated from mid-Sept. 1981 to mid-Sept. 1982; parameters added | 9-station daily network; operated from mid-Sept. 1982 to mid-Sept. 1983; air quality monitoring initiated at all sites | 7-station network; 3 daily and 4 weekly, operated from mid-Sept. 1983 to mid-Sept. 1984, air monitoring continued | Analysis of data for all phases |
| Source Attribution | Comprehensive literature search | Review available model results; perform 1980 emissions inventory for $SO_x$ and $NO_x$ | Evaluation and selection of source attribution techniques; development of Phase III emissions inventory | Implementation of two source attribution techniques; continue developing emissions inventory; biogenic sulfur emissions study* | Development and evaluation of source attribution techniques; performed illustrative model calculations |
| Ecological Effects | Comprehensive literature search | Evaluation of the geographical distribution of lake and soil chemistry | Four major studies performed: sulfate adsorption in surficial soils; buffing capacity of lake sediments; geographical distribution of Florida fish species; simulated acidic deposition effects on certain terrestrial plants | Four major studies performed: Lake McCloud soil studies; nutrient and pH relationships in softwater lakes; sulfate reduction/adsorption in lake sediments; and diagnostic model development for lake acidification in Florida | Integration of studies performed in Phases II through IV with current literature |
| Emissions Reduction Scenarios | No major activity | Control technology review; preliminary cost estimates | Participation in DER report: "Acid Deposition Issues" | No additional activities required | No additional activities required |

*To be completed in mid-1986.

Source: ESE, 1986.

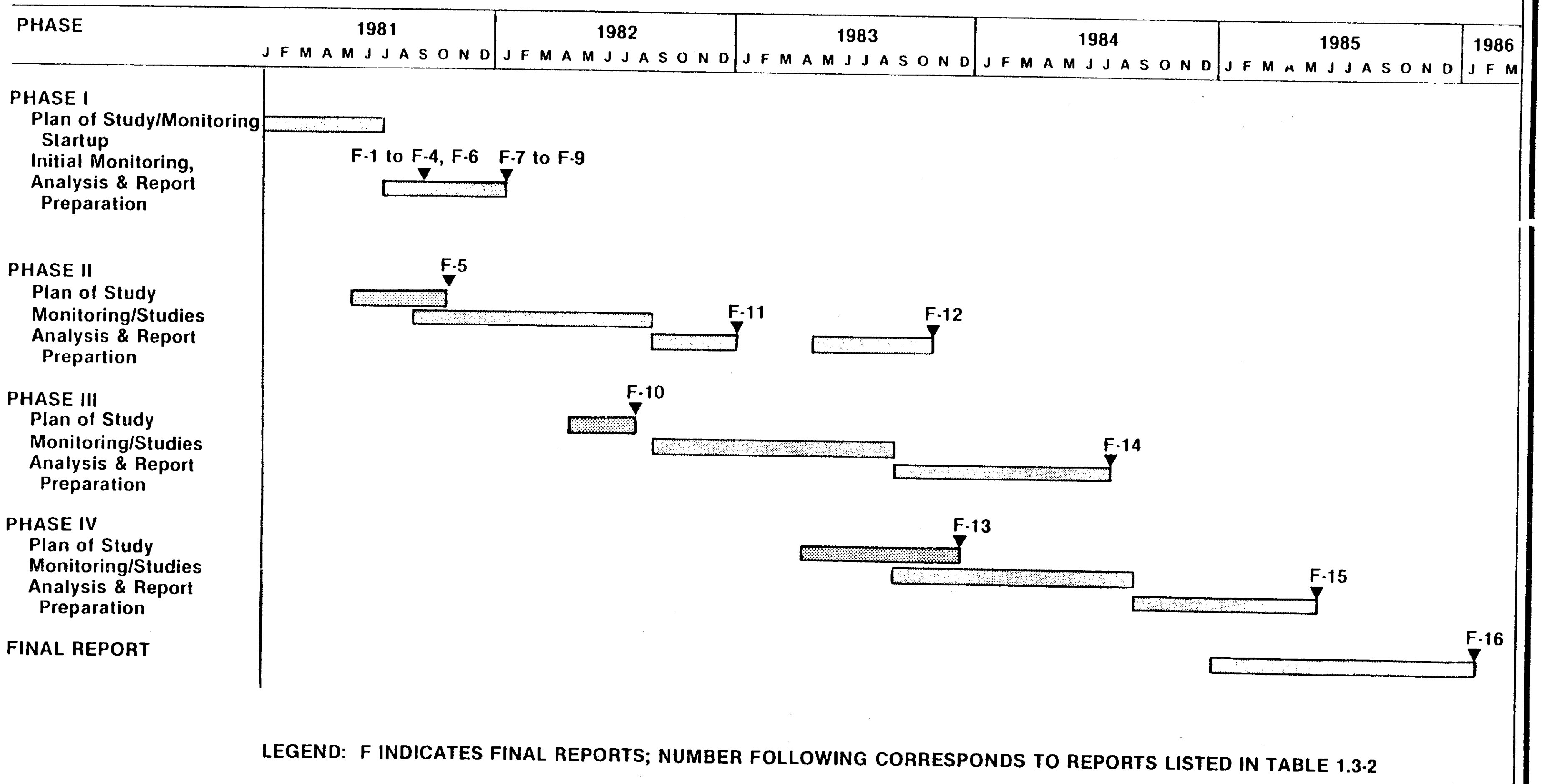

Figure 1.3-1
SCHEDULE AND MAJOR MILESTONES FOR THE FLORIDA ACID DEPOSITION STUDY

ENVIRONMENTAL SCIENCE
AND ENGINEERING, INC.

Table 1.3-2. Major Reports for the Florida Acid Deposition Study

| Report Number | Title | Date Issued |
|---|---|---|
| 1 | Plan of Study | September 1981 |
| 2 | Field Operator's Manual | September 1981 |
| 3 | Laboratory Operations Manual | September 1981 |
| 4 | Project QA Plan | September 1981 |
| 5 | Plan of Study--Phase II | October 1981 |
| 6 | Phase I Summary Report | September 1981 |
| 7 | Monitoring Report: Phase I Summary | January 1982 |
| 8 | Source Attribution: Phase I Summary | January 1982 |
| 9 | A Literature Review of the Ecological and Material Effects of Acid Deposition | January 1982 |
| 10 | Phase III Plan of Study | August 1982 |
| 11 | Phase II Report | January 1983 |
| 12 | Phase II Report Addendum | November 1983 |
| 13 | Phase IV Plan of Study | December 1983 |
| 14 | Phase III Report | August 1984 |
| 15 | Phase IV Report | June 1985 |
| 16 | Final Report--A Synthesis of the Florida Acid Deposition Study | March 1986 |

Source: ESE, 1986.

## 1.4 REFERENCES CITED

The following references are cited in Section 1.0.

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# 2.0 ACID DEPOSITION IN FLORIDA

## 2.1 INTRODUCTION AND OBJECTIVES

### 2.1.1 HISTORICAL AND NATIONAL PERSPECTIVE

Although acidic deposition was recognized in England as far back as the mid-1800s, it was not until the late 1940s and mid-1950s that precipitation chemistry networks were established in Europe and North America, respectively (Smith, 1872; Cowling, 1982; Cogbill, 1976). In Europe, Barrett and Brodin (1955) reported the pH of precipitation from a 19-station network (1953 to 1954) located in Sweden and an expanded network of 44 stations (November through December, 1954) covering Norway, Denmark, Finland, and Sweden. Data from this latter period indicated monthly pH values from 4.7 near the coast to 6.0 inland[1]. Both anthropogenic and natural (maritime) sources were considered potentially responsible for observed acidity.

In the United States, Junge and Werby (1958) measured major ions [sulfate anion ($SO_4^{-2}$), nitrate anion ($NO_3^-$), chloride anion ($Cl^-$), ammonium cation ($NH_4^+$), sodium cation ($Na^+$), potassium cation ($K^+$), and calcium cation ($Ca^{+2}$); magnesium cation ($Mg^{+2}$) and $H^+$ were not measured] in precipitation at 67 nationwide stations from July 1955 to July 1956. During the period 1960-1966, samples were collected at 33 stations nationwide operated by the U.S. Public Health Service and the National Center for Atmospheric Research (NCAR) (Lodge et al., 1968). The U.S. Geological Survey (USGS) operated a 27-station network from August 1962 to July 1963 in eastern North Carolina and southeastern Virginia and an 18-station network from mid-1965 to 1966 [Environmental Research and Technology (ERT), 1980]. The data from these networks were evaluated by Cogbill and Likens (1974) by superimposing hand-drawn isopleths on maps

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[1] pH is defined as $-\log_{10} (H^+)$, where $H^+$ is the hydrogen ion activity in equivalents per liter (eq/L) (Weast, 1984). The pH level of pure water in equlibrium with atmospheric carbon dioxide ($CO_2$) is approximately 5.6.

of annual volume-weighted precipitation pH for the periods 1955-1956 and 1965-1966. The pH values from 1955-1956 and 1965-1966 were calculated based on the ionic balance principle. A comparison of the pH isopleth maps for the two time periods suggested to Cogbill and Likens that precipitation acidity in northeast United States had increased since the mid-1950s to the mid-1960s, and the area receiving acidic precipitation (i.e., pH <5.6) had likewise increased (e.g., the 1965-1966 isopleths of pH 4.7 appeared to have increased in area over those calculated for 1955-1956.) A comparison of observed pH for 1972 and 1973 obtained from 8 stations in the eastern United States and 12 stations in southeastern Canada (Kramer, 1975; Cogbill and Likens, 1974), suggested to Cogbill and Likens that the spread of acidic precipitation again increased from the 1960s. In a subsequent analysis, Likens and Butler (1981) compared the 1955-1956 and 1965-1966 pH isopleth maps with one developed for 1975-1976 and concluded that the extent and intensity of precipitation acidity (as reflected in pH) had again increased between the mid-1960s and mid-1970s.

The existence of a trend in precipitation pH (Cogbill and Likens, 1974; Likens and Butler, 1981) has been challenged in several studies. Stensland and Semonin (1982) examined the concentrations of major ions in the 1955-1956 precipitation and concluded that various metals, especially calcium and magnesium, were present at anomalously high levels. High concentrations of calcium and magnesium in 1950s precipitation were attributed to intense duststorms across the Plains States as well as drought conditions in the southeast (Stensland and Semonin, 1982). Following adjustment of pH values for high calcium and magnesium concentrations, and with an empirical correction factor to improve agreement between measured and calculated pH values, the authors produced pH isopleth maps indicating similar distribution of pH for the periods 1955-1956 and 1980. Finally, Stensland and Semonin (1982) suggested that any increases in precipitation acidity between the 1950s and the 1970s were more likely due to a regionwide decrease in concentration of basic cations rather than to an increase in concentration of acidic anions (e.g., $NO_3^-$ and $SO_4^{-2}$) which were insufficient to account for apparent increases in $H^+$.

Hansen et al. (1981) analyzed the precipitation collection, handling, and analysis methodologies employed by each network in operation during 1955-1956, 1965-1966, and 1973-1975 and concluded that significant differences in reported pH values could be attributed both to uncertainties in calculation of pH and the lag time in analyzing pH. Moreover, the authors suggested that meteorological variability from year to year could very likely obscure point estimates of historical trends based on only 3 years of precipitation data collected over 3 decades.

Hansen et al. (1981) also concluded that a small downward trend in precipitation pH (approximately 0.25 unit) may have occurred in the southeast between the 1950s and 1980s. Rather than attribute this to the availability of basic cations, Hansen et al. (1981) suggested that substantial increases of $NO_3^-$ in precipitation may be the cause. Similarly, Barrie and Hales (1984) have recently concluded that increased $SO_4^{-2}$ and $NO_3^-$ concentrations since the 1950s have increased the acidity of precipitation by 30 to 37 micro-normal (µN) in the southeastern United States.

### 2.1.2 HISTORICAL PRECIPITATION CHEMISTRY FOR FLORIDA

In the 1950s, several of the stations measuring wet-only precipitation chemistry were located in Florida (Junge, 1958). The first comprehensive precipitation monitoring network established in Florida consisted of 21 bulk collectors and 4 wet/dry collectors (Brezonik et al., 1980; Brezonik et al., 1983). Comparing the Junge data with data taken from five bulk-precipitation collectors (collector open to the atmosphere at all times) during 1979, Brezonik et al. (1980) concluded that the acidity of rainfall in Florida had increased markedly in the past 25 years, and the average $SO_4^{-2}$ and $NO_3^-$ concentrations had increased by factors of 1.6 and 4.5, respectively. Although the collection procedures between these methods differed (i.e., wet-only compared to bulk), Brezonik et al. (1980) concluded that the differences in collector type did not explain the apparent increase in $SO_4^{-2}$ and $NO_3^-$ from 1956 to 1979. The studies by Brezonik et al. (1980) also suggested a general north-to-south gradient of pH, $SO_4^{-2}$, and $NO_3^-$ concentrations (i.e., decreasing acidity and $SO_4^{-2}$ and $NO_3^-$ concentrations from north Florida to south Florida).

The first reported measurements of wet-only precipitation pH were made near Tallahassee in 1974 (Burton, 1977). From 1976 through 1981, three monitoring networks collected wet-only precipitation during different periods and in various parts of the state: the University of Florida (UF) network from 1976 through 1980, the National Aeronautics and Space Administration (NASA) network from 1977 through 1980, and the National Acid Deposition Program (NADP) network from 1980 through 1981. Results of some of these investigations (Table 2.1-1) suggest that precipitation pH, as measured in the laboratory, has generally remained stable during this period and the various monitoring efforts produce data which are generally consistent. At Tallahassee, the location with the longest time interval between measurements, the annual volume-weighted mean (VWM) pH was 4.53 in 1974 and 4.59 in 1980. At Gainesville, the site with the longest continuous period of analysis (1976 to 1981), annual pH values ranged from 4.51 to 4.66.

### 2.1.3 MONITORING PROGRAM OBJECTIVES

At the study inception, the primary objectives of the monitoring effort were to provide information necessary to:

1. Quantify the current levels of acidity and related chemical species in wet deposition at regionally representative sites in the State of Florida;
2. Identify the spatial and temporal variabilities of these species over a 3-year period;

Table 2.1-1. Summary of Historical VWM pH Data* for Florida Wet-Only Precipitation (Laboratory Measurements Only), 1974 Through 1981

| General Sampling Area | Time Period<br>1974 | 1976-77 | 1977 | 1978 | 1979 | 1980 | 1981 |
|---|---|---|---|---|---|---|---|
| Panhandle | | | | | | | |
| Jay | | | | | $4.63^{a}$ | $4.51^{b}$ | $4.52^{c}$ |
| Tallahassee-Monticello | $4.53^{d}$ | | | | | $4.59^{b}$ | |
| Northern Peninsula | | | | | | | |
| Bradford Forest | | | | | | $4.69^{e}$ | $4.65^{e}$ |
| Austin-Carey Forest | | | | | | $4.66^{e}$ | $4.76^{e}$ |
| Gainesville | | $4.53^{f}$ | | $4.66^{a}$ | $4.53^{a}$ | $4.54^{b}$ | $4.51^{c}$ |
| Cedar Key-Cross City | | | | | $4.51^{a}$ | $4.53^{b}$ | |
| Central Peninsula | | | | | | | |
| Apopka-Leesburg | | | | $4.57^{a}$ | | | |
| Tampa | | | | | | $4.53^{b}$ | |
| Orlando-University of Central Florida | | | $4.44^{g}$ | $4.47^{g}$ | $4.49^{g}$ | $4.54^{g}$ | $4.54^{g}$ |
| Kennedy Space Center | | | $4.70^{g}$ | $4.49^{g}$ | $4.60^{g}$ | $4.48^{g}$ | $4.40^{g}$ |
| Southern Peninsula | | | | | | | |
| Belle Glade | | | | $5.24^{a}$ | $5.49^{a}$ | | |
| Corkscrew Swamp | | | | | | $4.82^{b}$ | |
| Tamiami Trail | | | | | | $4.83^{b}$ | |
| Homestead | | | | | $4.95^{e}$ | $5.34^{e}$ | |

*VWM pH = $-\log_{10}[\Sigma(H^{+}_{i} \times R_{i}) \div \Sigma R_{i}]$, where $R_{i}$ = rainfall amount.

a = Brezonik _et al._, 1983.
b = Edgerton and Brezonik, 1981.
c = Edgerton, 1981.
d = Likens, 1976.
e = Peden, 1983.
f = Hendry and Brezonik, 1980.
g = Madsen, 1983.

Source: ESE, 1986.

3. Provide a limited set of complementary data to the electric utility industry's UAPSP study; and
4. Establish the accuracy, precision, and overall uncertainty of the data obtained (ESE, 1981c).

In addition to these four objectives, a major purpose of the monitoring program was to provide a body of useful precipitation and air chemistry data to the Source Attribution and Ecological Effects Programs. The Source Attribution Program, in turn, was designed to analyze the relationships between the various sources of acid precursors and the observed precipitation acidity (refer to Section 3.0). The Ecological Effects Program was designed to evaluate potential ecological effects of the observed deposition (refer to Section 4.0).

During the course of the study, the monitoring program evolved to focus efforts on meeting the study's objectives while modifying the network number, frequency, and type of monitoring to meet specific research needs. Quality assurance standards were maintained throughout the monitoring program to ensure that results from different years would be comparable.

Specific questions concerning precipitation and air chemistry in Florida were addressed during each phase of the monitoring program.

1. What is the accuracy, precision, and overall uncertainty of the data obtained?
2. What procedural and equipment factors influence data quality?
3. What are the spatial patterns in chemical composition and atmospheric deposition of acidity and related parameters in Florida precipitation?
4. What are the seasonal differences in the chemistry of precipitation and ambient air throughout Florida?
5. What chemical factors relate to (and presumably cause or mediate) precipitation acidity over Florida?

6. What are the relationships between ambient air concentrations and precipitation chemistry?

Each of these questions was addressed in detail in the phase reports listed in Table 1.3-2 and Figure 1.3-1 (specifically Reports 12, 14, and 15) and formed the underlying basis of the key research questions listed in Table 1.2-1 for the monitoring program.

### 2.1.4 PURPOSE AND ORGANIZATION

The purpose of this subsection is to address the key research questions outlined in Table 1.2-1 for the Acid Deposition Monitoring Program through the presentation and analysis of the data collected during the course of the study.

Subsection 2.2 presents a summary of the design of, and methods for, the precipitation and air monitoring network.

The findings of the monitoring program are discussed in six subsections: monitoring data overview (2.3), quality control/quality assurance (QA/QC) results (2.4), spatial patterns in precipitation/air chemistry (2.5), temporal variability in precipitation/air chemistry (2.6), relationships among chemical species in precipitation (2.7), and meteorological influences on precipitation/ air chemistry (2.8).

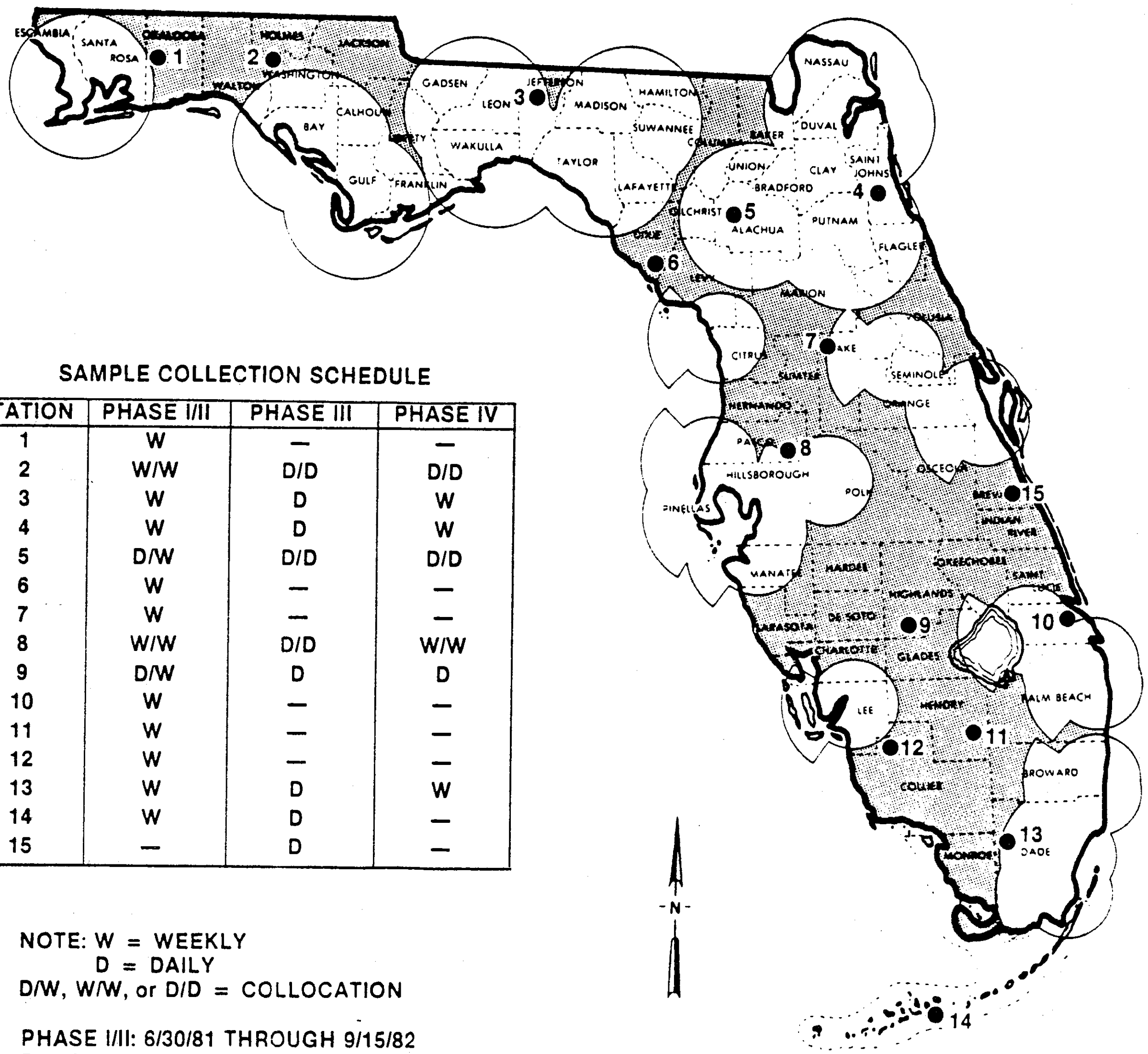
## 2.2 SUMMARY OF METHODS

This subsection provides a summary of the monitoring program. More detailed information can be found in Reports 1, 2, 3, 4, 5, 10, and 13 as listed in Table 1.3-2.

### 2.2.1 NETWORK DESIGN AND CONFIGURATION

The monitoring network was designed to provide a broad geographic coverage of the state which would address the principal monitoring program objectives and also to supply information on deposition and air quality to the Source Attribution and Ecological Effects Programs. The network design encompasses the following broad criteria: (1) the level and variability of acidic deposition to previously identified, potentially sensitive aquatic and terrestrial resources in the state, (2) the relationship between coastal proximity and precipitation chemistry, and (3) the historical database by providing continuity of monitoring at or near locations used in previous monitoring networks. Station locations and equipment configurations conformed to NADP criteria in terms of distances to nearby obstacles, roads, dwellings, and, with two exceptions, large point sources of $SO_x$ and/or $NO_x$ (NADP, 1982).

A 14-station monitoring network was established to meet the requirements of the monitoring program (see Figure 2.2-1). This original network began weekly (i.e., Tuesday-to-Tuesday) operation on July 1, 1981 with four stations instrumented for collocated W/W (Sites 2 and 8) and D/W (Sites 5 and 9) precipitation sampling. W/W collocation involved weekly collection of samples from two adjacent wet/dry precipitation samplers. D/W collocation involved weekly collection of samples from one sampler and daily collection from another sampler at the same site. The purpose of collocated sampling was to quantify: 1) the overall precision of precipitation measurements, and 2) the effects of collection frequency on precipitation chemistry.



**SAMPLE COLLECTION SCHEDULE**

| STATION | PHASE I/II | PHASE III | PHASE IV |
|---|---|---|---|
| 1 | W | — | — |
| 2 | W/W | D/D | D/D |
| 3 | W | D | W |
| 4 | W | D | W |
| 5 | D/W | D/D | D/D |
| 6 | W | — | — |
| 7 | W | — | — |
| 8 | W/W | D/D | W/W |
| 9 | D/W | D | D |
| 10 | W | — | — |
| 11 | W | — | — |
| 12 | W | — | — |
| 13 | W | D | W |
| 14 | W | D | — |
| 15 | — | D | — |

NOTE: W = WEEKLY
D = DAILY
D/W, W/W, or D/D = COLLOCATION

PHASE I/II: 6/30/81 THROUGH 9/15/82
PHASE III: 9/15/82 THROUGH 9/14/83
PHASE IV: 9/14/83 THROUGH 12/31/84

● FLORIDA ACID DEPOSITION STUDY MONITORING SITE

0 50 100 MILES

0 50 100 KILOMETERS

NOTE: CLEAR AREAS (e.g., DESIGNATED BY CIRCLES) ARE AREAS OF MAJOR $SO_2$ AND $NO_x$ SOURCES.

Figure 2.2-1
LOCATION OF MONITORING SITES AND POINT-SOURCE EXCLUSIONS ZONES

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The 14-station network provided broad geographic coverage of Florida and met the program's initial siting goals. Sites 1, 2, 3, 4, 5, and 6 provided coverage across the panhandle and northern portions of the state, while Sites 5, 7, 9, 11, and 13 provided coverage along the center of the Florida peninsula. Sites 5, 7, and 9 also were established to provide information on atmospheric deposition in the potentially sensitive ecological areas located within the Trail Ridge and Highlands lake district of north-central Florida, and Sites 11, 12, and 13 were established to provide similar information for the Florida Everglades. Sites 4, 6, 10, and 14 were established to assess coastal influences on precipitation chemistry, and Sites 5, 9, 12, and 13 were established for comparison with monitoring begun in the late 1970s by Brezonik et al. (1981).

Beginning in September 1982, the network was reduced to nine stations, including a new site (Site 15), and operated on a daily sampling schedule. The decision to reduce the number of monitoring sites was based on an evaluation of the first 15 months of monitoring data. Statistical analyses of these data indicated that, because of the degree of redundancy in the network, numerous sites could be eliminated without significantly impairing the ability to detect spatial patterns (ESE, 1983a). However, Site 15 was added for two reasons. First, this site would provide information on precipitation chemistry between two statistically different groups of sites: northern peninsula of Florida (Sites 4, 5, 6, 7, and 8) and southern peninsula of Florida (Sites 9, 10, 11, 12, 13, and 14) (ESE, 1983a). Second, Site 15 would continue to obtain monitoring data from a southern peninsula coastal site necessary for source attribution evaluations and eliminate the need for Site 10, which had come under the influence of fugitive particulate emissions from highway construction. Daily precipitation sampling was initiated at all sites to support air mass trajectory calculations performed under the Source Attribution Program and to increase the sample population used in the analysis of spatial trends.

Routine sampling of atmospheric concentrations of particulate $SO_4^{-2}$, sulfur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), and nitric acid ($HNO_3$) was begun in mid-November 1982. There were three main reasons for this addition to the monitoring program. First, it was recognized that assessment of ecological effects would require information on total deposition (i.e., precipitation plus dry deposition) rather than deposition from precipitation only. Ambient concentration data throughout the state were therefore needed to estimate dry deposition via application of the deposition velocity concept. Although ambient $NO_2$, $SO_2$, and particulate $SO_4^{-2}$ data were available for a number of areas within the state, it was determined that such data were of limited usefulness for the purposes of this study. This was due either to inadequate sensitivity of instrumentation (especially for $SO_2$) or inadequate locations due to the typically urban or industrial settings of most ambient monitoring programs (i.e., not regionally representative). Second, acquisition of air data, especially near state boundaries, was essential for estimation of atmospheric sulfur and nitrogen budgets for the Florida atmosphere (Edgerton, 1981). Third, the ambient database would lend itself to the evaluation and refinement of model parameterizations used in the Source Attribution Program. For example, comparison of predicted versus observed $SO_2$ and particulate $SO_4^{-2}$ would serve as an intermediate checkpoint in the evaluation of model calculations.

In September 1983, the network was again modified in response to the overall needs of the study. The number of monitoring stations was reduced to seven, of which four (Sites 3, 4, 8, and 13) were operated on a weekly sampling schedule and three (Sites 2, 5, and 9) were operated on a daily schedule. Ambient air sampling (every third day) was continued at all seven stations from September 1983 through December 1984. The seven ambient air monitors were operated on the originally established sampling schedule (i.e., once every third day). This configuration remained intact through December 1984, with the exception of Site 13, which was converted to daily operation in September 1984.

The rationale for the additional reduction in monitoring locations (i.e., from nine to seven sites) stemmed mainly from comparison of separate analyses of the first 2 years of chemistry data. Results of these analyses (ESE, 1984) showed that precipitation chemistry across the state could be resolved into three or four statistically distinct regimes, depending on the year and the analyte in question. These regimes, however, could be distinguished at a high confidence level (i.e., ≥95-percent confidence level) only if the data from at least two sites were grouped together prior to statistical treatment. Seven monitoring locations were therefore retained to permit continued investigation, on an annual basis, of chemical regimes across Florida. The weekly sites were operated primarily for evaluation of long-term trends and spatial patterns, while daily sites provided more detailed chemical information for analysis of single precipitation events.

### 2.2.2 SITE CONFIGURATION AND EQUIPMENT

Each site was equipped with an Aerochem-Metrics Model 301 wet/dry collector, a Belfort weighing-type 8-day rain gage modified to accommodate a precipitation event marker, and a 12-volt battery for backup power in the event of electrical outages (see Figure 2.2-2). Both wetfall and dryfall were collected in buckets made of linear polyethylene. The collector was fitted with a bird-off ring, developed by ESE, to prevent avian contamination of dryfall buckets. A 6-foot (ft) chain-link fence, or a similar security measure, was installed at each site to discourage vandalism and tampering. The size of each site was typically 40 ft x 40 ft; collocated sites were 40 ft x 80 ft. Collocated precipitation samplers were separated by 2 meters (m).

A special field laboratory was developed and located in residences of field technicians. These laboratories were lockable to prevent tampering and equipped with a conductivity bridge (Beckman Model RC-16C) with a conductivity cell [Yellow Springs Instruments (YSI) Model 3403], a digital pH meter (Corning Model 125) with a combination pH electrode

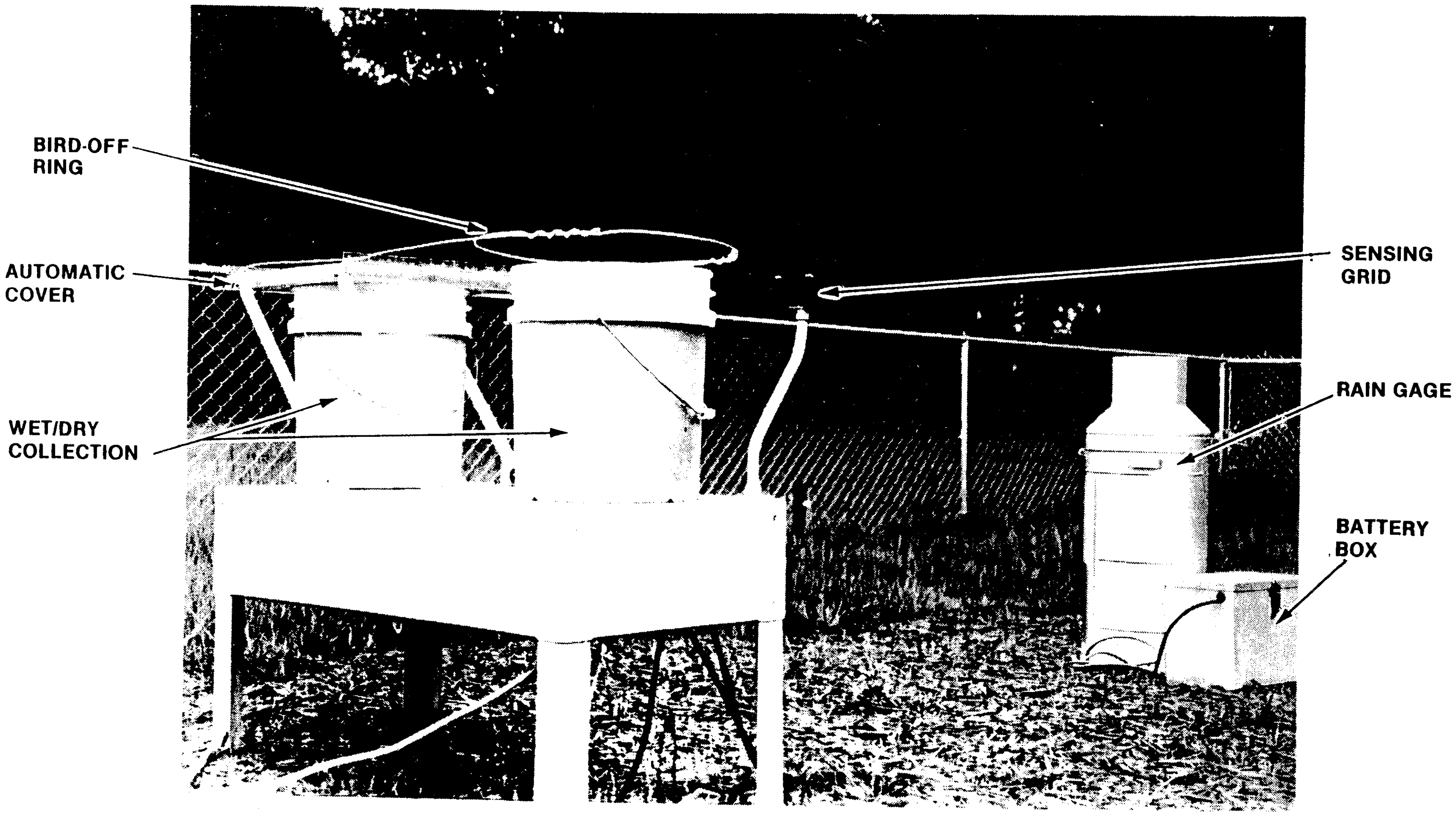

Figure 2.2-2
AEROCHEM-METRICS MODEL 301 WET/DRY COLLECTOR, BELFORT WEIGHING-TYPE 8-DAY RAIN GAGE, AND SITE LAYOUT

SOURCE: ESE, 1985.

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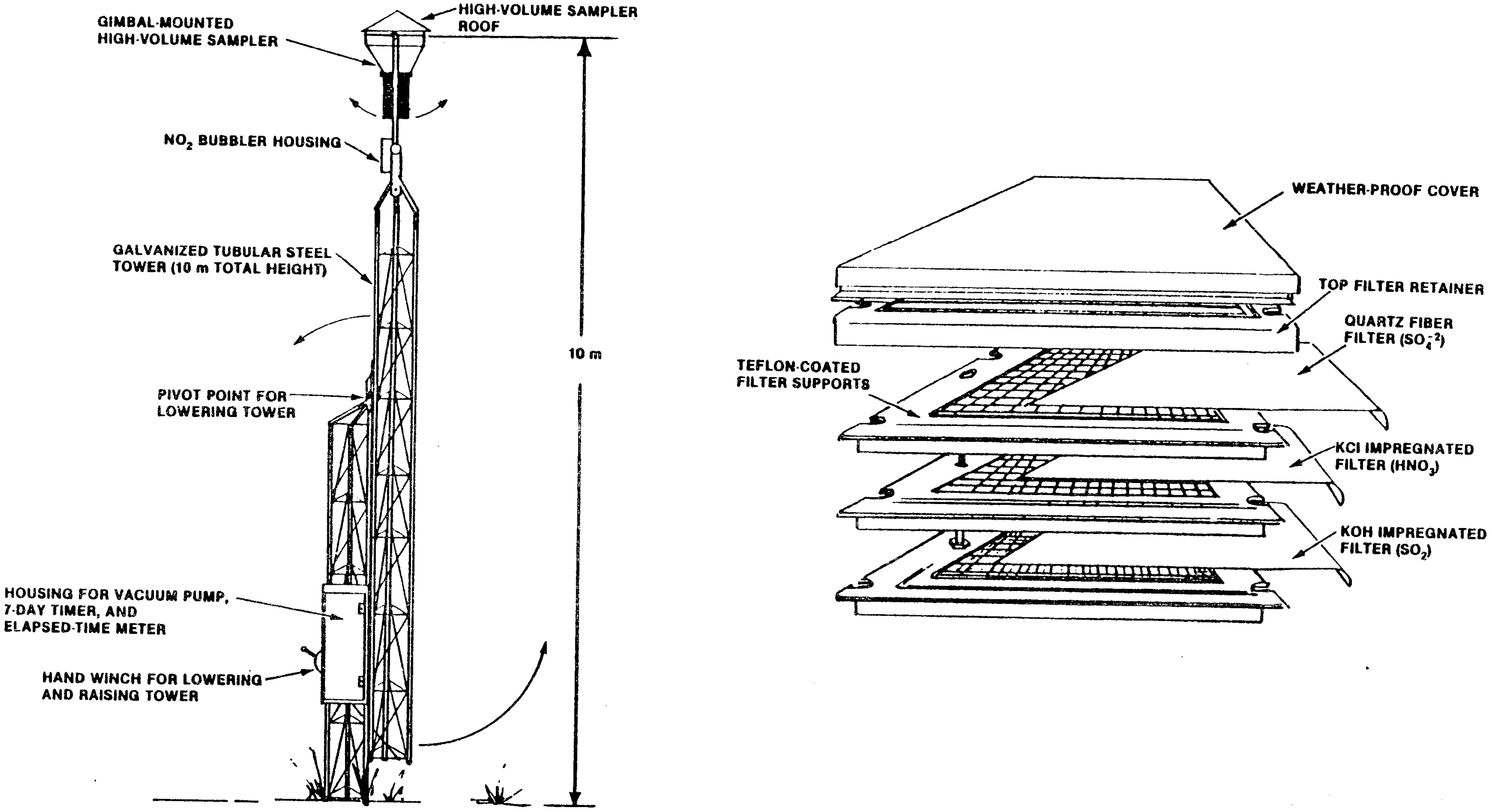
(Corning Model 476223), and an Ohaus 20-kilogram (kg) triple-beam solution balance. Field laboratories also were supplied with a 1.4-cubic-foot ($ft^3$) refrigerator for storage of test solutions, as well as necessary supplies for the collection, analysis, and shipment of samples.

Twenty-four-hour integrated air samples for particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ analysis were collected using 10-m cantilever towers. These towers were designed to lower for ground-level servicing and to raise into vertical position for air sampling (see Figure 2.2-3 and ESE, 1984).

Particulate $SO_4^{-2}$, $SO_2$, and $HNO_3$ were sampled once every 3 days using the high-volume triple-filter-pack technique pioneered by Forrest et al. (1979) (see Figure 2.2-3). Particulate $SO_4^{-2}$ samples were collected on the first stage of the filter pack using untreated quartz micro-fiber filters (Pallflex 2500 QAO). $HNO_3$ was collected on the second stage of the filter pack using a cellulose filter (Schleicher and Schuell #589 black ribbon) impregnated with potassium chloride (KCl). $SO_2$ was collected on the final stage with a Teflon®-coated quartz-fiber filter (Pallflex TX40H120-WW) impregnated with a 10-percent potassium hydroxide (KOH)/5-percent glycerol ($C_3H_8O_3$) solution. Filter supports between stages consisted of Teflon®-coated 1/4-inch stainless steel mesh custom ordered from General Metal Work Corporation. Teflon® coatings were color-coded to aid field technicians in the proper sequencing of filters. Filters were stored in airtight resealable bags before and after exposure.

$NO_2$ air samples were collected using the EPA Christie method (EPA, 1973). Air was bubbled through 50 milliliter (mL) of basic arsenic trioxide ($As_2O_3$) in an impinger tube at a flow rate between 180 and 220 milliliters per minute (mL/min). Flow rates were controlled by a critical orifice and accurately determined with a bubble tube certified by the National Bureau of Standards (NBS) and a calibrated digital stopwatch.



AIR SAMPLING TOWER

AMBIENT AIR QUALITY FILTER PACK TO MEASURE PARTICULATE $SO_4^{-2}$, $HNO_3$, AND $SO_2$

Figure 2.2-3
AIR SAMPLING EQUIPMENT

SOURCE: ESE, 1985.

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### 2.2.3 FIELD OPERATIONS

Prior to initiating field sample collection, each field technician was given extensive training that included 2 days of classroom instruction and several days of in-field operation review. In addition, semiannual audits were scheduled to ensure standard operating procedures were followed.

Weekly precipitation samples were collected every Tuesday between 8:00 to 10:00 a.m. Daily precipitation samples were collected during the same time period each day (8:00 to 10:00 a.m.), provided the precipitation event marker had been triggered. Dry buckets were collected every 2 months. In the event no precipitation occurred during the course of a week, wetfall buckets were collected each Tuesday regardless of when the bucket was placed in the field. These "dry" wetfall buckets were used as part of the Quality Assurance (QA) Program.

Precipitation samples were analyzed in the field laboratory for sample weight, pH, and conductivity. Precipitation samples (whole bucket) were shipped at ambient temperature to ESE, via United Parcel Service (UPS), on the day of collection.

Ambient air sampling was performed for a 24-hour period once every 3 days beginning at midnight. The exposed filters were removed from the high-volume air sampler the morning following a sampling run. Sample changeout was facilitated by providing each field technician with a duplicate filter pack assembly, which permitted handling of exposed/fresh filters exclusively in the field laboratory. Filter samples were sent to the ESE laboratory within 1 week of collection (ESE, 1982).

### 2.2.4 LABORATORY OPERATIONS

Precipitation samples were analyzed on the day of receipt for weight, pH, and conductivity, then filtered through a prewashed 0.45-micrometer (µm) Millipore HA cellulose-acetate filter supported on an all-plastic vacuum filtration apparatus. After filtration, samples were analyzed again for pH and conductivity, then for $NH_4^+$, $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, $NO_3^-$, $SO_4^{-2}$, and $Cl^-$. $Na^+$, $Ca^{+2}$, and $Mg^{+2}$ were analyzed on a Jarrel-Ash Atomcomp 1200 inductively coupled argon plasma (ICAP) emission spectrometer. $NH_4^+$, $NO_3^-$, $SO_4^{-2}$, and $Cl^-$ were analyzed via automated colorimetry on a Technicon AutoAnalyzer® II system. $K^+$ was analyzed via atomic emission on a Perkin-Elmer Model 703 atomic absorption spectrophotometer (AAS). In the event sample volume was limited (i.e., <100 mL), analyses were performed in the following order: pH, conductivity, $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, $Ca^{+2}$, $Na^+$, $Mg^{+2}$, $Cl^-$, and $K^+$ (see also ESE, 1981, 1983, 1984, and 1985). Samples were refrigerated to 4 degrees Celsius (°C) until analyses were complete (generally less than 2 weeks). During the period September 15, 1981, through September 14, 1982, orthophosphate anion ($PO_4^{-3}$), flouride anion ($F^-$), vanadium cation ($V^{+4}$), aluminum cation ($Al^{+3}$), total/strong acidity, alkalinity, and dissolved organic carbon (DOC) were analyzed at all sites (see ESE, 1983b). Formic acid (HCOON) and acetic acid ($CH_3COOH$) were analyzed in precipitation at Site 5 from March 1982 through August 1982.

Dryfall samples were extracted from the dryfall bucket by rinsing with 250 mL of deionized water. Samples were analyzed for pH, conductivity, $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, $Ca^{+2}$, $Na^+$, $Mg^{+2}$, $Cl^-$, and $K^+$. Only dryfall samples collected over the period September 15, 1981, through September 14, 1982, were anlyzed (see ESE, 1984); the remaining dryfall samples were archived.

Sample extracts from ambient air filters were made by equilibrating them overnight with 200 mL of deionized water, heating to 85°C, and shaking vigorously for 30 seconds. After cooling to room temperature, the solutions were filtered through a Millipore 0.45-µm cellulose-acetate filter, then refrigerated until analysis.

Particulate $SO_4^{-2}$ and $SO_2$ extracts were analyzed (as $SO_4^{-2}$) using the automated methylthymol blue technique (Lazrus et al., 1965). $HNO_3$

extracts were anlyzed (as $NO_3^-$) using the automated cadmium-reduction technique (EPA, 1974). $NO_2$ samples were analyzed (less than 2 weeks) using the automated $NO_2$ method (EPA, 1973). Particulate $SO_4^{-2}$ values were not corrected for sea-salt $SO_4^{-2}$ contributions.

### 2.2.5 QUALITY ASSURANCE PROGRAM

In order to ensure and document the quality of monitoring data, numerous QA/QC activities were performed. The activities included both field and laboratory quality control (QC) practices, as well as scheduled and unscheduled performance audits. The major elements of the program are summarized in Table 2.2-1 and discussed in the following paragraphs.

Accuracy of field pH and conductivity measurements was maintained by calibration of the pH meter and conductivity bridge with known reference standards. Calibration was performed before each field measurement. To evaluate accuracy, a low ionic strength (LIS) reference solution was analyzed for pH and conductivity each time a precipitation sample was analyzed. LIS solutions ranging from approximately pH 4.0 to 5.0 were randomly distributed every quarter to each field operator during the monitoring period.

Field operator performance was determined through bimonthly measurements of unknown reference solutions and semiannual audits. Two unknown reference solutions (one in the pH range 4.5 to 5.0 and one in the pH range 4.0 to 4.5) were sent to each field operator approximately every 2 months and analyzed in the same manner as precipitation samples. Semiannual audits were performed during scheduled monitor servicing to observe field operator technique for sample handling; measurement of pH, weight, and conductivity; and maintenance procedures. An unknown reference sample was given to each field operator during each semiannual audit. Laboratory operators also measured LIS solutions and were included in performance audits for pH and conductivity measurements.

Table 2.2-1. Summary of QA/QC Program

| Location | QA/QC Activity | Frequency | Remarks |
|---|---|---|---|
| Field | Instrument Calibration | D/W* | Reference standards: pH 7.0 and 4.0 (or 3.0 if sample was below pH 4.0), and conductivity 75 and 30 µS/cm |
| | LIS Solution Measurement | D/W* | Reference samples: pH approximately, 4.0 to 5.0 |
| | Unknown Reference Solutions | Bimonthly (2 samples) | References samples: pH 4.0 to 5.0 |
| | Performance Audits | Semiannually | Performed on sample recovery |
| | Collocated Samplers | W/W:<br>D/W:<br>D/D: | Sites 2 and 8 from 7/81 to 9/82<br>Site 9 from 7/81 to 9/82<br>Sites 2, 5, and 8 from 9/82 to 12/84 |
| Laboratory | Instrument Calibration | Daily* | 5 calibration standards and 1 blank |
| | Field Bucket Blanks | Varied, about once/month | Dry wetfall buckets |
| | Bucket Blanks | Biweekly | 50 mL of deionized water in clean bucket |
| | Filter Blanks | Biweekly | 50 mL of deionized water filtered |
| | Reference Samples | D/W* | Known solutions of cations and anions of similar chemistry as observed in precipitation |
| | Spikes | D/W* | 5 percent of precipitation samples |
| | Duplicates | D/W* | 10 percent of precipitation samples |
| | Cation/Anion Balances | D/W* | Performed on each precipitation sample |
| | Predicted Versus Calculated Conductivity | D/W* | Performed on each precipitation sample |
| | Performance Audit | Monthly | Evaluate performance with specified criteria and include 4 reference samples |

Note: µS/cm = microsiemens per centimeter.
*Performed D/W or when precipitation sample was analyzed.

Source: ESE, 1986.

Collocated samplers were used to investigate the precision of D/W, W/W, and D/D sampling schedules (see Figure 2.2-1). During the study, the collocated samplers at Sites 2 and 5 were operated off separate precipitation sensors, and those at Sites 8 and 9 were operated off a single sensor. Collocated rain gages were used to evaluate precision of precipitation measurements. The amount of precipitation determined from rain gages and wet/dry collectors was used to evaluate differences in precipitation measurements. Precision of ambient air measurements from collocated monitoring was evaluated at Site 5 by collection of duplicate samples from adjacent monitoring towers.

The effect of physical filtration on precipitation samples was evaluated through laboratory pH and conductivity measurements of samples both before and after filtering. In addition, potential contamination by filters was evaluated by analysis of filter blanks for pH, conductivity, and all cations and anions normally measured. Three filter blanks were generated each week by passing 50 mL of distilled water through separate filters. Analyses were made after filtration.

Potential contamination of precipitation samples by contact with sample buckets was determined by generating two types of bucket "blanks" and measuring pH, conductivity, and the major cations and anions. Each week, clean bucket blanks were generated by adding 50 mL of deionized water to a freshly washed and air-dried bucket. A field bucket blank was generated from "dry" wet buckets by adding 50 mL of deionized water to a bucket that was returned from the field. After ensuring that the deionized water contacted the walls of the bucket, the blank sample was decanted and analyzed by the same procedures as precipitation samples.

Accuracy of all cation and anion measurements was maintained by calibrating each instrument with five calibration standards and one blank. A reference sample was analyzed after instrument calibration to determine accuracy. Unknown reference samples, from EPA and generated internally, were also incorporated into the analytical scheme. In addition, 5 percent of the precipitation samples were spiked with known concentrations of cations and anions to evaluate analyte recoveries.

Laboratory precision in cation and anion measurements was determined by performing duplicate analyses on 10 percent of the precipitation samples.

In order to validate sample measurements, analytical results were evaluated using two interparameter relationships: cation/anion ratio and predicted versus measured conductivity. Based on the electroneutrality condition, the ratio of the major cations and anions should be nearly equal to 1.0. Predicted conductivity can be calculated based on the concentration of cations and anions in solution and compared with observed conductivity. If either of these interparameter consistency checks exceeded specified tolerances, the sample was reanalyzed for pH and conductivity. If a tolerance was still exceeded, the sample was reanalyzed for all cations and anions. Tolerance ranges for the percent difference interparameter consistency checks were as follows:

$\pm 15$ percent for pH $<4.80$ or conductivity $\geq 15.0$ micromhos per centimeter (µmho/cm), and

$\pm 30$ percent for pH $\geq 4.80$ or conductivity $<15.0$ µmho/cm.

Rerun data were used to recalculate ionic and conductivity balances. If ionic and conductivity balance criteria were satisfied, the original data were replaced. If ionic balance criteria were not met, then the average of rerun and original data was entered in the database, and the sample was flagged.

The QA/QC program for air monitoring was similar to that established for the precipitation chemistry monitoring. This is because the analytical matrix for air samples is essentially the same as for precipitation samples (i.e., aqueous). Field equipment was calibrated monthly and semiannual performance audits were conducted. Collocated air sampling towers were installed at Site 5 to obtain an estimate of overall air sample precision. Dynamic ambient filter blanks were analyzed from all sites quarterly. A portion of the air sample from each site was analyzed as a duplicate (10 percent) and samples were spiked (5 percent). Reference samples (NBS filter strips) were extracted and analyzed monthly, and laboratory performance audits were performed quarterly.

## 2.2.6 STATISTICAL METHODS

### 2.2.6.1 General

The Statistical Analysis System (SAS) (SAS Institute, 1982) computer program was used to reduce and analyze precipitation and air chemistry data. All of the statistical procedures used to evaluate and draw conclusions from the monitoring data were parametric in nature.

Although the decision to use parametric procedures as a basis for the conclusions was believed to be warranted, it would be incorrect to assume that the precipitation monitoring data had no skewness or outliers that affected the analyses. For this reason, most analyses were performed on both the monitoring data and their logarithmic transforms. The purpose of the transform is to convert the observed distribution into a lognormal distribution, thereby tending to allow for some "extreme" positive values. Analysis of residuals, on both the monitoring data and its logarithmic transforms, indicated that the error variances were stabilized (i.e. made homogeneous) with the logarithmic transforms. For most of the data, the lognormal distribution was supported (probability level $>0.15$), an important finding considering that the number of observations (n) was often very large (e.g., $n > 100$). Bar, box, and normal probability plots also supported an assumption of lognormality. Residual plots of the "models" tested indicated that variances of errors were generally homogeneous for the logarithmic transform of the monitoring data, whereas the monitoring data alone produced residual plots with considerable skewness.

In most cases, the analyses yielded consistent results for the two distributional assumptions. However, because of the strength of the residual analysis, the results reported herein are those resulting from the lognormal rather than the normal analyses. Where results differed enough to be important, both analyses are reported and discussed.

Throughout this analysis, a 95-percent confidence level has been required for differences between sites and seasons to be declared significantly different. This implies that in only 1 out of 20 cases would the observed differences be an expected result of random variability. For multiple comparisons, such as differences between sites or groups of sites across seasons, a 99-percent confidence level has been required. The purpose of this measure is to ensure an overall protection level of at least 95 percent for statements concerning groups of comparisons.

### 2.2.6.2 Collocated Sampling

The network design incorporated various procedures into the sampling protocol to evaluate the overall precision of precipitation chemistry measurements.

Comparisons were made of D/D, W/W, and D/W precision using the t-test and the t-test on logarithms. The t-test is used to detect statistically significant differences between means of parameters and thus make comparisons between a single pair of means. The t-test on logarithms is also used to distinguish statistically significant differences between the geometric means (i.e., ratios) of the parameter concentrations. The t-test on untransformed parameter concentrations is statistically conservative if the true distribution is lognormal and is appropriate if the data are normally distributed. The t-test on logarithms is more discriminating for skewed distributions and is preferred if the data are lognormally distributed. Both types of t-tests are presented in the results.

It is important to note that these tests assume that the true chemical composition of precipitation collected by collocated samplers is identical. However, there is no way of knowing if the quality of rainfall is identical for each bucket. As a consequence, statistically significant differences between collocated collectors, if found, may be attributable to differences in the quality of received precipitation.

The network design also permitted comparison of collocated precision across sites using the same collection procedure (e.g., D/D at Site 5 versus D/D at Site 9). The test statistic employed was the absolute value of the difference between collocated samplers, which is analogous to the ratio of the larger observation to the smaller observation for each sampling interval. Thus, the overall precision of precipitation sampling was evaluated across sites.

### 2.2.6.3 Spatial and Temporal Variations in Precipitation and Air Chemistry

Spatial patterns of temporal trends of Florida precipitation were evaluated using analysis of variance (ANOVA). ANOVA models were designed for laboratory $H^+$ (computed from pH), excess $SO_4^{-2}$, $NO_3^-$, excess $Ca^{+2}$, and $NH_4^+$ to test the individual effects of site, site-group, season, and year, as well as 2-way and 3-way interactions of the above. Site-groups were selected based on results of cluster analysis, geographic location, and previous statistical evaluations (ESE, 1984; ESE, 1985). When significant differences were detected for an individual site versus all other sites, this site was always assigned to a unique site-group.

Seasonal effects were tested by division of the year into two 6-month seasons: summer (April through September) and winter (October through March). Annual periods have been defined for this analysis to begin in October and end in September. Although use of a meteorological year may somewhat restrict comparability of results between this and other networks, it enhances the internal consistency of the database by preserving the integrity (i.e., continuity) of the winter season.

Preliminary calculations of annual seasonal statistics for calendar and meteorological years showed generally lower variability within years and within winters using the concept of a meteorological year.

Spatial and temporal variability of air chemistry data was tested using similar ANOVA models, except that analyses were performed with blocking on sample date. Blocking is analogous to a paired t-test in which paired differences are calculated for all possible combinations of sites. This approach is typically more sensitive to systematic differences between sites and is possible because the timing of an air sample collection is controlled and simultaneous across the entire network.

Log-transformed precipitation and air concentrations were used as input to all ANOVA models. In addition, precipitation data were weighted by precipitation amount to give greater emphasis to larger samples, resulting in a volume-weighted geometric mean. Wet-only deposition was accumulated over weekly intervals (i.e., Tuesday to Tuesday) to account for sampling variability between sites and across years, then log-transformed before use in ANOVA models.

### 2.2.6.4 Chemical Relationships Between Laboratory $H^+$ and Other Chemical Species in Precipitation

Chemical relationship between laboratory $H^+$ and other chemical species in Florida precipitation were calculated using SAS stepwise multiple-regression. In this procedure, the relationship between $H^+$ (the dependent variable) and $SO_4^{-2}$, $NO_3^-$, $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$, and $NH_4^+$ (independent variables) were determined using untransformed chemical data. Observations were volume-weighted to give more importance to large precipitation events compared to small events.

For the multiple-regression analysis, $SO_4^{-2}$, $Cl^-$, and $Ca^{+2}$ were partitioned into their respective marine and nonmarine, or "excess," components, using sodium as a tracer of marine particulates. Equations for the excess components of precipitation analytes, expressed as milligrams per liter (mg/L), are as follows (Horne, 1969):

Excess $SO_4^{-2}$ = $SO_4^{-2}$ - 0.25 $Na^+$,
Excess $Cl^-$ = $Cl^-$ - 1.80 $Na^+$,
Excess $Ca^{+2}$ = $Ca^{+2}$ - 0.036 $Na^+$,
Excess $Mg^{+2}$ = $Mg^{+2}$ - 0.128 $Na^+$, and
Excess $K^+$ = $K^+$ - 0.033 $Na^+$.

### 2.2.6.5 Ambient Air Concentrations: Statistics and Relationships Between Precipitation Chemistry

The design of the monitoring network included the measurement of ambient air concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ at each precipitation monitoring site. A sampling frequency (once every third day) was selected that would establish both a statewide pattern and primary statistics for these ambient parameters, and develop a sufficient number of simultaneous observations to allow the comparison of ambient air concentrations with precipitation chemistry.

Spatial and temporal variability in ambient air concentrations between sites were evaluated using SAS ANOVA and Duncan's multiple-range test. In addition, the relationship between $SO_4^{-2}$ and $NO_3^-$ in precipitation and $SO_4^{-2}/SO_2$ and $HNO_3/NO_2$ concentrations in ambient air, respectively, were evaluated by performing SAS stepwise multiple-regression analysis procedure. The ambient air concentrations input into the model were those occurring the same day as precipitation. Precipitation amount was included in this latter model test as follows:

$$[\text{excess } SO_4^{-2}]_p = k_1 R^u [SO_4^{-2}]_a^v [SO_2]_a^w$$
$$[NO_3^-]_p = k_2 R^x [HNO_3]_a^y [NO_2]_a^z$$

where: $[\,]_p$ = concentration of $SO_4^{-2}$ or $NO_3^-$ in precipitation (mg/L),
$[\,]_a$ = concentration of $SO_4^{-2}/SO_2$ or $HNO_3/NO_2$ in ambient air [micrograms per cubic meter ($\mu g/m^3$)],
$k_1, k_2$ = regression-derived constants,
R = rainfall amount [grams (g)], and
u-z = regression-derived exponents.

## 2.3 MONITORING PROGRAM FINDINGS--OVERVIEW

During the course of the monitoring program, the network evolved from 14 to 7 stations with revisions in the frequency and type of monitoring performed (see Figure 2.2-1). The data collected from July 1, 1981, through September 11, 1984, consisted of over 3,000 individual precipitation samples, for which at least 12 chemical analyses were performed. In addition, approximately 7,000 chemical analyses were performed on ambient air samples collected from November 1, 1982, through September 11, 1984. Detailed analyses of these data were made on an annual basis (starting September 18, 1981) and presented in comprehensive study reports (see ESE, 1983b; ESE, 1984; and ESE, 1985). The annual data presented and analyzed in these reports were not analyzed together and will not be presented in this report.

Only data from certain sites were selected for presentation and analysis in this report. This selection of data was based on two factors: (1) the duration that monitoring was conducted at a particular site, and (2) the geographic representativeness of the site. However, the selection of any data required the presumption that it would be able to address the key research questions of the program.

Precipitation samples were collected over the 3-year period from September 15, 1981, through September 11, 1984, at seven sites (Sites 2, 3, 4, 5, 8, 9, and 13); during the same period, seven sites (Sites 1, 6, 7, 10, 11, 12, and 15) were operated for only 1 year. Site 14 was operated for a 2-year period: September 15, 1981, through September 13, 1983. Ambient air samples were collected from seven sites (Sites 2, 3, 4, 5, 8, 9, and 13) for a period of approximately 2 years (November 10, 1982, through September 11, 1984). Air monitoring was conducted at Sites 14 and 15 for only a 1-year period. The 3-year precipitation chemistry database and 2-year ambient air quality database for Sites 2, 3, 4, 5, 8, 9, and 13 formed the basis of the analysis presented in this report. These 7 sites would provide the best data to make statistical comparisons over a 3-year period; i.e., a temporally balanced statistical design. In addition, these data represent 76.4 percent of the precipitation chemistry data collected from all sites over the 3-year period and essentially all the ambient air monitoring data. Site 14 was included in the data overview and quality discussions, i.e., Subsections 2.3.1 and 2.4, respectively, since it had a 2-year precipitation chemistry database and was originally selected as a background site for both precipitation chemistry and air quality.

The sites selected for analysis in this report are regionally representative and provide broad geographic coverage of the state (see Figure 2.3-1). Sites 2, 3, 5, 8, 9, 13, and 14 span approximately 900 kilometers (km) from the Florida panhandle to the Florida Keys. Each site is also more than 100 km from the nearest site; for Sites 2, 3, 5, 8, 9, and 13, the distance between each site is within a range of approximately 140 km to 180 km. Thus, the relatively uniform distribution of sites provided a database that is geographically representative of the state as a whole and would provide a geographically balanced design for statistical comparisons.

Analysis of data from previous annual periods (see ESE, 1983b, 1984, and 1985) indicated that precipitation chemistry data can be divided into two seasons: winter (October 1 through March 31) and summer (April 1 through September 30). This seasonal division was also found in previous research (Brezonik et al., 1983). The winter and summer seasons thus describe the annual cycle of precipitation chemistry in Florida. In order to evaluate and analyze a 3-year database representative of precipitation chemistry in Florida, it was necessary to supplement the data beyond that obtained from Phase IV monitoring alone since that phase ended on September 11, 1984. However, since September 11, 1984, the operation of the Phase IV monitoring network was continued at seven sites (Sites 2, 3, 4, 5, 8, 9, and 13). This "fourth-year monitoring" network was operated the same as the Phase IV network except that Site 13 was

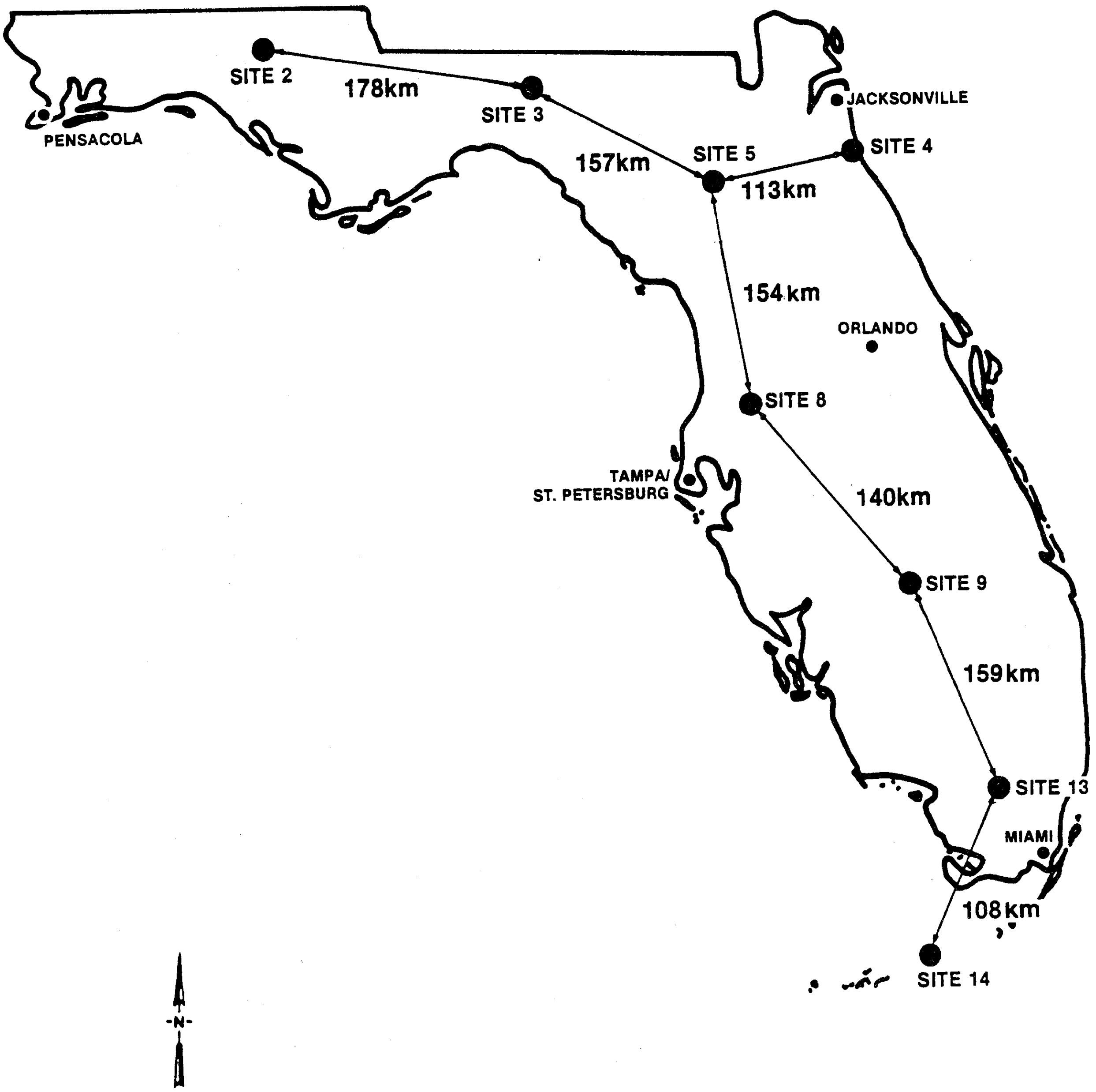

Figure 2.3-1
PRECIPITATION CHEMISTRY AND AMBIENT AIR QUALITY MONITORING SITES EVALUATED

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operated on a daily (instead of weekly) basis after September 11, 1984 (see Figure 2.2-1). Data from the fourth-year monitoring network were required to complete the last of the three sampling years listed below.

Year 1 = October 1, 1981, through September 30, 1982
Year 2 = October 1, 1982, through September 30, 1983
Year 3 = October 1, 1983, through September 30, 1984

The selection of the monitoring stations and annual periods for statistical analysis required merging of precipitation chemistry databases that included daily and weekly samples. As a consequence, the possible effect on the statistical analysis can be twofold. First, the data from weekly-operated stations do not begin or end on the dates specified for the annual periods. This influence was considered insignificant since the beginning and ending dates for the weekly samples did not vary more than 4 days from the annual periods evaluated. Second, the effect of merging weekly and daily data could influence the analysis since the potential uncertainty associated with each sampling frequency may be different. This latter effect, however, was also considered insignificant since the data uncertainty was small compared to the variance in observed data (refer to Subsection 2.4.4 for further discussion).

Precipitation chemistry data collected by other organizations generally are presented in terms of calendar years. In order to compare data collected from other networks with data collected from this study's monitoring program, precipitation chemistry data were annualized for Calendar Years 1982, 1983, and 1984. Statistical analyses were not performed on these databases because rigorous evaluation of systematic differences in concentrations and deposition between networks was beyond the scope of this study.

## 2.3.1 GENERAL DATA OVERVIEW

### 2.3.1.1 Volume-Weighted Mean Concentrations and Depositions

The VWM is the most appropriate summary statistic describing a time sequence of precipitation chemistry in the context of an acid deposition study. Through this statistic, the ionic composition of heavy storms is weighted proportionally greater than lighter rainfall events.

Table 2.3-1 presents average VWM values of laboratory and field pH and major cations and anions for precipitation collected over the 3-year period (October 1, 1981, through September 30, 1984) at seven stations. Data from Site 14 are presented for the period October 1, 1981, through September 14, 1983. The units presented in Table 2.3-1 are µN which are numerically equivalent to microequivalents per liter (µeq/L) (i.e., 1 µN = 1 µeq/L).

VWMs were calculated based on the volume (weight) of rainfall in the sample bucket. Volume-weighted pH values were derived from volume-weighted $H^+$ concentrations. Ionic depositions were calculated from VWM concentrations and total rainfall amount collected in sample buckets.

The data in Table 2.3-1 suggest a spatial pattern of decreasing precipitation acidity from sites located in northern and central Florida (Sites 2, 3, 4, 5, and 8) to sites located in southern Florida (Sites 9, 13, and 14); however, this gradient is not uniform. For VWM field pH, a low of 4.52 was observed in north-central Florida (Site 5), and a high of 4.73 was observed in south Florida (Site 13). Sites 5 and 8 located in north-central Florida exhibited slightly lower pH than the more northern and western sites (Sites 2 and 3).

For each annual period, a similar pattern for pH emerged, but its strength was highly variable (see also ESE, 1983b; ESE, 1984; and ESE, 1985). For example, field pH during the three annual periods ranged from 4.33 (Site 2) to 4.69 (Site 13) for the first year, from 4.51 (Site 5) to 4.77 (Site 13) for the second year, and from 4.60 (Site 5) to 4.74

Table 2.3-1. VWM* Concentrations† for Wet-Only Precipitation for the 3-Year Period from 10/01/81 Through 09/30/84

| Site | pH |  | $H^+$ |  | $Ca^{+2}$ | Excess $Ca^{+2}$ | $Mg^{+2}$ | $K^+$ | $Na^+$ | $NH_4^+$ | $NO_3^-$ | $Cl^-$ | Excess $Cl^-$ | $SO_4^{-2}$ | Excess $SO_4^{-2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Field | Lab | Field | Lab |  |  |  |  |  |  |  |  |  |  |  |
| 2 | 4.53 | 4.64 | 29.5 | 23.0 | 4.7 | 4.2 | 3.8 | 0.8 | 11.7 | 5.9 | 9.9 | 14.4 | 0.9 | 22.3 | 21.0 |
| 3 | 4.56 | 4.68 | 27.5 | 21.1 | 4.8 | 4.4 | 3.7 | 0.9 | 11.8 | 5.7 | 9.2 | 15.6 | 1.8 | 20.7 | 19.3 |
| 4 | 4.56 | 4.67 | 27.6 | 21.4 | 5.9 | 4.4 | 10.1 | 1.3 | 40.0 | 4.2 | 9.5 | 47.2 | 0.8 | 23.9 | 19.1 |
| 5 | 4.52 | 4.57 | 30.3 | 26.9 | 5.1 | 4.8 | 3.1 | 0.8 | 9.9 | 5.7 | 10.5 | 12.6 | 1.1 | 24.2 | 23.2 |
| 8 | 4.57 | 4.62 | 26.8 | 23.7 | 7.6 | 7.1 | 4.2 | 0.8 | 13.0 | 9.5 | 11.8 | 16.4 | 1.3 | 30.4 | 28.9 |
| 9 | 4.63 | 4.80 | 23.2 | 15.9 | 6.3 | 5.7 | 4.8 | 0.7 | 14.7 | 4.6 | 9.2 | 18.7 | 1.6 | 17.4 | 15.5 |
| 13 | 4.73 | 4.86 | 18.6 | 13.7 | 8.9 | 8.2 | 5.5 | 1.7 | 19.0 | 5.1 | 9.1 | 23.7 | 1.9 | 15.8 | 13.5 |
| 14** | 4.68 | 4.96 | 21.1 | 11.0 | 7.3 | 5.3 | 13.4 | 1.4 | 53.7 | 2.7 | 6.0 | 62.8 | 0.8 | 17.3 | 10.9 |

*VWM is calculated as follows:

$$C_{VWM} = \Sigma(C_i \cdot R_i)/\Sigma R_i$$

where: $C_{VWM}$ = VWM concentration;
$C_i$ = concentration of the species of interest for the $i^{th}$ sample; and
$R_i$ = rainfall amount for the $i^{th}$ sample as determined from sample volume.

†All concentrations are µN, except pH which is unitless.
**Data for Site 14 are for the 2-year period 10/01/81 through 09/13/83.

Source: ESE, 1986.

(Site 13) for the third year (see Table 2.3-2). In terms of field $H^+$ concentrations (see Table 2.3-3), the range was 46.7 to 20.5 µN for the first year, 30.9 to 17.1 µN for the second year, and 25.2 to 18.1 µN for the third year. For laboratory $H^+$, the suggested patterns were similar to field $H^+$ with the lowest pH observed for the sites in northern and central Florida and highest pH observed in southern Florida (see Tables 2.3-1 and 2.3-3).

Year-to-year variations in pH and $H^+$ concentrations for both the field and laboratory for each site are also apparent from the data presented in Table 2.3-2 and Table 2.3-3. The field and laboratory pH for the northern and central Florida sites (Sites 2, 3, 4, 5, and 8) generally increased from Year 1 to Year 3, with the greatest increases occurring for Sites 2 and 3. Indeed, in terms of $H^+$ concentrations, over the 3-year period the northern sites experienced an average decrease of 17.4 µN (43.1 percent) in field $H^+$ and an average decrease of 10.4 µN (32.5 percent) in laboratory $H^+$. In contrast, field and laboratory $H^+$ concentrations remained essentially constant in southern Florida (Sites 9 and 13). Field $H^+$, for example, decreased by less than 3.0 µN (12 percent) in the southern Florida sites.

Excess $SO_4^{-2}$ is that portion of the total $SO_4^{-2}$ concentration which is presumed to be derived from nonmarine sources. This distinction is meaningful because of Florida's proximity to the Atlantic Ocean and the Gulf of Mexico. These bodies of water act as large sources of $SO_4^{-2}$, hence it is important to subtract marine sources of $SO_4^{-2}$. (Refer to Subsection 2.3.1.2 for further discussion.) Average excess $SO_4^{-2}$ [total $SO_4^{-2}$ minus $(0.25 \times Na^+)$] concentrations appeared to follow $H^+$ concentrations and were highest in the north-central portion of the state (Sites 5 and 8) and decreased toward the panhandle and southern portions of the state (Sites 2 and 3 and Sites 9 and 13, respectively). Average excess $SO_4^{-2}$ concentrations in the panhandle and north-central portions of Florida were greater than 19 µN; the corresponding levels in the southern portion of Florida (Sites 9 and 13) were less than 16 µN.

Table 2.3-2. Annual VWM Field and Laboratory pH for the 3-Year Period from 10/01/81 Through 09/30/84

| Site | Field pH | | | Laboratory pH | | |
|---|---|---|---|---|---|---|
| | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 |
| 2 | 4.33 | 4.58 | 4.69 | 4.43 | 4.71 | 4.73 |
| 3 | 4.35 | 4.63 | 4.67 | 4.49 | 4.79 | 4.73 |
| 4 | 4.42 | 4.64 | 4.69 | 4.56 | 4.74 | 4.73 |
| 5 | 4.47 | 4.51 | 4.60 | 4.52 | 4.60 | 4.62 |
| 8 | 4.50 | 4.55 | 4.69 | 4.58 | 4.65 | 4.64 |
| 9 | 4.61 | 4.65 | 4.65 | 4.78 | 4.84 | 4.74 |
| 13 | 4.69 | 4.77 | 4.74 | 4.85 | 4.96 | 4.78 |
| 14* | 4.61 | 4.74 | -- | 4.90 | 5.02 | -- |

*Data for Site 14 are for the 2-year period 10/01/81 through 09/13/83.

Note: Year 1 = October 1, 1981, through September 30, 1982.
Year 2 = October 1, 1982, through September 30, 1983.
Year 3 = October 1, 1983, through September 30, 1984.

Source: ESE, 1986.

Table 2.3-3. Annual VWM Concentrations* of Field H$^+$, Laboratory H$^+$, Excess $SO_4^{-2}$, $NO_3^-$, and Excess Ca$^{+2}$ for the 3-Year Period from 10/01/81 Through 09/30/84

| | Field H$^+$ | | | Laboratory H$^+$ | | | Excess $SO_4^{-2}$ | | | $NO_3^-$ | | | Excess Ca$^{+2}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 |
| 2 | 46.7 | 26.1 | 20.2 | 37.1 | 19.3 | 18.5 | 29.9 | 17.5 | 17.9 | 13.2 | 8.5 | 8.8 | 3.7 | 3.5 | 5.4 |
| 3 | 44.4 | 23.5 | 21.3 | 32.7 | 16.4 | 18.7 | 21.6 | 19.0 | 18.3 | 9.7 | 9.2 | 8.8 | 4.1 | 4.5 | 4.5 |
| 4 | 38.2 | 22.9 | 20.2 | 26.6 | 18.3 | 16.8 | 18.9 | 20.0 | 18.3 | 8.5 | 10.7 | 9.4 | 3.3 | 5.2 | 4.8 |
| 5 | 33.5 | 30.9 | 25.2 | 30.1 | 25.4 | 24.0 | 26.1 | 21.6 | 20.7 | 10.1 | 10.9 | 10.6 | 4.0 | 4.1 | 6.4 |
| 8 | 31.6 | 27.9 | 20.6 | 26.3 | 22.3 | 23.0 | 31.6 | 28.1 | 27.2 | 12.5 | 10.7 | 12.4 | 6.7 | 6.3 | 8.4 |
| 9 | 24.7 | 22.3 | 22.4 | 16.6 | 14.6 | 16.3 | 14.9 | 15.8 | 15.9 | 8.8 | 8.9 | 10.0 | 5.0 | 5.2 | 7.0 |
| 13 | 20.5 | 17.1 | 18.1 | 14.0 | 10.9 | 16.7 | 13.7 | 13.3 | 13.6 | 9.5 | 8.6 | 9.2 | 9.7 | 8.5 | 6.0 |
| 14† | 24.3 | 18.2 | -- | 12.5 | 9.6 | — | 9.5 | 12.2 | -- | 5.3 | 6.7 | — | 4.7 | 5.8 | — |

*All concentrations are µN.
†Data for Site 14 are for the 2-year period 10/01/81 through 09/13/83.

Note: Year 1 = October 1, 1981, through September 30, 1982.
Year 2 = October 1, 1982, through September 30, 1983.
Year 3 = October 1, 1983, through September 30, 1984.

Source: ESE, 1986.

Similar to the observation made for field pH, excess $SO_4^{-2}$ concentration varied from year to year, but an apparent gradient in concentrations remained. During the three annual periods, the highest excess $SO_4^{-2}$ concentrations were observed in central Florida (Site 8), with the southern Florida sites having the lowest observed concentrations (see Table 2.3-3). The maximum site-to-site differences observed within specific annual periods (excluding Site 14) were 17.9 μN for the first year, 14.8 μN for the second year, and 13.6 μN for the third year.

For each site located in northern and central Florida, there was also a general decrease in excess $SO_4^{-2}$ concentrations similar, but less pronounced, to that observed for $H^+$ concentrations. Over the 3-year period, excess $SO_4^{-2}$ concentrations decreased an average of 5.1 μN (18.6 percent) for those sites. For the southern Florida sites, excess $SO_4^{-2}$ concentrations at Site 9 increased slightly (1.0 μN, or 6.7 percent) and at Site 13 remained about the same. The statistical significance of these observed annual differences is addressed in Subsection 2.6.

Average nitrate concentrations also followed laboratory $H^+$ for the 3-year period and were highest at Sites 5 and 8 and decreased toward both the panhandle and southern peninsula. The average $NO_3^-$ concentrations in the north-central portion of the state (Sites 5 and 8) were above 10 μN, and $NO_3^-$ concentrations in the panhandle (Sites 2 and 3) and the southern portions (Sites 9 and 13) of Florida were below 10 μN.

Year-to-year variations in observed $NO_3^-$ concentrations both within and across sites were less pronounced than variations in field $H^+$ or excess $SO_4^{-2}$ concentrations. During the 3-year period, the observed differences across the state (excluding Site 14) were 4.7 μN or 43.3 percent for the first year, 2.4 μN or 24.7 percent for the second year, and 3.6 μN or 34.0 percent for the third year. Within sites, a decrease in $NO_3^-$ concentrations over the 3-year period was observed for Site 2 (4.4 μN or

33.3 percent) and Site 3 (0.9 µN or 9.2 percent); however, $NO_3^-$ concentrations at Sites 4 and 9 increased slightly (an average of 1.1 µN or 12.1 percent) and at Sites 5, 8, and 13, remained about the same.

Average concentrations of excess $Ca^{+2}$ over the 3-year period generally increased from north to south, perhaps reflecting higher levels of $Ca^{+2}$ and $Mg^{+2}$ carbonates in central and southern Florida soils. The maximum site-to-site differences of excess $Ca^{+2}$ concentrations for the three annual periods were 6.4 µN or 98.5 percent for Year 1, 5.0 µN or 83.3 percent for Year 2, and 3.9 µN or 60.5 percent for Year 3. Over the 3-year period, excess $Ca^{+2}$ concentrations observed at Sites 2, 3, 5, 8, and 9 increased 1.5 µN or more from Year 1 to Year 3 with an average increase of 43.4 percent. Only excess $Ca^{+2}$ at Site 13 decreased over the 3-year period, a corresponding 3.0 µN or 31-percent decrease.

The 3-year average concentrations of $Mg^{+2}$, $Na^+$, and $Cl^-$ increased slightly from north to south (at inland sites) and were highest at the coastal sites (Sites 4 and 14). Excess $Cl^-$ concentrations [total $Cl^-$ minus (1.8 x $Na^+$)] were not significant (i.e., <2 µN) at any site. Wind at the northern Florida locations is from many different directions, but the southern peninsula of Florida is generally under the influence of wind predominantly from the east and southeast [National Oceanic and Atmospheric Administration (NOAA), 1980]. This easterly and southeasterly flow brings moisture-laden marine air from the Atlantic Ocean, which results in higher $Na^+$ and $Cl^-$ concentrations at southern peninsula sites (refer to Subsection 2.3.1.2 on sea-salt influences on precipitation chemistry).

The average rainfall and deposition of major cations and anions over the 3-year period for the seven sites are presented in Table 2.3-4. The patterns for average deposition across the state generally followed the observed concentration patterns. The highest depositions of field and laboratory $H^+$ were observed at the more northern sites. Depositions of

Table 2.3-4. Mean Annual Rainfall and Wet Deposition* for the 3-Year Period from 10/01/81 Through 09/30/84

| Site | Rainfall† (cm/yr) | $H^+$ Field | $H^+$ Lab | $Ca^{+2}$ | Excess $Ca^{+2}$ | $Mg^{+2}$ | $K^+$ | $Na^+$ | $NH_4^+$ | $NO_3^-$ | $Cl^-$ | Excess $Cl^-$ | $SO_4^{-2}$ | Excess $SO_4^{-2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 153 | 451 | 349 | 71 | 64 | 57 | 11 | 177 | 90 | 150 | 218 | 13 | 337 | 316 |
| 3 | 144 | 396 | 304 | 69 | 62 | 53 | 13 | 168 | 80 | 129 | 221 | 25 | 293 | 273 |
| 4 | 150 | 414 | 319 | 86 | 64 | 148 | 19 | 588 | 62 | 139 | 695 | 11 | 352 | 281 |
| 5 | 138 | 415 | 369 | 69 | 64 | 42 | 11 | 134 | 78 | 143 | 172 | 15 | 331 | 314 |
| 8 | 127 | 340 | 301 | 95 | 89 | 53 | 10 | 163 | 119 | 148 | 206 | 17 | 383 | 363 |
| 9 | 127 | 295 | 202 | 79 | 72 | 60 | 8 | 184 | 58 | 116 | 236 | 21 | 219 | 195 |
| 13 | 131 | 241 | 180 | 117 | 108 | 72 | 17 | 248 | 63 | 119 | 309 | 25 | 207 | 178 |
| 14** | 117 | 246 | 128 | 85 | 62 | 155 | 16 | 623 | 32 | 70 | 728 | 9 | 201 | 126 |

*All ion deposition rates are eq/ha-yr.
†Based on volume of precipitation samples.
**Data for Site 14 are for the 2-year period from 10/01/81 through 09/13/83.

cm/yr = centimeters per year.

Source: ESE, 1986.

field $H^+$ averaged more than approximately 400 equivalents per hectare per year (eq/ha-yr) at Sites 2, 3, 4, and 5 and less than 350 eq/ha-yr at Sites 8, 9, 13, and 14. The highest depositions of laboratory $H^+$ were observed at Sites 5 and 2 with values of 369 and 349 eq/ha-yr, respectively. The lowest observed deposition of laboratory $H^+$ was less than 200 eq/ha-yr or 50 percent less than the highest deposition. Excess $SO_4^{-2}$ deposition averaged more than 300 eq/ha-yr for the northern and central Florida sites and less than 200 eq/ha-yr for the southern Florida sites. Deposition of $NO_3^-$ was generally about one-half that of excess $SO_4^{-2}$. The difference in $NO_3^-$ deposition between the northern and southern sites was less than that for field and laboratory $H^+$ and excess $SO_4^{-2}$.

The effects of both concentration and rainfall amount can in some cases confound differences among sites. For example, the highest average observed field $H^+$ concentration for the 3-year period was 30.3 µN at Site 5 and the second highest was 29.5 µN at Site 2, a difference of only 2.7 percent. However, wet deposition at Site 5 was 36 equivalents per hectare (eq/ha) or 8 percent less than Site 2, which was accounted for by 9 percent more rainfall at Site 2 that at Site 5. In contrast, the lowest concentration of excess $SO_4^{-2}$ and rainfall amount was observed at Site 14, thus enhancing the differences in deposition of that site relative to other sites.

Rainfall amount and deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ for each site are presented in Table 2.3-5. Rainfall amount was highly variable across sites and years. Depositions of laboratory $H^+$ and excess $SO_4^{-2}$, in general, decreased from Year 1 to Year 3 with more northern sites observing a greater decrease than southern sites. For example, deposition of laboratory $H^+$ at Site 2 decreased from 449 to 297 eq/ha-yr (35 percent) and deposition of excess $SO_4^{-2}$ decreased from 362 to 283 eq/ha-yr (21 percent) over the 3-year period. Conversely, the deposition of excess $SO_4^{-2}$ increased from 217 to 307 eq/ha-yr (46 percent) at Site 3. $NO_3^-$ deposition varied from year to year but was generally

Table 2.3-5. Annual Rainfall* and Deposition† of Laboratory $H^+$, Excess $SO_4^{-2}$, and $NO_3^-$ for the 3-Year Period from 10/01/81 Through 09/30/84

| Site | Rainfall | | | Laboratory $H^+$ | | | Excess $SO_4^{-2}$ | | | $NO_3^-$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 | Year 1 | Year 2 | Year 3 |
| 2 | 121 | 178 | 162 | 449 | 301 | 297 | 362 | 303 | 283 | 160 | 147 | 141 |
| 3 | 103 | 157 | 174 | 329 | 257 | 327 | 217 | 293 | 307 | 98 | 143 | 147 |
| 4 | 165 | 137 | 150 | 438 | 250 | 268 | 305 | 272 | 265 | 137 | 145 | 136 |
| 5 | 166 | 131 | 118 | 499 | 327 | 280 | 427 | 276 | 238 | 168 | 139 | 121 |
| 8 | 117 | 145 | 119 | 307 | 323 | 273 | 369 | 398 | 322 | 146 | 152 | 147 |
| 9 | 140 | 119 | 123 | 233 | 172 | 200 | 208 | 186 | 191 | 123 | 104 | 120 |
| 13 | 145 | 134 | 116 | 203 | 146 | 193 | 198 | 177 | 157 | 138 | 114 | 106 |
| 14** | 112 | 122 | — | 139 | 117 | — | 105 | 147 | — | 59 | 81 | — |

*Rainfall in cm/yr for volume of precipitation samples.
†Deposition in eq/ha-yr.
**Data for Site 14 are for the 2-Year Period 10/01/81 through 09/13/83.

Note: Year 1 = October 1, 1981, through September 30, 1982.
Year 2 = October 1, 1982, through September 30, 1983.
Year 3 = October 1, 1983, through September 30, 1984.

Source: ESE, 1986.

less than laboratory $H^+$ and excess $SO_4^{-2}$. Year 1 was relatively "wet" (i.e., large rainfall amount relative to other years) for Sites 4, 5, 9, and 13, but it was relatively dry for Sites 2 and 3. However, the highest deposition of laboratory $H^+$ and excess $SO_4^{-2}$ for Year 1 was at Sites 4, 5, and 2, which would not be expected considering rainfall amount alone, and relates to the higher VWM concentrations at these sites in Year 1 (see Table 2.3-3).

Although these data summaries suggest differences among sites and within sites for different annual periods, the inherent variability in observed precipitation chemistry must be evaluated carefully through statistical procedures that can account for such variability before conclusions can be drawn. Such analyses are presented in Subsections 2.5 and 2.6 of this report.

#### 2.3.1.2 Sea-Salt Influence on Precipitation Chemistry

Because of the marine influence on the atmosphere over Florida, sea salt can contribute significantly to observed cations and anions in precipitation. This contribution is illustrated by Table 2.3-6 which presents the sea-salt contribution to observed deposition of total ions, $SO_4^{-2}$, $Cl^-$, $Ca^{+2}$, $K^+$, and $Mg^{+2}$. As seen in this table, the sea-salt contribution to total ions ranges from 25.8 percent (Site 5) to 78.8 percent (Site 14). The sea-salt contribution of total ions at the coastal sites (Sites 4 and 14) is clearly evident. As noted previously, the inland southern Florida sites also have a higher sea-salt contribution than other inland sites.

Sea-salt contributes the majority of $Cl^-$ and $Mg^{+2}$ ions at all sites, with the coastal sites experiencing greater than a 95-percent contribution. Only at the coastal sites does sea salt contribute more than 50 percent of $K^+$. Sea-salt contributions to $SO_4^{-2}$ and $Ca^{+2}$ are generally 10 percent or less for the inland sites but are 20 percent or more for the coastal sites.

Table 2.3-6. Sea-Salt Contribution (%) to Observed Deposition of Total Ions, $SO_4^{-2}$, $Cl^-$, $Ca^{+2}$, $K^+$, and $Mg^{+2}$ for the 3-Year Period from 10/01/81 Through 09/30/84

| Site | Total Ions | $SO_4^{-2}$ | $Cl^-$ | $Ca^{+2}$ | $K^+$ | $Mg^{+2}$ |
|---|---|---|---|---|---|---|
| 2 | 31.2 | 6.1 | 93.9 | 9.5 | 33.0 | 76.1 |
| 3 | 32.7 | 6.7 | 88.7 | 9.3 | 27.3 | 78.1 |
| 4 | 63.1 | 20.0 | 98.4 | 25.8 | 67.0 | 97.9 |
| 5 | 25.8 | 4.8 | 91.3 | 7.3 | 26.9 | 78.8 |
| 8 | 28.6 | 5.1 | 91.9 | 6.3 | 36.1 | 76.8 |
| 9 | 41.4 | 10.1 | 91.2 | 8.9 | 48.1 | 77.3 |
| 13 | 47.6 | 14.3 | 91.9 | 8.2 | 23.4 | 84.9 |
| 14* | 78.8 | 37.1 | 98.8 | 27.7 | 83.8 | 99.1 |

*Data for Site 14 are for the 2-year period 10/01/81 through 09/13/83.

Note: $Na^+$ used as a sea-salt tracer. Sea-salt contributions of $NH_4^+$ and $NO_3^-$ are negligible (i.e., <<1 percent).

Source: ESE, 1986.

Although sea salt significantly contributes to the total ion loading observed in Florida's precipitation, it plays a minor role in the acid-base chemistry of precipitation. Sea-salt contains approximately 1 μN alkalinity for every 159 μN of $Na^+$ (assuming all $Na^+$ is of marine origin); the corresponding acid neutralizing capacity (ANC) of sea-salt at Site 14 amounts to only 0.33 μN and is much less at all other sites.

The results demonstrate that sea salt contributes significantly to the ionic loading in Florida's precipitation and should be considered in evaluating concentrations and depositions of non-sea-salt $SO_4^{-2}$ and $Ca^{+2}$. However, the effect of sea salt on precipitation acidity is minor.

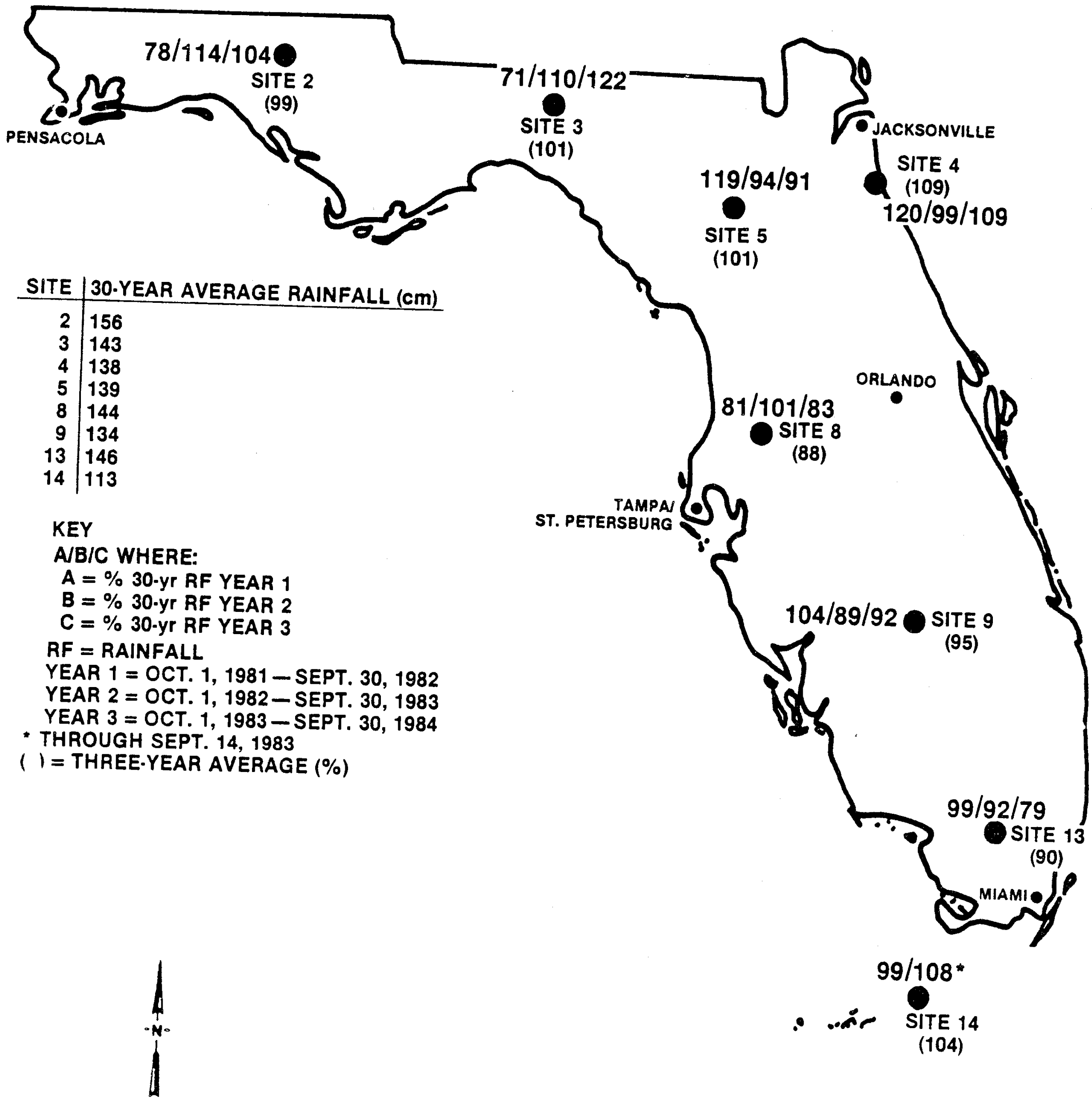
#### 2.3.1.3 Comparison of 3-Year Rainfall Amounts to 30-Year Average

A comparison of the precipitation amounts from each site with the 30-year average is presented for the 3-year period for each site in Figure 2.3-2. The average precipitation over the 3-year period ranged from 88 percent (Site 8) to 109 percent (Site 4) of the 30-year average rainfall. On the average, the coastal sites (Sites 4 and 14) experienced more rainfall than the 30-year average; inland sites located in central and south Florida (Sites 8, 9, and 13) experienced less rainfall than the 30-year average; and inland, more northern sites (Sites 2, 3, and 5) experienced about the same rainfall as the 30-year average.

The precipitation amount observed for individual annual periods was often considerably different than the 30-year average. For example, Site 3 had a 3-year average rainfall approximately equivalent to the 30-year average, but the year-to-year differences were greater than 50 percent. Similar, although not as distinct, differences were observed for the other sites.

#### 2.3.1.4 Annualized Air Chemistry

Annual average concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ in ambient air are presented in Table 2.3-7. Ambient air concentrations of



| SITE | 30-YEAR AVERAGE RAINFALL (cm) |
|---|---|
| 2 | 156 |
| 3 | 143 |
| 4 | 138 |
| 5 | 139 |
| 8 | 144 |
| 9 | 134 |
| 13 | 146 |
| 14 | 113 |

KEY
A/B/C WHERE:
A = % 30-yr RF YEAR 1
B = % 30-yr RF YEAR 2
C = % 30-yr RF YEAR 3
RF = RAINFALL
YEAR 1 = OCT. 1, 1981—SEPT. 30, 1982
YEAR 2 = OCT. 1, 1982—SEPT. 30, 1983
YEAR 3 = OCT. 1, 1983—SEPT. 30, 1984
* THROUGH SEPT. 14, 1983
( ) = THREE-YEAR AVERAGE (%)

Figure 2.3-2
ANNUAL RAINFALL AS A PERCENTAGE OF 30-YEAR AVERAGE FOR SITES 2, 3, 4, 5, 8, 9, 13, AND 14

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Table 2.3-7. Annual Average Concentrations* of Particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ for the 2-Year Period from 11/01/82 Through 09/11/84

| Site | Particulate $SO_4^{-2}$ | | $HNO_3$ | | $SO_2$ | | $NO_2$ | |
|---|---|---|---|---|---|---|---|---|
| | Year 1 | Year 2 | Year 1 | Year 2 | Year 1 | Year 2 | Year 1 | Year 2 |
| 2 | 5.6 | 4.9 | 1.2 | 1.1 | 2.9 | 3.0 | 6.6 | 9.5 |
| 3 | 5.1 | 4.7 | 1.0 | 1.0 | 2.4 | 2.7 | 4.2 | 4.2 |
| 4 | 4.4 | 4.6 | 1.0 | 1.1 | 2.4 | 2.6 | 7.1 | 8.3 |
| 5 | 4.6 | 4.5 | 1.2 | 1.2 | 3.0 | 3.1 | 9.0 | 10.3 |
| 8 | 4.4 | 4.4 | 1.0 | 1.2 | 4.4 | 4.4 | 10.3 | 11.1 |
| 9 | 3.5 | 3.7 | 0.94 | 1.0 | 2.8 | 2.6 | 4.7 | 5.0 |
| 13 | 3.2 | 3.2 | 0.86 | 0.84 | 1.6 | 1.3 | 3.1 | 2.9 |
| 14† | 3.5 | -- | 0.72 | -- | 1.5 | -- | 1.3 | -- |

*Concentrations are in $\mu g/m^3$.
†Data for Site 14 are for Year 1 only.

Note: Year 1 = October 1, 1982, through September 30, 1983; approximately 100 samples per site.
Year 2 = October 1, 1983, through September 30, 1984; approximately 120 samples per site.

Source: ESE, 1986.

$SO_2$ and $NO_2$ primarily reflect direct contributions from anthropogenic sources while particulate $SO_4^{-2}$ and $HNO_3$ reflect a component of their oxidized forms, respectively.

These data suggest a north-south gradient in mean concentrations for particulate $SO_4^{-2}$ during both annual periods. Particulate $SO_4^{-2}$ concentrations for Year 1 uniformly decreased over the inland sites, from 5.6 $\mu g/m^3$ at Site 2 to 3.2 $\mu g/m^3$ at Site 13. Similarly, during Year 2, particulate $SO_4^{-2}$ decreased from 4.9 $\mu g/m^3$ at Site 2 to 3.2 $\mu g/m^3$ at Site 13. Mean concentrations of particulate $SO_4^{-2}$ ranged from greater than 4.5 $\mu g/m^3$ for the panhandle and north-central sites (Sites 2, 3, 4, 5, and 8) to less than 4.4 $\mu g/m^3$ for the south Florida sites (Sites 9, 13, and 14). $HNO_3$ concentrations generally decreased from north to south over the 2-year period; the northern and central Florida sites were generally 1.0 $\mu g/m^3$ or more, and southern Florida sites were 1.0 $\mu g/m^3$ or less. However, there was only about a 0.3 $\mu g/m^3$ decrease (less than a 30-percent decrease) in $HNO_3$ concentrations for both years over all sites. In contrast, particulate $SO_4^{-2}$ decreased more than 2 $\mu g/m^3$ (more than a 40-percent decrease) for the same annual periods.

Concentrations of $SO_2$ in ambient air were highest at Site 8 with 4.4 $\mu g/m^3$ observed for both years and lowest at Site 13 with concentrations less than 2 $\mu g/m^3$. The pattern of $SO_2$ concentrations for northern and central Florida sites (Sites 2, 3, 4, 5, and 8) did not follow the uniform north-to-south gradient exhibited by particulate $SO_4^{-2}$. Ambient concentrations of $NO_2$ were highest at Site 8 and lowest at Site 13, with the general pattern similar to that observed for $SO_2$.

The different patterns between $SO_2$ and $NO_2$ and their oxidation products, particulate $SO_4^{-2}$ and $HNO_3$, may reflect the direct influence of local sources on observed concentrations of $SO_2$ and $NO_2$, whereas transformation mechanisms on a regional scale primarily influence particulate $SO_4^{-2}$ and $HNO_3$ concentrations.

#### 2.3.1.5 Estimates of Total Deposition

Wet deposition of $SO_4^{-2}$ and $NO_3^-$ is only one component of the transfer of acidic substances or their precursors to the landscape. Assessment of the potential effects on the ecology and manmade materials of acidic deposition requires information not only on wet deposition but on the total deposition of acidifying substances. The term total deposition commonly refers to the sum of wet plus dry deposition.

Dry deposition is the mass transfer of gases and aerosols to exposed surfaces and is caused by a complex set of physical, chemical, and biological processes. Sehmel (1980) and Hicks (1983) have summarized the factors that influence the rate of pollutant deposition upon exposed surfaces. These factors include:

1. Pollutant phase (i.e., gas, fine aerosol, or coarse aerosol),
2. Chemical reactivity (e.g., strongly acidic versus weakly acidic),
3. Micrometeorological characteristics including surface roughness, and
4. Surface characteristics (e.g., biological status, surface wetness, surface reactivity).

Measurements of dry deposition have been made through laboratory simulations and field studies. The laboratory studies performed to date have primarily focused on the evaluation of the relative importance of deposition mechanisms, as well as the response of certain surfaces, including biological, to the deposition of gases and aerosols. Field measurements have principally centered around the measurement of concentration gradients as well as micrometeorological conditions to obtain more direct estimates of dry deposition than laboratory studies.

Dry deposition mechanisms are highly temporally and spatially variable, which in turn complicates measurement. Currently, neither field nor laboratory measurements can fully account for this temporal and spatial variability. Out of necessity, therefore, the simulations of the dry-deposition processes used in models have tended to be simple in form, and the use of a deposition velocity (Vd) to account for a combination of dry-deposition mechanisms has been widely accepted. A deposition velocity is the apparent vertical velocity at which a specific gas or aerosol is deposited on a surface and can be used to estimate the mass transfer if the airborne concentration (c) is known (i.e., dry deposition = Vd x c).

The use of currently available deposition velocities is not without significant uncertainties for several reasons. First, the dry-deposition process is sufficiently complex to make the direct applicability of both laboratory and field-derived deposition velocities uncertain. Second, since dry-deposition measurements are only available for selected surfaces, the direct transfer of such information to other surfaces may not be appropriate. Finally, the time scale for available measurements is limited and may not reflect actual temporal variability in the deposition processes.

Taken together, the uncertainties in the available dry-deposition measurements provide sufficient reason to consider any long-term, spatial estimate of dry deposition as extremely preliminary. Only with such qualification can an annual estimate of total deposition be made for Florida using the data obtained from the monitoring network and assuming a literature-based deposition velocity.

During the course of this study, it was recognized that the data collected from the dry-bucket portion of wet/dry collectors could not be usefully interpreted to provide estimates of dry deposition. For this reason, ambient air concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ were collected at each monitoring site (refer to Subsection 2.2) in order to estimate dry deposition. Although there are considerable uncertainties associated with this approach, the measurement of particulate $SO_4^{-2}$, $SO_2$, $NO_2$, and $HNO_3$ would provide considerably better dry-deposition estimates than the dry bucket. Recent initiatives to establish a national monitoring network for estimating dry deposition from airborne concentrations (NAPAP, 1984) demonstrate the general acceptance of this approach as the best available for routine measurements.

Dry-deposition rates for particulate $SO_4^{-2}$ and $SO_2$ were estimated using deposition velocities calculated by the Eastern North American Model of Air Pollution (ENAMAP) model (see Subsection 3.2.3 and Subsection 3.3.2). Monthly average deposition velocities were calculated by ENAMAP based on Sheih et al. (1979) and Sheih (1984) and take into account the land-use type, atmospheric stability, time of day, and season. Dry deposition in ENAMAP is calculated based on 12 land use types, six atmospheric stabilities, time of day, and five seasons: winter, spring, summer, early fall, and late fall. However, because the extent and assignment of seasons vary over the eastern United States, the seasons were modified for Florida. For the panhandle and northern peninsula of Florida [i.e., above 27.8 degrees north (°N) latitude], only spring, summer, early fall, and late fall met the surface descriptions by Sheih et al. (1979) and Sheih (1984). Only summer, early fall, and spring would meet the surface description for the southern peninsula (i.e., below latitude 27.8°N). Daytime dry-deposition velocities of particulate $SO_4^{-2}$ and $SO_2$ for three atmospheric stabilities and two seasons are presented in Table 2.3-8 to illustrate the range of dry-deposition velocities calculated by ENAMAP. To account for the prevalent stable atmospheric conditions which occur at night, the particulate $SO_4^{-2}$ and $SO_2$ dry-deposition velocities used were 0.07 cm/sec for all nighttime conditions. Monthly average deposition velocities were calculated for each monitoring site using ENAMAP for: February, March, April, June, July, and August 1983. The resultant deposition velocities were then used to calculate total deposition at seven monitoring sites using the corresponding monthly average ambient

Table 2.3-8. Example of Daytime $SO_2$ and Particulate $SO_4^{-2}$ Dry Deposition Velocities by Land-Use Category, Atmospheric Stability, and Season

| Land-Use Category | $SO_2$ Dry Deposition Velocities (cm/sec) | | | | | | Particulate $SO_4^{-2}$ Dry Deposition Velocities (cm/sec) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Summer | | | Winter | | | Summer | | | Winter | | |
| | Slightly Stable | Neutral | Slightly Unstable | Slightly Stable | Neutral | Slightly Unstable | Slightly Stable | Neutral | Slightly Unstable | Slightly Stable | Neutral | Slightly Unstable |
| 1. Cropland and pasture | 0.05 | 0.35 | 0.75 | 0.25 | 0.45 | 0.45 | 0.05 | 0.30 | 0.30 | 0.05 | 0.20 | 0.05 |
| 2. Cropland, woodland, and grazing land | 0.05 | 0.35 | 0.75 | 0.55 | 0.75 | 0.75 | 0.05 | 0.30 | 0.30 | 0.05 | 0.20 | 0.05 |
| 3. Irrigated crops | 0.05 | 0.25 | 0.65 | 0.25 | 0.45 | 0.35 | 0.05 | 0.30 | 0.30 | 0.05 | 0.20 | 0.05 |
| 4. Forest and woodland grazed | 0.05 | 0.35 | 0.85 | 0.25 | 0.35 | 0.35 | 0.05 | 0.30 | 0.40 | 0.05 | 0.10 | 0.05 |
| 5. Forest and woodland ungrazed | 0.05 | 0.35 | 0.85 | 0.25 | 0.35 | 0.35 | 0.05 | 0.30 | 0.20 | 0.05 | 0.20 | 0.10 |
| 6. Subhumid grasslands and semiarid grazing land | 0.05 | 0.25 | 0.75 | 0.25 | 0.45 | 0.45 | 0.05 | 0.20 | 0.10 | 0.05 | 0.20 | 0.05 |
| 7. Open woodland grazed | 0.05 | 0.35 | 0.75 | 0.45 | 0.55 | 0.55 | 0.05 | 0.20 | 0.20 | 0.10 | 0.20 | 0.05 |
| 8. Desert shrubland | 0.05 | 0.15 | 0.45 | 0.55 | 0.75 | 0.75 | 0.20 | 0.30 | 0.30 | 0.20 | 0.30 | 0.30 |
| 9. Swamp | 0.55 | 0.95 | 1.25 | 0.45 | 0.65 | 0.65 | 0.05 | 0.30 | 0.40 | 0.05 | 0.10 | 0.05 |
| 10. Marshland | 0.05 | 0.35 | 1.05 | 0.25 | 0.25 | 0.25 | 0.20 | 0.70 | 0.40 | 0.10 | 0.20 | 0.05 |
| 11. Metropolitan city | 0.05 | 0.05 | 0.05 | 0.55 | 0.65 | 0.65 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| 12. Lake or ocean | 0.35 | 0.75 | 0.35 | 0.35 | 0.75 | 0.55 | 0.20 | 0.30 | 0.30 | 0.20 | 0.30 | 0.30 |

Note: cm/sec = centimeters per second.

Sources: Sheih, 1984.
ESE, 1986.

air concentrations of particulate $SO_4^{-2}$ and $SO_2$. Annual dry deposition was calculated using the 6-month average deposition velocity and annual average concentrations of particulate $SO_4^{-2}$ and $SO_2$.

Deposition velocities similar to those suggested by Sheih _et al_. (1979) and Sheih (1984) for particulate $SO_4^{-2}$ and $SO_2$ are not available for $HNO_3$ and $NO_2$. Consequently, the literature was reviewed to obtain a reasonable first approximation of deposition velocities for these species.

For $HNO_3$, Huebert (1983) found an average deposition velocity of 2.9 cm/sec to pasture for 8 days of concentrated sampling. Although inappropriate for Florida, Cadle _et al_. (1985) found average deposition velocity of 1.4 cm/sec to snow over two winter periods. For $NO_2$, Wesely _et al_. (1982) found deposition velocities to a soybean field to average 0.6 cm/sec during the daytime. Meszaros and Horvath (1984) reported an average deposition velocity from Varhelyi (1980) of 0.5 cm/sec for $NO_2$. Deposition velocities of total $NO_x$ [$NO_2$, NO, peroxyacetylnitrate (PAN), and $HNO_3$] to a deciduous forest canopy were found by Hicks _et al_. (1983) to be highly variable, ranging from 0.8 cm/sec during the day and negligible at night. Based on these studies and information on deposition velocities derived for other pollutants (e.g., the nighttime deposition velocity for particulate $SO_4^{-2}$ and $SO_2$ was assumed to be only 0.07 cm/sec due to stable atmospheric conditions), deposition velocities of $HNO_3$ and $NO_2$ were assumed to be 1.5 cm/sec and 0.3 cm/sec, respectively. For $HNO_3$, a value of 1.5 cm/sec reflects the relatively high daytime values of Huebert (1983) plus an assumed nighttime deposition velocity that would be neglible. Similarly, the assumed deposition velocity fo $NO_2$ of 0.3 cm/sec reflects the a daytime value of 0.6 cm/sec and neglible value at night.

The results of the dry-deposition calculations as well as estimates of total deposition are presented in Table 2.3-9. For $SO_x$, total estimated deposition ranged from 640 eq/ha-yr at Site 8 to about 306 eq/ha-yr at

Table 2.3-9. Observed Wet, Calculated Dry, and Estimated Total Deposition (eq/ha-yr) of $SO_x$ and $NO_x$ Measured in Florida (October 1982 Through October 1983)

| | | Calculated Dry $SO_x$* | | | | | | Calculated Dry $NO_x$* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Observed Wet $SO_4^{-2}$ | As Particulate $SO_4^{-2}$ | As $SO_2$ | Total | % as Particulate $SO_4^{-2}$ | Total (Wet and Dry) | Observed Wet | As $HNO_3$ | As $NO_2$ | Total | % As $HNO_3$ | Total (Wet and Dry) |
| 2 | 328 | 91 | 88 | 179 | 51 | 507 | 147 | 90 | 135 | 225 | 40 | 372 |
| 3 | 320 | 82 | 72 | 154 | 53 | 474 | 143 | 75 | 86 | 161 | 47 | 304 |
| 4 | 352 | 67 | 72 | 139 | 48 | 491 | 145 | 75 | 146 | 221 | 34 | 366 |
| 5 | 294 | 71 | 99 | 170 | 42 | 464 | 139 | 90 | 184 | 274 | 33 | 413 |
| 8 | 419 | 67 | 157 | 224 | 30 | 643 | 152 | 75 | 211 | 286 | 26 | 438 |
| 9 | 211 | 53 | 89 | 142 | 37 | 353 | 104 | 71 | 96 | 167 | 43 | 271 |
| 13 | 206 | 46 | 54 | 100 | 46 | 306 | 114 | 65 | 64 | 129 | 50 | 243 |

*$SO_x$ = particulate $SO_4^{-2}$ and $SO_2$.
$NO_x$ = $HNO_3$ + $NO_2$.

Source: ESE, 1986.

Site 13 and was about 33-percent dry which is consistent with the estimated portion of dry deposition for the eastern United States (NAS, 1983) as a whole. The calculated dry deposition of particulate $SO_4^{-2}$ and $SO_2$ for Sites 2, 3, 4, and 13 were nearly equal while calculated dry deposition of $SO_2$ was higher than particulate $SO_4^{-2}$ for Sites 5, 8, and 9. Mean seasonal differences between summer (April, June, July, and August) and winter (February and March) of calculated dry depositions of particulate $SO_4^{-2}$ and $SO_2$ were 34.1 and 9.4 percent, respectively, over the state with calculated summer depositon higher than winter. Total deposition for $NO_x$ was estimated to range from 438 eq/ha at Site 8 to 243 eq/ha at Site 13. Calculated dry deposition of $NO_x$ was about 50 percent higher than the observed wet deposition over the state. Except at Site 13, calculated dry deposition of $NO_2$ was higher than $HNO_3$. The ultimate accuracy of these results is unknown but provides a first approximation of total deposition of $SO_x$ and $NO_x$ in Florida.

Table 2.3-10 presents the results obtained for the dry bucket during the period September 15, 1981, through September 14, 1982. In general, the amount of dry deposition calculated from ambient concentrations is about twice as high as the dry-bucket measurements for $SO_4^{-2}$ and more than five times as high as the dry-bucket measurements for $NO_3^-$. The highest depositions, however, were obtained at Site 8 for both methods. Dry-bucket depositions of $SO_4^{-2}$ and $NO_3^-$ were generally higher in the north than the south as was the calculated dry depositions. This pattern may be due, in part, to higher sea-salt contributions which are indicated by higher $Na^+$ depositions in the dry buckets. Since aerosol $Na^+$ was not measured, the significance of sea-salt contributions to particulate $SO_4^{-2}$ depositions over the network is unknown.

Table 2.3-10. Dry-Bucket Measurements* from September 15, 1981, Through September 14, 1982

| Site | $Ca^{+2}$ | $Mg^{+2}$ | $K^+$ | $Na^+$ | $NH_4^+$ | $NO_3^-$ | $Cl^-$ | $SO_4^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| 2 | 40.3 | 22.3 | 16.4 | 46.9 | 26.9 | 15.4 | 54.6 | 71.4 |
| 3 | 154.6 | 36.1 | 29.5 | 48.1 | 27.5 | 31.1 | 56.0 | 83.7 |
| 4 | 78.0 | 48.7 | 15.6 | 197.5 | 19.2 | 23.5 | 230.0 | 83.7 |
| 5 | 116.5 | 29.9 | 12.7 | 77.0 | 5.8 | 31.0 | 89.7 | 75.1 |
| 8 | 318.3 | 45.7 | 32.7 | 102.3 | 82.0 | 39.0 | 119.1 | 139.5 |
| 9 | 90.9 | 34.7 | 11.9 | 82.5 | 30.0 | 15.1 | 96.1 | 59.7 |
| 13 | 273.0 | 49.3 | 33.7 | 131.3 | 23.7 | 12.7 | 152.9 | 66.1 |

*Units are eq/ha-yr.

Source: ESE, 1986.

### 2.3.1.6 Special Parameter Monitoring

Parameters other than the major cations and anions, pH, and conductivity mentioned previously were also analyzed in one year of precipitation samples. During the period September 15, 1981, through September 14, 1982, analyses were performed for $PO_4^{-3}$, $F^-$, $V^{+4}$, $Al^{+3}$, total strong acidity, alkalinity, and DOC. $PO_4^{-3}$ and $F^-$ were measured as tracer or indicator species of phosphate chemical emissions while $V^{+4}$ was measured as an indicator of fuel oil combustion (ESE, 1982). $Al^{+3}$ was measured because of its importance to potential aquatic effects in Florida. Total/strong acidity was measured (by titration) to evaluate the influence of weak acids, possibly of organic origin, in Florida's precipitation. DOC was measured to provide data on the organic content in Florida's precipitation.

Results of these analyses on precipitation samples from 14 sites indicated that $PO_4^{-3}$, $F^-$, $Al^{+3}$, and $V^{+4}$ are consistently at or below their respective analytical detection limits at most sites (Table 2.3-11). Higher levels of these trace constituents were observed at Site 8 which may reflect the phosphate mines that are operating nearby (ESE, 1983b). Such mining activities are well-known sources of airborne $F^-$ and $PO_4^{-3}$. Elevated $Al^{+3}$ and $V^{+4}$, likewise, might represent soil constituents disturbed by such mining operations.

Total acidity and bound acidity (total minus free acidity) decreased from northern sites (Sites 1 through 8) to southern sites (Sites 10 through 14); however, most of the observed decrease in total acidity was due to free acidity (i.e., dissolved $H^+$) (ESE, 1983b). For all sites, bound acidity accounts for approximately 50 percent of total acidity (Table 2.3-11). Currently, no data are available to determine whether the bound acidity component is of natural or anthropogenic origin.

The observed DOC concentrations were somewhat higher for the more northern sites (Sites 1 through 8) than the southern sites (Sites 9

Table 2.3-11. Summary of VWM Concentrations* for $PO_4^{-3}$, $F^-$, $Al^{+3}$, $V^{+4}$, DOC, Total and Bound Acidity, and Alkalinity (September 15, 1981, to September 14, 1982).

| Parameter | Average VWM Over All Sites | Maximum VWM | Minimum VWM |
|---|---|---|---|
| $PO_4^{-3}$ | <0.9 | 1.4 | <0.9 |
| $F^-$ | <0.2 | 0.8 | <0.2 |
| $Al^{+3}$ | 0.33 | 0.47 | <0.22 |
| $V^{+4}$ | <0.05 | 0.05 | <0.05 |
| DOC | 1.14 | 1.68 | 0.85 |
| Total Acidity | 43.0 | 57.1 | 32.0 |
| Bound Acidity | 23.3 | 29.9 | 18.1 |
| Alkalinity | <2 | <2 | <2 |

*All concentrations are µN except DOC (mg/L).

Note: Less than (<) indicates that the observed value was less than the detection limit.

Source: ESE, 1986.

through 14; ESE, 1983b). Organic carbon was determined to be the most abundant element in statewide precipitation (excluding, of course, hydrogen and oxygen).

Despite the abundance of DOC observed in Florida precipitation, its relevance to the acidic deposition phenomenon was unknown because the chemical speciation of the DOC was not characterized during the sampling. Although considerable research has focused on the inorganic chemistry of precipitation in the United States and elsewhere, relatively few studies have attempted to evaluate the contribution of organic acids to acidic deposition. Galloway _et al_. (1982) reported the presence of formic acid and acetic acid in remote global precipitation; Likens _et al_. (1983) observed a variety of organic acids in precipitation collected at Ithaca, New York, and Hubbard Brook, New Hampshire. These studies indicate that organic acids can contribute significantly (up to 66 percent) to background precipitation acidity, but probably play a minor role in northeastern United States precipitation chemistry. Results of a free-radical cloud droplet model indicate that formic acid can be produced via aqueous-phase formaldehyde oxidation (Chameides, 1983). As a result, a pilot investigation of organic acids in Florida's precipitation was performed during the period September 14, 1982, to September 13, 1983, at Site 5.

The pilot study analyzed low-molecular-weight organic acids in precipitation samples. The study showed that _in situ_ preservation was necessary to prevent loss of formic and acetic acids from natural precipitation. Losses of organic acids from unpreserved samples average 4 to 6 percent per day, while losses of acids from samples preserved with chloroform ($CHCl_3$) plus base average less than 1 percent per day. Formic and acetic acids were observed in 61 and 27 percent, respectively, of preserved precipitation samples collected at Gainesville. VWM concentrations of formic and acetic acids were 2.5 and <1.0 µN, respectively, and could have contributed approximately 8 percent of the laboratory $H^+$ observed in precipitation at Site 5.

## 2.3.2 RELATIONSHIPS WITH OTHER PRECIPITATION CHEMISTRY DATA

### 2.3.2.1 In-State Networks

The data collected from the Florida Acid Deposition Study monitoring network were contemporaneous with data collected through NADP and NASA over the Calendar Years 1982, 1983, and 1984. Two NADP stations were located in the Bradford Forest in north-central Florida and at the entrance of the Everglades National Park. These stations collected wet-only precipitation on a weekly basis with laboratory measurements of pH and major cations and anions. The NASA network was located in the Cape Canaveral-Orlando area and measured wet-only precipitation on a daily basis with laboratory measurements of pH and major cations and anions.

VWM measurements of laboratory pH, laboratory $H^+$, $SO_4^{-2}$, and $NO_3^-$ observed at the NADP and NASA monitoring sites for the years 1982, 1983, and 1984 are presented in Table 2.3-12. This table also presents data collected from the Florida Acid Deposition Study monitoring network for selected sites that are in proximity ($\leq$75 km) of the NADP and NASA monitoring sites.

In general, these data indicate that the observed pattern of pH, $SO_4^{-2}$, and $NO_3^-$ concentrations across the state are similar across networks. However, data from both NADP sites appear to have lower laboratory $H^+$ concentrations than those observed at the Florida Acid Deposition Study sites. This is the case despite similar concentrations of $SO_4^{-2}$ and $NO_3^-$, especially in northern Florida. Although measurement bias cannot be ruled out, differences between NADP and Florida Acid Deposition Study laboratory $H^+$ concentrations could reflect differences in sample collection frequencies (i.e., weekly collection for NADP versus daily collection for the Florida Acid Deposition Study) or differences within observed spatial variability of the networks. The NASA site exhibited higher acidity, $SO_4^{-2}$, and $NO_3^-$ concentrations than the nearby Florida Acid Deposition Study site in 1982, but had similar values in 1983 and 1984.

Table 2.3-12. VWM Laboratory pH, Laboratory $H^+$, $SO_4^{-2}$, and $NO_3^-$ Concentrations* for Selected Sites in the Florida Acid Deposition Study Network and Nearby Sites of the NADP and NASA Networks

| | Parameter | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Laboratory pH | | | Laboratory $H^+$ | | | $SO_4^{-2}$ | | | $NO_3^-$ | | |
| Region/Network† | 1982 | 1983 | 1984 | 1982 | 1983 | 1984 | 1982 | 1983 | 1984 | 1982 | 1983 | 1984 |
| North Central Florida | | | | | | | | | | | | |
| FADS (Site 5) | 4.52 | 4.62 | 4.60 | 30.2 | 24.0 | 25.1 | 25.8 | 19.6 | 22.3 | 10.4 | 9.7 | 11.9 |
| NADP (Bradford Forest) | 4.69 | 4.71 | 4.73 | 20.4 | 19.5 | 18.6 | 25.1 | 22.4 | 24.7 | 10.8 | 10.6 | 11.9 |
| Central Florida | | | | | | | | | | | | |
| FADS (Site 8) | 4.60 | 4.64 | 4.64 | 25.1 | 22.9 | 22.9 | 31.5 | 26.5 | 29.1 | 12.4 | 10.5 | 13.6 |
| NASA (Orlando)** | 4.47 | 4.72 | 4.71 | 33.9 | 19.1 | 19.5 | 34.9 | 19.2 | 24.6 | 16.2 | 12.2 | 13.8 |
| South Florida | | | | | | | | | | | | |
| FADS (Site 13) | 4.86 | 4.88 | 4.86 | 13.8 | 13.1 | 13.8 | 13.8 | 13.6 | 12.1 | 9.7 | 8.4 | 8.9 |
| NADP (Everglades National Park) | 4.96 | 4.98 | 5.05 | 11.0 | 10.5 | 8.9 | 12.4 | 13.6 | 11.7 | 9.0 | 7.1 | 7.4 |

*All concentrations are µN, except pH (unitless).

†Networks: FADS = Florida Acid Deposition Study.
NADP = National Acid Deposition Program.
NASA = National Atmospheric and Space Administration.

**Only the NASA site in Orlando was operated during 1982-1984.

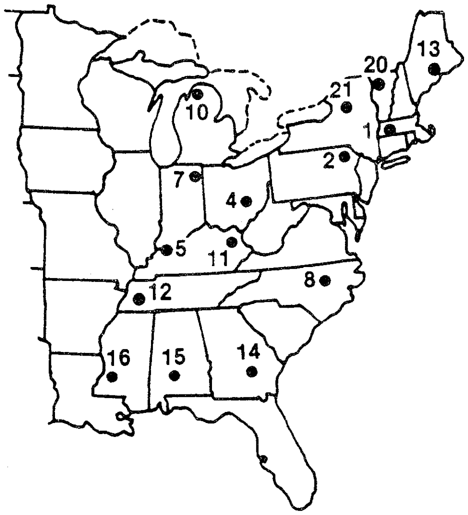
Source: ESE, 1986.

### 2.3.2.2 Out-of-State Networks

Three major precipitation chemistry monitoring networks have been operating in the eastern United States since the late 1970s: NADP, UAPSP, and Multistate Atmospheric Power Production Pollution Study (MAP3S) [sponsored by the U.S. Department of Energy (DOE) and EPA]. Precipitation chemistry data from these networks are obtained using wet-only collectors on either a weekly or daily basis (NADP = weekly; UAPSP and MAP3S = daily). Precipitation chemistry data from these networks were selected for comparison with the Florida data because each network used comparable field and analytical procedures and had a broad geographic coverage over the eastern United States. In addition, data from these networks have been previously used in describing the concentrations and depositions of acidic species in precipitation over the eastern United States. Figure 2.3-3 presents the location of each station used in the evaluation.

Average concentrations and depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$ within four geographic regions are shown in Figures 2.3-4 and 2.3-5 for Calendar Years 1982, 1983, and 1984. Concentrations of $H^+$, $SO_4^{-2}$, and $NO_3^-$ observed in the northeastern and midwestern United States were a factor of approximately 2 higher than concentrations observed for Florida for the Calendar Years 1982, 1983, and 1984. Sites located in the southeastern United States had concentrations of $H^+$, $SO_4^{-2}$, and $NO_3^-$ that were a factor of approximately 1.2 higher than Florida.

Presumably because of Florida's higher rainfall and coastal influence, differences in deposition of $H^+$, $SO_4^{-2}$, and $NO_3^-$ are not quite as great between the northeast and midwest United States and Florida. Northeast and midwest regions had depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$ generally in the range of 1.5 to 2 times higher than depositions for Florida (Figure 2.3-5). In contrast, differences in depositions between the southeastern region and Florida were roughly proportional to concentration differences.



### UAPSP SITES

MIDWEST:
4 ZANESVILLE, OH
5 ROCKPORT, IN
7 FT. WAYNE, IN
10 GAYLORD, MI
11 CLEARFIELD, KY

NORTHEAST:
1 TURNER FALLS, MA
2 TUNKHANNOCK, PA
13 WINTERPORT, ME
20 UNDERHILL, VT
21 BIG MOOSE, NY

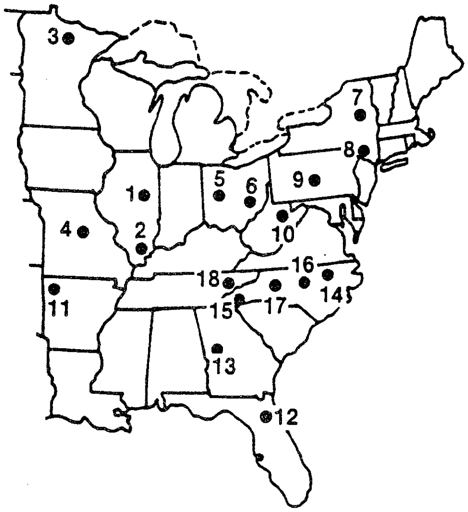
SOUTHEAST:
8 RALEIGH, NC
12 ALAMO, TN
14 UVALDA, GA
15 SELMA, AL
16 CLINTON, MS

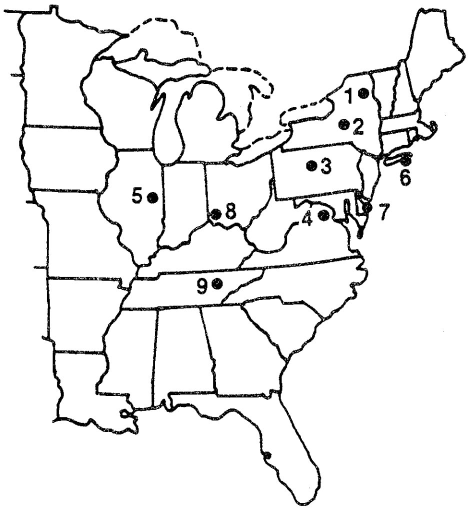
### NADP SITES

MIDWEST:
1 BONDVILLE, IL
2 DIXON SPRINGS, IL
3 MARCELL FOREST, MN
4 ASHLANDS WILDLIFE AREA, MO
5 DELAWARE, OH
6 CALDWELL, OH

NORTHEAST:
7 HUNTINGTON WILDLIFE AREA, NY
8 STILWELL LAKE, NY
9 LEADING RIDGE, PA
10 PARSONS, WV

SOUTHERN:
11 FAYETTEVILLE, AR
12 BRADFORD FOREST, FL
13 GEORGIA STATION
14 LEWISTON, NC
15 COWEETA, NC
16 RTP, NC
17 PIEDMENT RESEARCH, NC
18 WALKER BRANCH, TN





### MAP3S SITES

MIDWEST:
5 ILLINOIS
8 OXFORD, OH

NORTHEAST:
1 WHITEFACE, NY
2 ITHACA, NY
3 PENN STATE, PA
4 VIRGINIA
6 BROOKHAVEN, NY
7 LEWES, DE

SOUTHERN:
9 OAK RIDGE, TN

Figure 2.3-3
SITE LOCATIONS FOR UAPSP, NADP, AND MAP3S USED TO COMPARE WITH FLORIDA ACID DEPOSITION STUDY

ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.

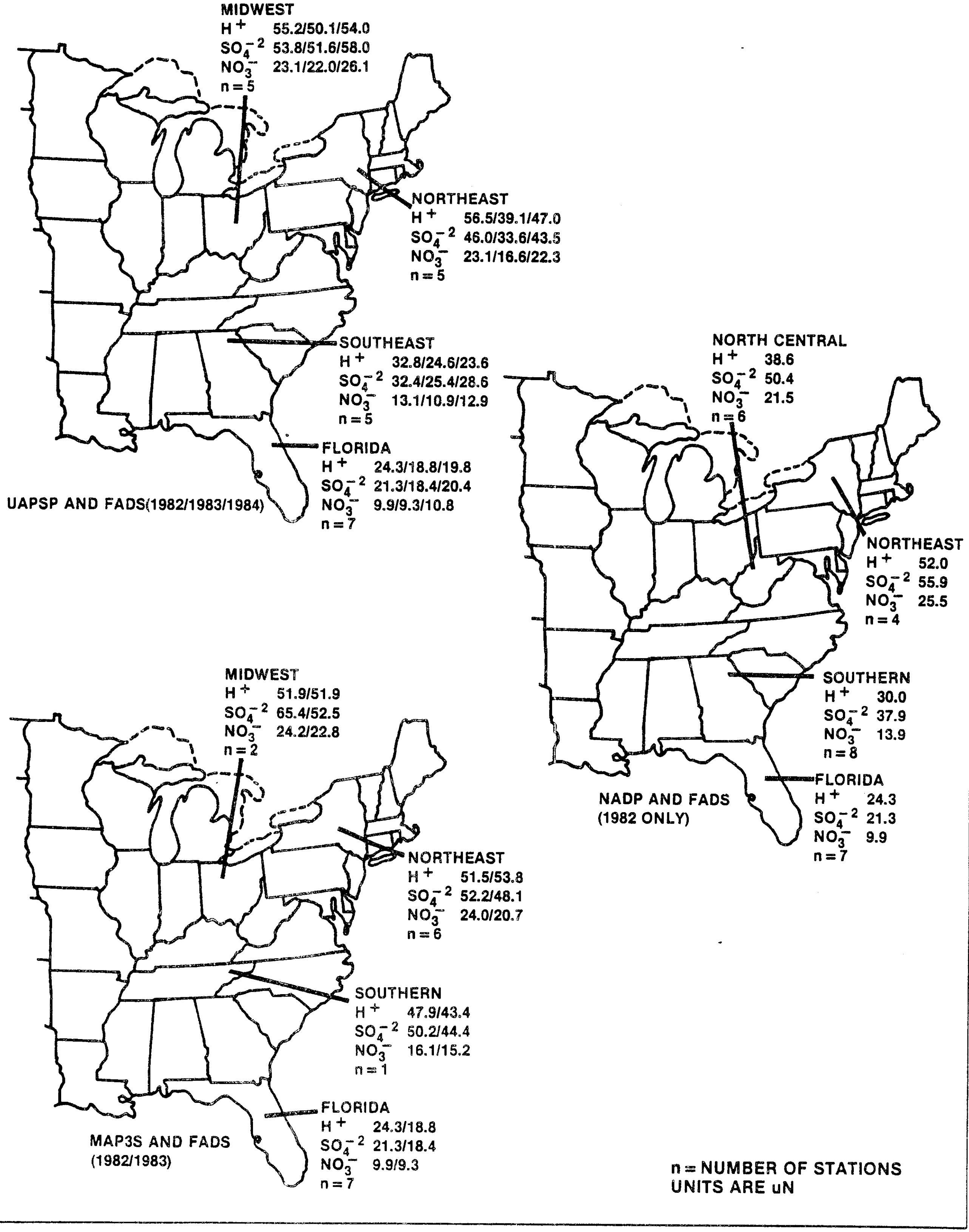
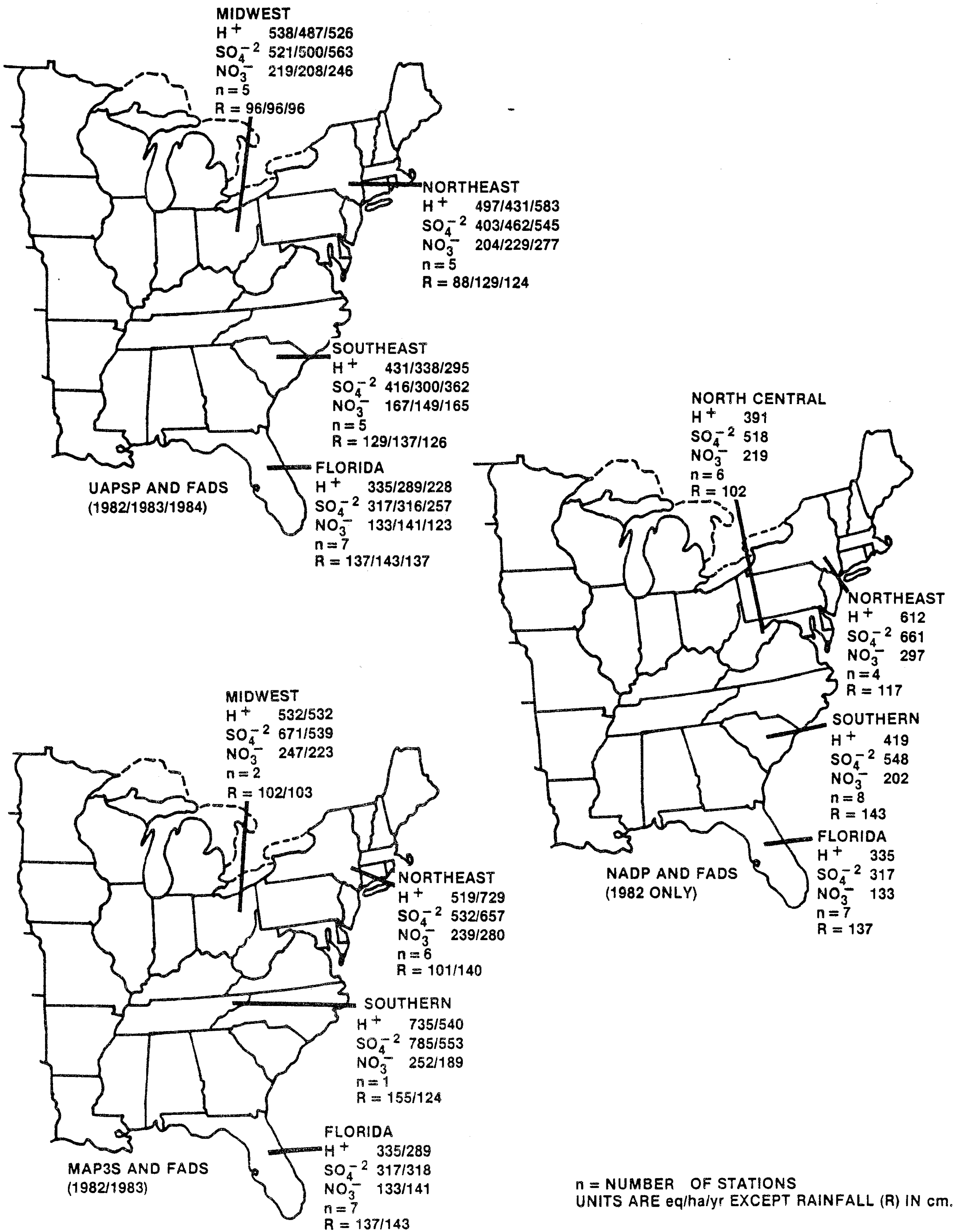


Figure 2.3-4
COMPARISON OF CONCENTRATION DATA COLLECTED FROM THE FLORIDA ACID DEPOSITION STUDY WITH AVAILABLE DATA FROM THE UAPSP, NADP, AND MAP3S NETWORKS FOR CONCENTRATIONS OF $H^+$, $SO_4^{-2}$, AND $NO_3^-$

ENVIRONMENTAL SCIENCE AND ENGINEERING, INC.



n = NUMBER OF STATIONS
UNITS ARE eq/ha/yr EXCEPT RAINFALL (R) IN cm.

Figure 2.3-5
COMPARISON OF DEPOSITION DATA COLLECTED FROM THE FLORIDA ACID DEPOSITION STUDY WITH AVAILABLE DATA FROM THE UAPSP, NADP, AND MAP3S NETWORKS FOR DEPOSITIONS OF $H^+$, $SO_4^{-2}$, AND $NO_3^-$

In a broad sense, these data demonstrate a continental gradient (i.e., decrease from north to south) of acidity and concentrations of $SO_4^{-2}$ and $NO_3^-$ that has been observed in previous studies (NAS, 1983). This gradient was also observed in Florida's precipitation chemistry and may suggest that the acidic deposition phenomena in Florida is part of an atmospheric process that is of continental scale. Such a hypothesis has been explored by evaluating precipitation chemistry data obtained from the Florida Acid Deposition Study with meteorological data and predictive models. The results of these analyses are presented in Subsections 2.8 and 3.3.

### 2.3.2.3 Historical Precipitation Chemistry for Florida

As indicated previously (see Subsection 2.1.1), the existence of historical trends in precipitation chemistry based upon data collected in the mid-1950s and mid-1960s has been challenged on two fronts. First, by examining the concentrations of major ions in 1955-1956 precipitation, Stensland and Semonin (1982) concluded that the apparent increase in acidity from the mid-1950s to the mid-1970s is much smaller than previously estimated because of anomalously high levels of base cations (i.e., $Ca^{+2}$ and $Mg^{+2}$). Second, by evaluating precipitation collection, handling, and analytical methodologies of data collected in the mid-1950s, mid-1960s, and mid-1970s, Hansen et al. (1981) concluded that the available data are not of sufficient quantity and quality to determine whether or not long-term trends have occurred.

For similar reasons, a detailed analysis of historical data has not been performed for Florida. The sampling techniques, analytical techniques, and sampling locations of available data differ sufficiently enough from study to study to warrant avoidance of a detailed analysis. In addition, since most of the earlier work does not have associated quality control data for evaluation of the overall consistency of analytical results, a rigorous analysis is of questionable value. As a consequence, this section briefly summarizes, for comparison purposes only, historical wet-only precipitation chemistry for Florida.

The first measurements of wet-only precipitation chemistry in Florida were made from July 1955 through July 1956 as part of a nationwide precipitation chemistry network (Junge and Werby, 1958). Precipitation samples were collected using manually operated systems at four Florida locations: Quincy, Jacksonville, Tampa, and West Palm Beach. Monthly composites of precipitation were analyzed for $NH_4^+$, $NO_3^-$, $SO_4^{-2}$, $Cl^-$, $Ca^{+2}$, and $K^+$, but not for pH (Junge and Gustafson, 1956). NCAR operated a nationwide 33-station network with one station in Florida (Tampa) from 1960 through 1966. Wet-only precipitation samples were collected on an event (probably daily) basis and pooled for monthly analysis of total inorganic nitrogen ($NH_4^+$ and $NO_3^-$), $SO_4^{-2}$, $Na^+$, $Mg^{+2}$, $Ca^{+2}$, $K^+$, and $Cl^-$ (Lodge et al., 1968).

The first measurements of wet-only pH in Florida were made near Tallahassee in 1974 (Burton, 1977). Since then, four monitoring networks have collected wet-only precipitation for pH measurement in various parts of the state: UF, NASA, NADP, and this program. All four networks have used similar precipitation samplers operated on a weekly or daily schedule, and all have measured the major cations and anions necessary for calculation of ionic balances.

Although pH was not measured during the 1950 and 1960 networks, excess $SO_4^{-2}$ and $NO_3^-$ data are available for comparison of presumably acidic anions with present values. Results for the 1955-1956, 1960-1966, 1980, 1982, 1983, and 1984 time periods (Table 2.3-13) indicate that only small differences in excess $SO_4^{-2}$ occur between 1955-1956 and 1982-1984 for north Florida and south Florida. In contrast, $NO_3^-$ concentrations may have increased by 200 to 400 percent over the same time period. These data indicate a reduction of the south-to-north ratio from approximately 7:1 during 1955-1956 to approximately 2:1 during 1982-1984.

Tampa data for 1960-1966 and 1980 are roughly twice those for 1955-1956 and 1982-1984, suggesting that all values for Tampa may be dependent on

Table 2.3-13. VWM Excess $SO_4^{-2}$ and $NO_3^-$ Concentrations for Available Historical Data Located in the Same General Sampling Area in Florida

| General Sampling Area | Analyte | Time Period | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1955-1956* | 1960-1966† | 1980** | 1982†† | 1983†† | 1984†† |
| Quincy-Monticello- | Excess $SO_4^{-2}$ | 18.8 | ND | 27.3 | 21.6 | 19.0 | 18.3 |
| Tallahassee (Site 3) | $NO_3^-$ | 2.9 | ND | 11.3 | 9.7 | 9.2 | 8.8 |
| Tampa-Zephyrhills | Excess $SO_4^{-2}$ | 28.8 | 65.0 | 66.5 | 31.6 | 29.5 | 28.6 |
| (Site 8) | $NO_3^-$ | 2.7 | ND | 20.7 | 12.5 | 10.7 | 12.4 |
| West Palm Beach- | Excess $SO_4^{-2}$ | 13.5 | ND | ND | 16.9 | 15.8 | 15.9 |
| Archbold (Site 9) | $NO_3^-$ | 4.1 | ND | ND | 8.8 | 8.9 | 10.0 |

Notes: All concentrations are µN.
ND = No data.

*Junge and Werby, 1958.
†Lodge _et al_., 1968.
**Edgerton and Brezonik, 1981.
††ESE, 1985.

Source: ESE, 1986.

the specific location of the precipitation collector. The 1980 data, for example, were collected in downtown Tampa and may be representative of only a limited, highly industrialized, urban area. Since collector locations and site descriptions are not readily available for the 1955-1956 data, it is impossible to evaluate whether sites were likely to have been locally or regionally representative.

The above comparisons, however, may be influenced by differences in field equipment and procedures and analytical methods between networks; therefore these comparisons should be viewed with caution.

Historical pH data for the period 1974-1984 is presented (Table 2.3-14) for data available within eight general sampling areas. A comparison of these data indicate different pH levels between sites located in north and central Florida and those located in south Florida. Also indicated is a slight increase in north Florida precipitation pH since 1982. Data from NASA and from Sites 3 and 5 of this study suggest pH values approximately 0.1 to 0.2 unit higher for 1983 and 1984 compared with previous years. NADP data for Bradford Forest (northeast of Gainesville) show little or no variability since 1980, but are currently in agreement with data from NASA and Site 3. Over all networks, it appears the precipitation pH in north Florida and south Florida are currently in the range of 4.6 to 4.7 and 4.8 to 5.0, respectively. This finding agrees with ANOVA results presented in the previous section.

The comparison of the more recent and comparable data suggests that rainfall acidity in Florida generally follows a north-to-south gradient and that no substantial increase in acidity has occurred over the last 5 to 8 years.

Table 2.3-14. Summary of Historical VWM pH Data for Florida Wet-Only Precipitation (Laboratory Measurements Only)

| General Sampling Area | Time Period | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1974 | 1976-1977 | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 |
| North Florida | | | | | | | | | |
| Tallahassee-Monticello (Site 3) | 4.53[a] | | | | 4.59[b] | | 4.54[c] | 4.77[c] | 4.69[c] |
| Bradford Forest | | | | | 4.69[d] | 4.65[d] | 4.69[c] | 4.71[c] | 4.73[c] |
| Gainesville (Site 5) | | 4.53[e] | 4.66[f] | 4.53[f] | 4.54[b] | 4.51[g] | 4.52[c] | 4.62[c] | 4.60[c] |
| Central Florida | | | | | | | | | |
| Tampa-Zephyrhills (Site 8) | | | | | 4.53[b] | | 4.60[c] | 4.64[c] | 4.64[c] |
| Orlando-UCF | | | 4.47[h] | 4.49[h] | 4.54[h] | 4.54[h] | 4.47[h] | 4.72[h] | 4.71[h] |
| Kennedy Space Center-Melbourne (Site 13) | | | 4.49[h] | 4.60[h] | 4.48[h] | 4.40[h] | | 4.85c | |
| South Florida | | | | | | | | | |
| Tamiami Trail-Pinecrest (Site 13) | | | | | 4.83[b] | | 4.86[c] | 4.88[c] | 4.86[c] |
| Homestead | | | | | 4.95[d] | 5.34[d] | 4.98[d] | 5.05[d] | 4.95[d] |

[a] = Likens, 1976.
[b] = Edgerton and Brezonik, 1981.
[c] = Florida Acid Deposition Study (ESE, 1982, 1983b, and 1984)
[d] = Peden, 1983.
[e] = Hendry and Brezonik, 1980.
[f] = Brezonik et al., 1983.
[g] = Edgerton, 1981.
[h] = Madsen, 1983.

Source: ESE, 1986.

## 2.4 DATA QUALITY AND UNCERTAINTY (VARIABILITY)

A detailed description of all QA/QC activities performed for the monitoring program can be found in the Project QA Plan (ESE, 1981d). These activities were implemented for each annual monitoring period and the results summarized in the Phase II, Phase III, and Phase IV Reports (ESE, 1983b, 1984, and 1985, respectively). An overall summary of the QA/QC data and evaluation of the overall uncertainty in the observed precipitation chemistry database are presented in this section.

### 2.4.1 FIELD DATA QUALITY

During the course of monitoring, an LIS solution was analyzed in the field each time a precipitation sample was analyzed. A total of 2,293 observations was made for LIS solutions within five pH ranges. The overall results of these observations were:

| pH Range of LIS Solution | Number of Samples | Percent Recovery (as $H^+$) |
|---|---|---|
| 3.90 to 4.00 | 187 | 94.9 |
| 4.15 to 4.25 | 587 | 95.1 |
| 4.30 to 4.40 | 619 | 95.3 |
| 4.50 to 4.60 | 416 | 95.2 |
| 4.70 to 4.80 | 484 | 100.0 |

Mean recoveries ranged from 94.9 percent to 100.0 percent. Standard deviations of observed recoveries generally increased with increasing LIS solution pH: from approximately 5 to $\geq$15 percent for the pH ranges of 3.90 to 4.00 and 4.70 to 4.80, respectively.

Over 80 percent of the LIS observations were within ±15 percent or ±0.065 pH unit. For the lower-pH LIS solution ranges (3.90 to 4.00, 4.15 to 4.25, and 4.30 to 4.40), over 90 percent of the observations were within ±0.065 pH unit. With the higher-pH LIS solutions (greater than pH 4.7), the variation in the number of observations within ±15 percent increased. This is to be expected as pH readings of approximately 4.75 or greater tend to be relatively difficult to measure (NBS, 1982).

For the 4.70 to 4.80 range in pH LIS solution measurements, approximately 70 percent of the observations were within $\pm 15$ percent or $\pm 0.065$ pH unit. During a 3-year period, 92.6 percent of all LIS solution measurements were within $\pm 0.1$ pH unit.

The two bimonthly QA audit samples in the range of pH 4.0 to pH 5.0 were analyzed during each annual period. The mean pH recovery ranged from approximately 85 to 115 percent for the audit samples. For all audit samples, over 95 percent of the data were within $\pm 0.1$ pH unit. Similar to that observed with LIS solution measurements, standard deviations generally increased with increasing pH.

### 2.4.2 LABORATORY DATA QUALITY

#### 2.4.2.1 Precipitation Chemistry

In order to evaluate the accuracy and precision of analyte measurements of precipitation samples, four types of associated analyses were performed along with the analysis of precipitation samples. Accuracy was determined by analyzing EPA reference samples, unknown reference samples, and spiked precipitation samples. Precision was determined by analyzing replicated precipitation samples. The results of these analyses over the 3-year period are presented in Table 2.4-1.

Unknown EPA reference samples were analyzed for each major cation [$H^+$ (as measured from pH), $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$, and $NH_4^+$] and major anion ($NO_3^-$, $SO_4^{-2}$, and $Cl^-$). Mean recoveries of $H^+$, $Ca^{+2}$, $Na^+$, $K^+$, $NH_4^+$, $SO_4^{-2}$, and $NO_3^-$ were approximately 100 $\pm 5$ percent or less. Mean recoveries for $Mg^{+2}$ and $Cl^-$ were 112.1 and 93.6 percent, respectively. Mean recoveries for over 110 unknown QA reference samples were all within 100 $\pm 5$ percent for all parameters.

At least 200 analyses for $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $SO_4^{-2}$, and $Cl^-$ were made for spiked precipitation samples. Spiked precipitation samples were not measured for pH and conductivity since the possible presence of

Table 2.4-1. Summary of Laboratory QA/QC Results for EPA Reference Samples, Unknown Reference Samples, Replicated Samples, and Spiked Samples

| Analyte | Percent Recovery of EPA Reference Samples |  | Percent Recovery of Unknown* Reference Samples |  | Percent Difference for Replicated Samples |  | Percent Total Recovery for Spiked Samples† |  |
|---|---|---|---|---|---|---|---|---|
|  | n | Mean | n | Mean | n | Mean | n | Mean |
| pH ($H^+$) | 12 | 94.9 | 118 | 99.8 | 274 | 5.3 | -- | -- |
| $Ca^{+2}$ | 14 | 103.6 | 112 | 102.5 | 405 | 5.2 | 216 | 104.7 |
| $Mg^{+2}$ | 14 | 112.1 | 110 | 104.1 | 395 | 9.1 | 228 | 101.7 |
| $Na^+$ | 14 | 102.0 | 112 | 101.1 | 402 | 4.8 | 217 | 102.5 |
| $K^+$ | 13 | 99.7 | 116 | 100.8 | 446 | 3.8 | 253 | 103.7 |
| $NH_4^+$ | 14 | 103.0 | 115 | 102.4 | 477 | 5.1 | 314 | 101.0 |
| $SO_4^{-2}$ | 14 | 103.0 | 114 | 98.9 | 435 | 2.2 | 245 | 100.6 |
| $Cl^-$ | 14 | 93.6 | 111 | 99.5 | 462 | 4.3 | 334 | 100.3 |
| $NO_3^-$ | 14 | 99.4 | 115 | 101.9 | 504 | 2.3 | 318 | 100.0 |

*Concentration unknown to the analyst.
†Precipitation plus spikes.

Note: For EPA and unknown reference samples and spiked samples, a percent recovery of 100 indicates "ideal" accuracy; for replicated samples, a percent diference of 0.0 indicates "ideal" precision.

Source: ESE, 1986.

weak acids would confound interpretation of recoveries. The results for total recovery of spiked precipitation samples, which evaluates the analyte concentrations in the precipitation sample plus the spike, provide a method to evaluate the influence of spike concentrations that are lower than the concentration of the the same analyte in the precipitation sample. Mean total recoveries for spiked samples were within 100 ±5 percent for all parameters. Standard deviations of total spike recoveries for all parameters were less than 10 percent.

Analyte precision was determined during the course of the study with approximately 400 replicate analyses of each major cation and major anion and conductivity in precipitation samples. Mean percent differences of replicate analyses were uniformly less than 10 percent with $Na^+$, $K^+$, $SO_4^{-2}$, $Cl^-$, and $NO_3^-$ having mean reproducibilities of better than ±5 percent.

### 2.4.2.2 Air Chemistry

For air chemistry parameters, analyses of reference, spiked, and replicate samples were performed to determine accuracy and precision of laboratory analyses for particulate $SO_4^{-2}$, $SO_2$, $HNO_3^-$, and $NO_2$ ambient air samples. Mean recovery for particulate $SO_4^{-2}$ and $SO_2$ in ambient air samples was 100.3 percent for 12 reference samples and 101.3 for 455 spike samples. Mean percent differences for particulate $SO_4^{-2}$ and $SO_2$ in ambient air samples for 715 replicate analyses were less than 2 percent. Over 99 percent of all particulate $SO_4^{-2}$ and $SO_2$ QC samples were within ±15 percent of the expected value. For $NO_2$ and $HNO_3$, mean recoveries were 94.4 and 103.7 percent for 12 reference samples and 304 spike samples, respectively. Replicate analyses of 536 samples produced a mean percent difference of 2 percent for $HNO_3$ and $NO_2$. Approximately 98 percent of all $HNO_3$ and $NO_2$ QC samples were within ±15 percent of the expected value.

### 2.4.3 OVERALL SAMPLE CONTAMINATION

Potential contamination from cleaning buckets alone was determined during the course of the study from blank samples generated by rinsing freshly cleaned buckets with 50 mL of deionized water (referred to as wash blanks). Potential contamination from the combined effects of cleaning, sample handling, field placement, and sampler operation was determined by rinsing "dry" wetfall buckets with 50 mL of deionized water (referred to as dynamic or field blanks). Potential contamination from filtering samples was determined with 50 mL of filtrate rinse (referred to as filter blanks). Wash, dynamic, and filter blanks were measured for pH, conductivity, and all major cations and anions.

The mean concentration observed from the wash and field bucket blanks were at or near the average detection limits of the measurement methods. Individual observed variations were occasionally large (i.e., greater than an order of magnitude difference between maximum and minimum values). This result is expected, however, since the variation in interparameter replicate concentrations was also large for samples near the detection limit.

Mean concentrations observed for filter blanks were also at or near the detection limit of the measurement methods except for $K^+$. The quantity of filtered water did not appear to influence observed parameter concentrations; e.g., the mean pH values for the different quantities of filtrate were in the range of that expected for $CO_2$ in equilibrium with pure water (i.e., pH of 5.6).

An overall potential for sample contamination can be determined by accounting for the overall effects in sampling chain: cleaning buckets, sample handling in the field, shipment, field placement, sample filtering, and laboratory handling. Although the results of blank analyses were at or near the detection limits of the methods (i.e., apparent concentrations were actually less than a specified value), a conservative estimate of overall contamination was determined by summing the results from dynamic (field) and filter blanks. The significance of this overall contamination potential for the 3-year period was determined by calculating the potential deposition due to sample contamination for each site and each major cation and anion and comparing the result to the actual deposition observed at each site over the 3-year period. The results of these calculations are presented in Table 2.4-2. As seen from this table, the contamination potential for $Ca^{+2}$, $Na^{+}$, $NH_4^{+}$, $SO_4^{-2}$, $Cl^{-}$, $NO_3^{-}$, and $H^{+}$ are 2 percent or less of the total deposition at any site. In fact, for $SO_4^{-2}$, $NO_3^{-}$, and $H^{+}$, the contamination potential is generally less than 1.0 percent for most sites. Only $Mg^{+2}$ and $K^{+}$ have a contamination potential of more than 5 percent at some sites. As noted previously, $Mg^{+2}$ is primarily of sea-salt origin which has little effect chemically, and $K^{+}$ has the lowest concentrations and deposition of any of the major cations or anions by a factor of more than 5.

### 2.4.4 OVERALL SAMPLE UNCERTAINTY

Collocated sampling was performed during the course of the study to evaluate the overall precision of the combined effects of field sampling and laboratory analysis for the two different precipitation monitoring protocols: weekly and daily. To determine the precision of weekly sampling, collocated monitors were operated at two sites (Sites 2 and 8) over a 63-week period. During the same 63-week period, the precision between daily and weekly sampling was determined with collocated monitors at two sites (Sites 5 and 9). The precision of daily sampling was determined through collocated monitors (Sites 2 and 5) operated over 2 years. Detailed discussions of the results of this sampling are included in previous reports (ESE, 1983b; ESE, 1984; and ESE, 1985) and are summarized in this subsection.

Results of all collocated sampling are summarized in Table 2.4-3 which presents both the mean percent difference and mean absolute difference for the major cations and anions measured during the course of the study.

Table 2.4-2. Maximum Potential Deposition* Due to Sample Contamination Over the 3-Year Period from 10/01/81 Through 09/30/84

| | $Ca^{+2}$ | | $Mg^{+2}$ | | $Na^+$ | | $K^+$ | | $NH_4^+$ | | $SO_4^{-2}$ | | $Cl^-$ | | $NO_3^-$ | | $H^+$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | D | %TD | D | %TD | D | %TD | D | %TD | D | %TD | D | %TD | D | %TD | D | %TD | D | %TD |
| 2 | 3.5 | 1.7 | 7.4 | 4.3 | 4.6 | 0.9 | 2.8 | 8.2 | 2.5 | 0.9 | 7.4 | 0.7 | 7.4 | 1.1 | 1.4 | 0.3 | 5.7 | 0.5 |
| 3 | 2.7 | 1.3 | 5.7 | 3.6 | 3.5 | 0.7 | 2.2 | 5.6 | 1.9 | 0.8 | 5.7 | 0.7 | 5.7 | 0.9 | 1.1 | 0.3 | 4.3 | 0.5 |
| 4 | 2.9 | 1.1 | 6.2 | 1.4 | 3.8 | 0.2 | 2.4 | 4.3 | 2.1 | 1.1 | 6.2 | 0.6 | 6.2 | 0.3 | 1.2 | 0.3 | 4.7 | 0.5 |
| 5 | 4.2 | 2.0 | 8.9 | 7.1 | 5.5 | 1.4 | 3.4 | 10.7 | 3.0 | 1.3 | 8.9 | 0.9 | 8.9 | 1.7 | 1.7 | 0.4 | 6.8 | 0.6 |
| 8 | 2.7 | 1.0 | 5.6 | 3.6 | 3.5 | 0.7 | 2.1 | 7.2 | 1.9 | 0.5 | 5.6 | 0.5 | 5.6 | 0.9 | 1.1 | 0.3 | 4.3 | 0.5 |
| 9 | 4.6 | 2.0 | 9.7 | 5.5 | 6.0 | 1.1 | 3.7 | 15.0 | 3.2 | 1.9 | 9.7 | 1.5 | 9.7 | 1.4 | 1.9 | 0.5 | 7.4 | 1.2 |
| 13 | 2.9 | 0.8 | 6.1 | 2.8 | 3.8 | 0.5 | 2.3 | 9.4 | 2.0 | 1.1 | 6.1 | 1.0 | 6.1 | 0.7 | 1.2 | 0.3 | 4.7 | 0.9 |
| 14† | 2.4 | 1.4 | 5.1 | 1.7 | 3.1 | 0.3 | 1.9 | 5.9 | 1.7 | 2.7 | 5.1 | 1.3 | 5.1 | 0.4 | 1.0 | 0.7 | 3.9 | 1.5 |

* D = deposition in eq/ha over 3-year period.
%TD = percent of total deposition for each site.
†Data for Site 14 are for the 2-year period from 10/01/81 through 09/14/83.

Note: Calculations based on the sum of the potential contamination from field blanks and filter blanks, number of samples, and actual deposition at each site.

Source: ESE, 1986.

Table 2.4-3. Percent Mean Difference and Mean Absolute Difference in W/W, D/D, and D/W Collocated Sampling*

| Analyte | Mean Percent Difference | | | Mean Absolute Difference (%)† | | |
|---|---|---|---|---|---|---|
| | W/W | D/D | D/W | W/W | D/D | D/W |
| Laboratory $H^+$ | 30.6 | 28.3 | 39.5 | 15.6 | 17.3 | 58.2 |
| $Ca^{+2}$ | 26.5 | 24.3 | 26.4 | 10.0 | 11.7 | 18.9 |
| $Mg^{+2}$ | 29.4 | 26.7 | 49.5 | 13.2 | 24.7 | 34.2 |
| $Na^+$ | 16.3 | 16.9 | 25.4 | 7.0 | 8.8 | 16.4 |
| $K^+$ | 32.0 | 49.6 | 51.9 | 14.3 | 29.3 | 27.6 |
| $NH_4^+$ | 37.8 | 31.8 | 71.8 | 25.0 | 33.0 | 39.0 |
| $Cl^-$ | 23.0 | 21.5 | 30.5 | 8.7 | 8.7 | 34.9 |
| $NO_3^-$ | 7.5 | 7.9 | 16.7 | 3.3 | 7.3 | 11.1 |
| $SO_4^{-2}$ | 6.1 | 10.4 | 14.4 | 4.4 | 11.2 | 11.6 |
| n | 126 | 755 | 126 | 126 | 755 | 126 |

*All collocated sampling included.
†Percent of mean concentration over all collocated sites.

Source: ESE, 1986.

These results suggest differences in precision between analyte measurements and monitoring frequency.

The highest precision for analyte measurements (as measured by the percent differences) was observed for $SO_4^{-2}$ and $NO_3^-$ (<15-percent difference), and the lowest was observed for $NH_4^+$, $Mg^{+2}$, and $K^+$ (>30-percent difference). Not surprisingly, the same general order for analyte measurements was observed for laboratory precision (see Table 2.4-1). Mean absolute differences as a percent of the observed concentration in precipitation (see Table 2.4-3) is a more representative measure of the significance of overall analyte and sampling frequency precision to the observed data. With the exception of laboratory $H^+$, $Mg^{+2}$, $K^+$, and $NH_4^+$, mean absolute differences were less than 15 percent and often less than 10 percent for most analytes for W/W and D/D collocated sampling. For D/W collocated sampling, mean absolute differences increased for all parameters except $K^+$.

The accuracy and precision of collecting rainfall amount can influence the uncertainty in the calculations of analyte deposition. The accuracy of rainfall amount collected in the wetfall bucket was determined by Belfort rain gages at all sites. Over a 3-year period, the mean recovery in rainfall amount collected by the wetfall bucket compared to the Belfort rain gage was 101.5 percent with a 95-percent confidence interval of ±1.8 percent. The precision of Belfort rain gages, as measured by collocated gages at Sites 2, 5, 8, and 9, was 1.14 percent ±0.86 percent (95-percent confidence interval). The precision between collocated wetfall bucket measurements of rainfall amount was 1.9 percent for W/W measurements, 2.1 percent for D/D measurements, and 1.4 percent for D/W measurements.

The variability in precipitation chemistry measurements is caused by analytical procedures, field procedures, and actual variability in analyte concentrations. Variability in analytical measurements was measured through replicate laboratory analyses. The combined variability of analytical and field procedures was measured through collocated sampling measurements. The coefficient of variation (CV) is the standard deviation divided by the mean, expressed in percent, and represents the relative magnitude of variability in measurements. A comparison of CV in laboratory replicates and collocated measurements with sample-to-sample variability provides information on the relative importance of each variability component and a measure of the overall uncertainty in the precipitation chemistry observations. A large CV for precipitation samples relative to that found in replicate and collocated measurements suggests that a majority of the observed variability is not a result of sampling imprecision, but primarily a result of actual variability in observed precipitation chemistry.

Table 2.4-4 presents CVs for the overall sample population, collocated samples, and laboratory replicates for a 3-year period. Included for the collocated sampling are results for W/W, D/D, and D/W sampling frequencies. For each analyte, the variability (expressed by the CV) in laboratory analysis is a small component of variability in the overall sample population. The combined variability caused by imprecision in both laboratory and field procedures is much larger than that caused by laboratory procedures alone. This result is expected since collocated sampling variability inherently contains the variability of laboratory analysis. The variability in collocated sampling is generally much smaller (i.e., by a factor of 4) than that observed in the sample population, and the relative differences between W/W, D/D, and D/W measurements compared to actual measurements are small. In general, collocated variability appeared to decrease in the following order: D/W > D/D > W/W.

Mean percent differences and mean absolute differences increased from W/W to D/D to D/W, possibly suggesting influences on observed precipitation

Table 2.4-4. Coefficient of Variation (%) for the Overall Sample Population, Collocated Sampling, and Laboratory Replicates Over 3 Years

| Parameter | Overall Sample Population[a] | Collocated Sampling | | | Laboratory Replicates[e] |
|---|---|---|---|---|---|
| | | W/W[b] | D/D[c] | D/W[d] | |
| Laboratory $H^+$ | 178 | 29.3 | 34.9 | 39.7 | 6.6 |
| $Ca^{+2}$ | 152 | 23.8 | 27.6 | 29.2 | 7.4 |
| $Mg^{+2}$ | 166 | 33.0 | 37.8 | 45.0 | 11.7 |
| $K^+$ | 198 | 41.0 | 51.1 | 46.3 | 5.9 |
| $Na^+$ | 467 | 18.0 | 32.5 | 32.9 | 7.9 |
| $NH_4^+$ | 189 | 47.8 | 46.1 | 62.3 | 8.4 |
| $NO_3^-$ | 86 | 14.1 | 21.5 | 34.7 | 6.2 |
| $Cl^-$ | 232 | 24.3 | 33.8 | 31.7 | 7.9 |
| $SO_4^{-2}$ | 88 | 7.7 | 25.0 | 24.1 | 3.5 |
| Sample Weight | 229 | 51.0 | 74.8 | 44.7 | NA |

[a] n = 1,594.
[b] n = 126.
[c] n = 755.
[d] n = 126.
[e] n = 274 to 504, depending on parameter.

NA = Not applicable.

Source: ESE, 1986.

chemistry from the two different sampling protocols. Paired t-tests on the logarithms of concentrations, depositions, and weighted concentrations for excess $Ca^{+2}$, excess $SO_4^{-2}$, $NH_4^+$, $NO_3^-$, laboratory $H^+$, and field $H^+$ and all collocated sampling performed were to further explore this possibility (see Table 2.4-5). These results suggest that overall precision may be influenced by location (i.e., field operator and site effects) and sampling frequency (i.e., weekly versus daily).

The influence of location is illustrated by statistically significant differences (for at least two tests) obtained for the following analyte concentrations and sites:

Excess $Ca^{+2}$--Site 5 D/D
Field $H^+$--Site 2 D/D
$NH_4^+$--Site 8 D/W
Laboratory $H^+$--Site 9 D/W

Conversely, no statistical differences were observed for their counterparts (e.g., excess $Ca^{+2}$ at Site 2--D/D sampling). Sampling frequency also appeared to have influenced at least one analyte significantly. Statistically significant differences were observed for $NH_4^+$ between D/W and W/W sampling but not D/D sampling. D/W variability of $NH_4^+$ was significantly greater than W/W variability. This finding suggests that $NH_4^+$ may be lost due to biological or chemical reactivity in weekly precipitation samples.

Results of ANOVA analyses on all collocated sampling further supported the potential influence of locations and sampling frequency on precision. These ANOVA results indicated statistically significant differences between locations (i.e., Sites 2, 5, 8, and 9) and sampling frequency (i.e., W/W, D/D, and D/W) for excess $Ca^{+2}$, $NH_4^+$, laboratory $H^+$, and field $H^+$. No statistical differences in either locations or sampling frequencies were observed for excess $SO_4^{-2}$ or $NO_3^-$.

Table 2.4-5. Comparison of Collocation Results Across Sites

|  |  | D/D |  | D/W |  | W/W |  |
|---|---|---|---|---|---|---|---|
| Parameter | Test Unit* | Site 2 | Site 5 | Site 5 | Site 9 | Site 2 | Site 8 |
| Excess $Ca^{+2}$ | C | ND | ND | ND | ND | ND | ND |
|  | D | ND | D | ND | ND | ND | ND |
|  | W | ND | D | ND | D | ND | ND |
| Excess $SO_4^{-2}$ | C | ND | ND | ND | ND | ND | ND |
|  | D | ND | ND | ND | ND | ND | ND |
|  | W | ND | ND | ND | ND | ND | ND |
| $NH_4^+$ | C | ND | ND | D | D | ND | D |
|  | D | ND | ND | D | D | ND | D |
|  | W | ND | ND | D | D | ND | D |
| $NO_3^-$ | C | ND | ND | ND | ND | ND | ND |
|  | D | ND | ND | ND | D | ND | ND |
|  | W | ND | ND | ND | ND | ND | ND |
| Laboratory $H^+$ | C | ND | ND | ND | D | ND | ND |
|  | D | ND | D | ND | D | ND | ND |
|  | W | ND | ND | ND | ND | ND | ND |
| Field $H^+$ | C | D | ND | ND | D | ND | ND |
|  | D | D | ND | ND | ND | ND | ND |
|  | W | D | ND | D | ND | ND | ND |

*Statistical tests: C = concentrations,
D = depositions, and
W = volume-weighted concentrations.

Note: ND = not statistically different at 95-percent confidence level.
D = statistically different at 95-percent confidence level.

Source: ESE, 1986.

The results of the statistical analysis indicate that the length of time a sample remains in the field as well as how an individual analyte responds to that exposure can influence observed sampling precision. In addition, the location of monitoring, inclusive of a particular field technician's practices, may also significantly influence sampling precision.

Although location, sampling frequency, and analytical error can influence observed variability of precipitation chemistry measurements, they are only some of the factors that could have influenced the observed variability in precipitation chemistry measurements over the network during the 3-year period. As demonstrated in previous reports, the variability caused by these factors accounts for only a relatively small percentage ($\leq$25 percent) of the total variability in overall measurements (ESE, 1983b; ESE, 1984; ESE, 1985). Nevertheless, ANOVA results presented in Subsections 2.5 and 2.6 accounted for collocated variability in the design of the statistical tests. These influences would tend to inflate overall variance estimates, thereby causing statistical inferences about the differences between sites and seasons to be conservative (i.e., no statistically significant difference observed when one actually exists).

### 2.4.5 FIELD VERSUS LABORATORY pH

Results for field pH and laboratory pH presented in Subsection 2.3 indicates that field pH is consistently lower than laboratory pH. The ratio of field $H^+$ to laboratory $H^+$ ranges from 113 to 190 percent (mean = 130 percent) and is statistically significant ($p < 0.001$) at all sites. This observation is fairly commonplace for networks with both field and laboratory analysis of pH; however, no satisfactory explanation has as yet been advanced.

By their nature, field measurements cannot undergo the rigorous scrutiny of laboratory chemical analyses. Nevertheless, comparison of field pH versus field conductivity can be used to monitor internal consistency and to verify conformance to ideal pH-conductivity relationships.

For dilute mineral acids [e.g., hydrochloric acid (HCl), $HNO_3$, and sulfuric acid ($H_2SO_4$)] in the pH range from approximately 2 to 5, the relationship between $H^+$ and conductivity at 25°C can be calculated from tabulated values (Weast, 1984) as follows:

$$H^+ = K\ (\text{conductivity})$$

where: $K = 2.36 \pm 0.02$, $H^+$ is expressed in μN, and conductivity is expressed in μS/cm.

For weak acid solutions and mixed solutions of strong acids and neutral salts, the coefficient of proportionality is always less than 2.36. Thus, an upper limit exists for the proportionality between pH and conductivity. Data which significantly exceed this upper limit of proportionality are inconsistent and may be presumed erroneous in at least one variable (i.e., pH and/or conductivity).

To test the internal consistency of field and laboratory measurements, linear regression was used to calculate coefficients of proportionality between $H^+$ and conductivity for all sites combined. Regression lines for field and laboratory data are shown in Figure 2.4-1, along with the theoretical relationship. Results are highly similar for field and laboratory data and indicate no clear inconsistency between pH and conductivity measurements. Coefficients of proportionality between $H^+$ and conductivity are 1.91 and 1.89 (not significantly different) for field and laboratory data, respectively, indicating that no inference of inconsistency can be drawn from these data.

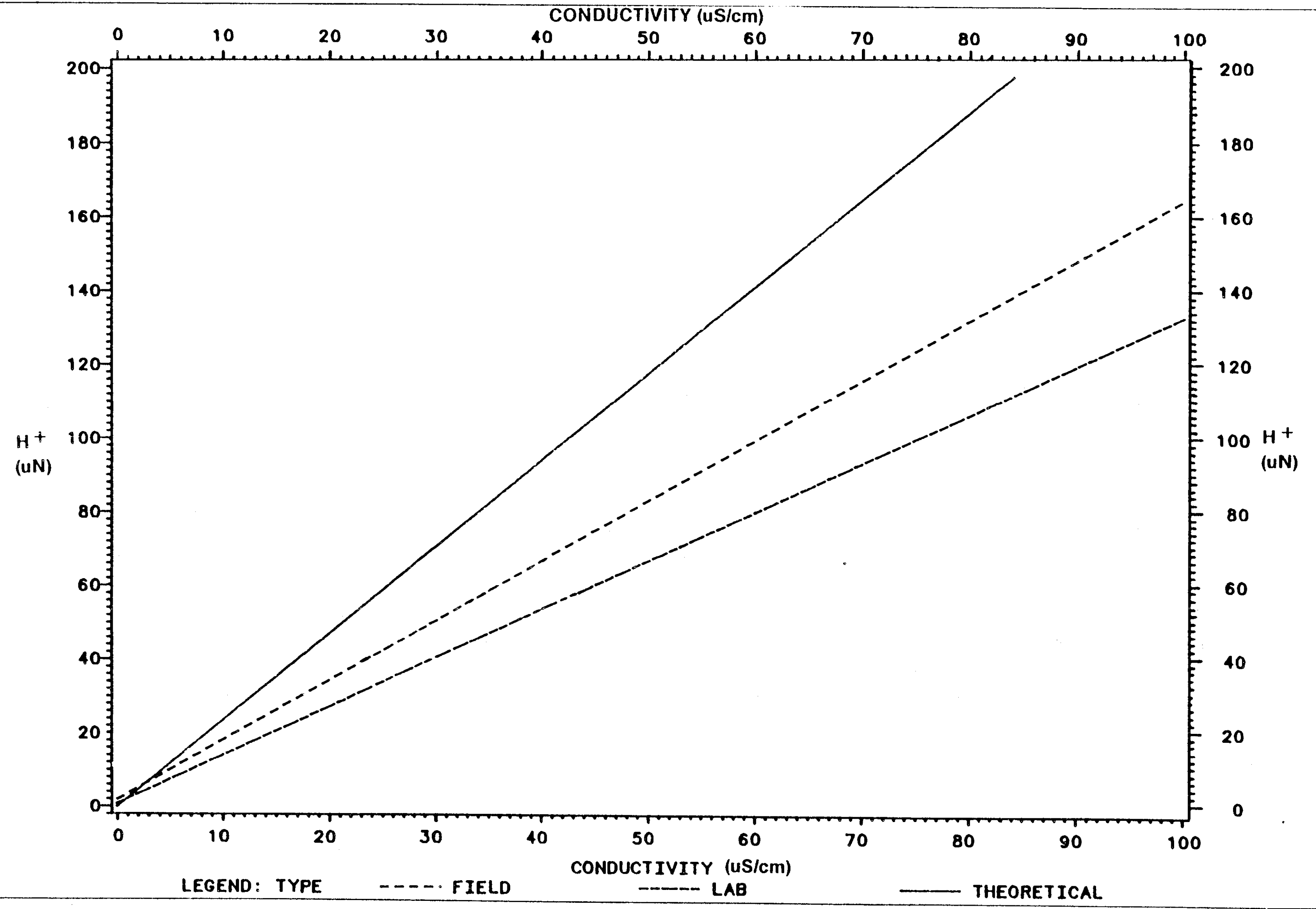


Figure 2.4-1
THEORETICAL, FIELD, AND LABORATORY RELATIONSHIPS BETWEEN $H^+$ CONCENTRATION AND CONDUCTIVITY

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## 2.5 SPATIAL VARIABILITY OF PRECIPITATION AND AIR CHEMISTRY IN FLORIDA

This section investigates the statistical significance of spatial variability in wet-only precipitation concentrations and deposition for the period from October 1981 through September 1984. Results of statistical models (i.e., ANOVA) are presented which resolve the precipitation network into spatially distinct sites or groups of sites for the following chemical species: laboratory $H^+$, excess $Ca^{+2}$, $NH_4^+$, excess $SO_4^{-2}$, and $NO_3^-$. The species excess $Ca^{+2}$, $NH_4^+$, excess $SO_4^{-2}$, and $NO_3^-$ have been selected because they frequently account for most of the variability (i.e., $\geq$80 percent) in laboratory $H^+$ (Brezonik *et al.*, 1981; ESE, 1982; ESE, 1983b; Madsen, 1985).

The non-sea-salt components of $Ca^{+2}$ and $SO_4^{-2}$ are used in this analysis to remove the spatial variability in these species associated with sea-salt influences. As discussed in Subsection 2.3.1.2, Florida precipitation chemistry is strongly affected by sea salt, especially in coastal areas (e.g., Sites 4 and 14). It should be noted that the statistical findings discussed in this section refer to the overall 3-year database, rather than its component annual or seasonal periods. The persistence of site-to-site or group-to-group differences across seasons and across years is discussed in Subsection 2.6.

### 2.5.1 WET-ONLY CONCENTRATIONS

Results of the analysis of variance on concentration data (Table 2.5-1) indicate that numerous statistically distinct (p >95 percent) site-groups exist for all analytes and that for each analyte a unique configuration of site(s) make up each site group. For laboratory $H^+$, three homogeneous groups can be resolved with corresponding VMW pH values of 4.59, 4.65, and 4.81. In general, the grouping of sites indicates a significant difference in laboratory $H^+$ between north Florida and south Florida. The north-south gradient of approximately 40 percent is not uniform, however, as shown by the distinction between Site 2 and Site 3 in extreme north Florida and between Site 4 and Site 5 in north-central Florida.

Table 2.5-1. ANOVA Results for VWM Concentrations* of Site-Groups During the 3-Year Period from 10/1/81 Through 9/30/84

| Analyte | Site-Group A | | Site-Group B | | Site-Group C | |
|---|---|---|---|---|---|---|
| | Sites | VWM | Sites | VWM | Sites | VWM |
| Laboratory $H^+$ (pH) | 2,5,8 | 25.6<br>(4.59) | 3,4 | 22.3<br>(4.65) | 9,13 | 15.5<br>(4.81) |
| Excess $Ca^{+2}$ | 8,9,13 | 7.3 | 2,3,4,5 | 4.6 | -- | -- |
| $NH_4^+$ | 8 | 9.5 | 2,3,5,9 | 5.7 | 4,13 | 4.6 |
| Excess $SO_4^{-2}$ | 5,8 | 26.9 | 2,3,4 | 20.4 | 9,13 | 15.2 |
| $NO_3^-$ | 2,5,8 | 11.1 | 3,4,9 | 9.6 | 13 | 9.1 |
| Excess $Cl^-$ | 3,4,5,<br>8,13 | 1.4 | 2,9 | 1.3 | -- | -- |

*All concentrations are µN.

Notes: Sites refer to the site(s) making up the site-group. VWM refers to the volume weighted mean for the site-group. Site-groups A, B, and C indicate statistically significant differences between site-groups at the 95-percent confidence level. Site-Group A denotes a significantly higher concentration than Site-Group B; Site-Group B denotes a significantly higher concentration than Site-Group C.

Source: ESE, 1986.

Site groupings for excess $SO_4^{-2}$ and $NO_3^-$ are similar to those observed for laboratory $H^+$. Three significant site-groups are resolved for excess $SO_4^{-2}$, and the sole difference in their composition regarding laboratory $H^+$ is the location of Site 2. Thus, the concentration pattern appears to be: north-central Florida > north Florida > south Florida. VWM concentrations of excess $SO_4^{-2}$ and laboratory $H^+$ also appear to vary together across site-groups. The high-, mid-, and low-level concentrations of excess $SO_4^{-2}$ are 105 percent, 91 percent, and 98 percent, respectively, of corresponding laboratory $H^+$ values. Statistical evidence of correlations between laboratory $H^+$ (as the dependent variable) and excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$ (as independent variables) is presented in Subsection 2.7. The only difference in site groupings between $NO_3^-$ and laboratory $H^+$ concerns the assignment of Site 9, which is grouped with Sites 3 and 4 for the former and with Site 13 for the latter. Unlike the results for laboratory $H^+$ and excess $SO_4^{-2}$, differences across groups are only 10 percent for $NO_3^-$ and cover a range of only 2.0 µN. This finding suggests that spatial variability in $NO_3^-$ plays only a minor role in the spatial variability of laboratory $H^+$ across Florida. It also shows that the results of the statistical analysis can be sensitive to small overall differences in concentrations. Although these differences are significant, they may not lend meaningful insight into spatial trends of acidic deposition.

A distinct north-south concentration gradient also is suggested in the ANOVA results for excess $Ca^{+2}$. In this case, two site-groups are resolved by ANOVA, and the trend is toward higher values in the southern portion of the state. As a group, Sites 8, 9, and 13 exhibit a VWM excess $Ca^{+2}$ concentration 59 percent higher than the group composed of Sites 2, 3, 4, and 5. Although not necessarily indicative of a causal relationship, this trend is in general agreement with the north-to-south increase in $Ca^{+2}$ content of Florida soils (ESE, 1984). Other factors which could potentially influence excess $Ca^{+2}$ concentrations include surface mining activity south of Site 8 and north of Site 9, as well as widespread agricultural activity (primarily citrus) near both sites.

Results for $NH_4^+$ indicate that it is the only variable with a range of concentrations (i.e., between site-groups) exceeding a factor of 2. The $NH_4^+$ concentration at Site 8 is significantly higher than all others, while the concentration for the group comprised of Sites 4 and 13 is lower than the concentration for Sites 2, 3, 5, and 9.

The fact that Site 4 is grouped with Site 13, rather than with Sites 2, 3, and 5, may reflect its proximity to the coast. Recent estimates of global ammonia emissions to the atmosphere have suggested that terrestrial sources far outweigh marine sources (Gras, 1983). Relatively low concentrations of ammonium in precipitation at Site 4 may thus reflect the influence of relatively unmodified marine air masses at this coastal site.

### 2.5.2 WET DEPOSITION

ANOVA results for rainfall amount and wet deposition of laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, excess $Ca^{+2}$, and $NH_4^+$ are listed in Table 2.5-2. Data for rainfall indicate two distinct site-groups covering the state. Sites 2, 3, 4, and 5 form a northern group with mean annual rainfall of 146 centimeters (cm), and Sites 8, 9, and 13 form a southern group with mean annual rainfall of 129 cm. Note that this finding shows a difference between groups over the 3-year monitoring period only and does not imply wet or dry conditions relative to long-term average precipitation. Given the ANOVA results on concentration data, the site groupings for rainfall amount suggest positive interaction (except for excess $Ca^{+2}$) and the likelihood of significant depositional gradients for numerous variables.

Indeed, results for laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ show identical site assignments to each of three groups. Sites 2, 5, and 8 form a homogeneous group with highest deposition; Sites 3 and 4 form a group of intermediate deposition; and Sites 9 and 13 form a group with lowest deposition. As an apparent result of the reduction in annual rainfall

Table 2.5-2. ANOVA Results for Mean Annual Rainfall and Deposition* of Site-Groups During the 3-Year Period from 10/1/81 Through 9/30/84

| Analyte | Site-Group A |  | Site-Group B |  | Site-Group C |  |
|---|---|---|---|---|---|---|
|  | Sites | Deposition | Sites | Deposition | Sites | Deposition |
| Rainfall (cm) | 2,3,4,5 | 146.4 | 8,9,13 | 128.6 | — | — |
| Laboratory $H^+$ | 2,5,8 | 340 | 3,4 | 311 | 9,13 | 191 |
| Excess $Ca^{+2}$ | 8,9,13 | 89.4 | 2,3,4,5 | 63.6 | — | — |
| $NH_4^+$ | 8 | 119 | 2,3,5 | 82.4 | 4,9,13 | 60.3 |
| Excess $SO_4^{-2}$ | 2,5,8 | 331 | 3,4 | 277 | 9,13 | 186 |
| $NO_3^-$ | 2,5,8 | 147 | 3,4 | 134 | 9,13 | 118 |
| Excess $Cl^-$ | 3,4,5,8,13 | 19 | 2,9 | 17 | — | — |

*All ion deposition rates are eq/ha-yr.

Notes: Sites refer to the site(s) making up the site-group. Deposition refers to the mean deposition for the site-group. Site-groups A, B, and C indicate statistically significant differences between site(s) at the 95-percent confidence level. The order for each site-group is as follows: Site-group A deposition > Site-Group B > Site-Group C.

Source: ESE, 1986.

from north Florida to south Florida, excess $SO_4^{-2}$ deposition at Site 2 (high rainfall) has been grouped with Sites 5 and 8, and $NO_3^-$ deposition at Site 9 (low rainfall) has been grouped with Site 13. This distinction between concentration and deposition site-groups suggests that spatial variability in rainfall amount can have an important influence on the determination of concentration and/or deposition fields.

ANOVA results for excess $Ca^{+2}$ and $NH_4^+$ deposition indicate that concentration groupings remain fairly intact in spite of the north-south rainfall gradient. Sites 8, 9, and 13 together exhibit higher deposition of excess $Ca^{+2}$ than Sites 2, 3, 4, and 5, and Site 8 persists as a maximum for $NH_4^+$. As with $NO_3^-$, Site 9 appears to have been displaced from the intermediate $NH_4^+$ group due to relatively low rainfall.

### 2.5.3 AIR CHEMISTRY DATA

ANOVA results for particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ are displayed in Table 2.5-3. Three site-groups are resolved for each of the above analytes, except $NO_2$. In all cases, Site 13 is classified uniquely in the lowest ranking group.

Data for particulate $SO_4^{-2}$ and $HNO_3$ reveal a significant north-south gradient through the state. Particulate $SO_4^{-2}$ and $HNO_3$ decrease by approximately 30 percent and 40 percent, respectively, from the northern site-group (A) to the southern site-group (C).

For $SO_2$ and especially $NO_2$, the organization of sites within groups suggests local influences superimposed on a north-south gradient. $SO_2$ concentrations exhibit a local maximum at Site 8 and a local minimum at Site 13, with all other sites grouped together. In general, these findings suggest that $SO_2$ levels in rural Florida are typically between 1 and 2 $\mu g/m^3$. Results for $NO_2$ also suggest local influence of the observed concentrations. This is not unexpected given the widely distributed sources for $NO_2$ (e.g., automotive exhaust). There appears to

Table 2.5-3. ANOVA Results for Geometric Mean Concentrations* for Particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$

| Analyte | Site-Group A |  | Site-Group B |  | Site-Group C |  | Site-Group D |  | Site-Group E |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | Sites | Mean | Sites | Mean | Sites | Mean | Sites | Mean | Sites | Mean |
| Particulate $SO_4^{-2}$ | 2,3,4,5,8 | 3.91 | 9 | 2.92 | 13 | 2.63 | — | — | — | — |
| $HNO_3$ | 2,3,5 | 0.93 | 4,8,9 | 0.69 | 13 | 0.57 | — | — | — | — |
| $SO_2$ | 8 | 3.21 | 2,3,4,5,9 | 1.88 | 13 | 1.09 | — | — | — | — |
| $NO_2$ | 5,8 | 8.16 | 2,4 | 6.37 | 9 | 4.33 | 3 | 3.59 | 13 | 2.24 |

*All concentrations are $\mu g/m^3$.

Notes: Sites refer to the site(s) making up the site-group. Mean refers to the geometric mean concentration for the site-group. Site-Groups A, B, C, D, and E indicate statistically significant differences between site(s) at the 95-percent confidence level. The order for each site-group is as follows: Site-Group A concentration > Site-Group B concentration; etc.

Source: ESE, 1986.

be little relationship between the $HNO_3$ and $NO_2$ distributions across the state which is readily seen by comparing the groupings for Site 3 and 8. Site 3 is in the next-to-the-lowest ranking group for $NO_2$ and the highest ranking group for $HNO_3$; Site 8 is ranked in the highest group for $NO_2$ but the intermediate group for $HNO_3$.

Intersite correlations for air data (Table 2.5-4) generally indicate that particulate $SO_4^{-2}$ and $HNO_3$ concentrations vary more uniformly across sites than do $SO_2$ and $NO_2$. This is especially true in the case of particulate $SO_4^{-2}$, for which site-to-site correlations are almost invariably highest between sites closest to each other. As the distance between sites increases (e.g., Site 2 and Site 13), correlation for particulate $SO_4^{-2}$ progressively decrease.

Interparameter correlations (Table 2.5-5) show a stronger relationship for $SO_4^{-2}$ versus $HNO_3$ than for $SO_2$ versus $NO_2$. This relationship also appears stronger than that between $SO_4^{-2}$ versus $SO_2$ and $HNO_3$ versus $NO_2$. In general, the strength of most correlations decreases from north Florida (Site 2) to south Florida (Site 13), and, in general, is a reflection of reduced variability in south Florida air chemistry. The implication of this relationship is explored further in Subsection 2.8.

Table 2.5-4. Intersite Correlation Coefficients (r) for Particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$

| Dependent Site | Analyte | Independent Site | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 2 | 3 | 4 | 5 | 8 | 9 | 13 |
| 2 | Particulate $SO_4^{-2}$ | — | 0.76 | 0.47 | 0.62 | 0.48 | 0.50 | 0.29 |
| | $HNO_3$ | — | 0.53 | 0.41 | 0.39 | 0.41 | 0.38 | 0.31 |
| | $SO_2$ | — | 0.60 | 0.40 | 0.30 | N.S. | 0.38 | 0.29 |
| | $NO_2$ | — | 0.44 | 0.39 | 0.45 | 0.29 | 0.34 | N.S. |
| 8 | Particulate $SO_4^{-2}$ | 0.49 | 0.55 | 0.76 | 0.74 | — | 0.76 | 0.64 |
| | $HNO_3$ | 0.41 | 0.49 | 0.64 | 0.53 | — | 0.64 | 0.50 |
| | $SO_2$ | N.S. | N.S. | N.S. | N.S. | — | N.S. | N.S. |
| | $NO_2$ | 0.29 | 0.28 | 0.58 | 0.32 | — | 0.46 | 0.15 |
| 13 | Particulate $SO_4^{-2}$ | 0.29 | 0.38 | 0.53 | 0.49 | 0.64 | 0.76 | — |
| | $HNO_3$ | 0.31 | 0.48 | 0.58 | 0.52 | 0.48 | 0.61 | — |
| | $SO_2$ | 0.29 | 0.40 | 0.55 | 0.26 | N.S. | 0.50 | — |
| | $NO_2$ | N.S. | 0.22 | 0.18 | 0.19 | 0.15 | 0.26 | — |

Note: N.S. = Not significant at 98-percent confidence level.

Source: ESE, 1986.

Table 2.5-5. Interparameter Correlation Coefficients (r) for Particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$

| | | Independent Variables | | | |
|---|---|---|---|---|---|
| Site | Dependent Variables | $SO_4^{-2}$ | $HNO_3$ | $SO_2$ | $NO_2$ |
| 2 | Particulate $SO_4^{-2}$ | -- | | | |
| | $HNO_3$ | 0.72 | -- | | |
| | $SO_2$ | 0.63 | 0.48 | -- | |
| | $NO_2$ | N.S. | 0.39 | 0.45 | -- |
| 8 | Particulate $SO_4^{-2}$ | -- | | | |
| | $HNO_3$ | 0.69 | -- | | |
| | $SO_2$ | 0.42 | N.S. | -- | |
| | $NO_2$ | 0.18 | 0.25 | 0.55 | -- |
| 13 | Particulate $SO_4^{-2}$ | -- | | | |
| | $HNO_3$ | 0.51 | -- | | |
| | $SO_2$ | 0.32 | N.S. | -- | |
| | $NO_2$ | N.S. | 0.28 | 0.43 | -- |

Note: N.S. = Not significant at 98-percent confidence level.

Source: ESE, 1986.

## 2.6 TEMPORAL VARIABILITY OF PRECIPITATION AND AIR CHEMISTRY

The short-term variability of Florida precipitation and air chemistry is examined in this section. The objective of this analysis is to determine whether the chemical data from this program suggest upward or downward changes in precipitation quality over time. Short-term trends (i.e., season-to-season, year-to-year) are evaluated statistically using the 3-year database from this study. Specifically, ANOVA is used to test the stability of and relationship between concentration of deposition site-groups presented in Subsection 2.5 for laboratory $H^+$, excess $Ca^{+2}$, $NH_4^+$, excess $SO_4^{-2}$, and $NO_3^-$. Mean concentrations and depositions are compared across seasons within the same year (i.e., summer versus winter), across seasons between years (e.g., summer 1982 versus summer 1983), and across years.

### 2.6.1 MONTHLY MEAN PRECIPITATION CONCENTRATIONS AND DEPOSITIONS

Monthly VWM concentrations and depositions of laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, excess $Ca^{+2}$, and $NH_4^+$ for statistically significant site-groups are shown in Figures 2.6-1 through 2.6-5. Note that site-groups vary from ion to ion and from concentration to deposition according to results of the statistical evaluation of spatial trends. In general, mean concentrations for all ions, except excess $Ca^{+2}$, show similar monthly patterns. Concentrations of laboratory $H^+$ and excess $SO_4^{-2}$ attain maximum values of 40 to 70 µN during summer (i.e., April through September) and minimum values of 5 to 20 µN during winter (i.e., October through March). Peak monthly concentrations of $NO_3^-$ and $NH_4^+$ are both on the order of 15 to 30 µN, whereas minimum monthly concentrations are on the order of 2 to 5 µN. Three-year average summer:winter concentration ratios are approximately 2.0 for laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$; however, monthly data show there is considerable variability in the relationship from year to year. Monthly mean concentrations of excess $Ca^{+2}$ show considerable month-to-month variability but no readily apparent seasonal variability. Monthly means for the southern and northern site-groups are approximately 7.5 µN and 5.0 µN, respectively.

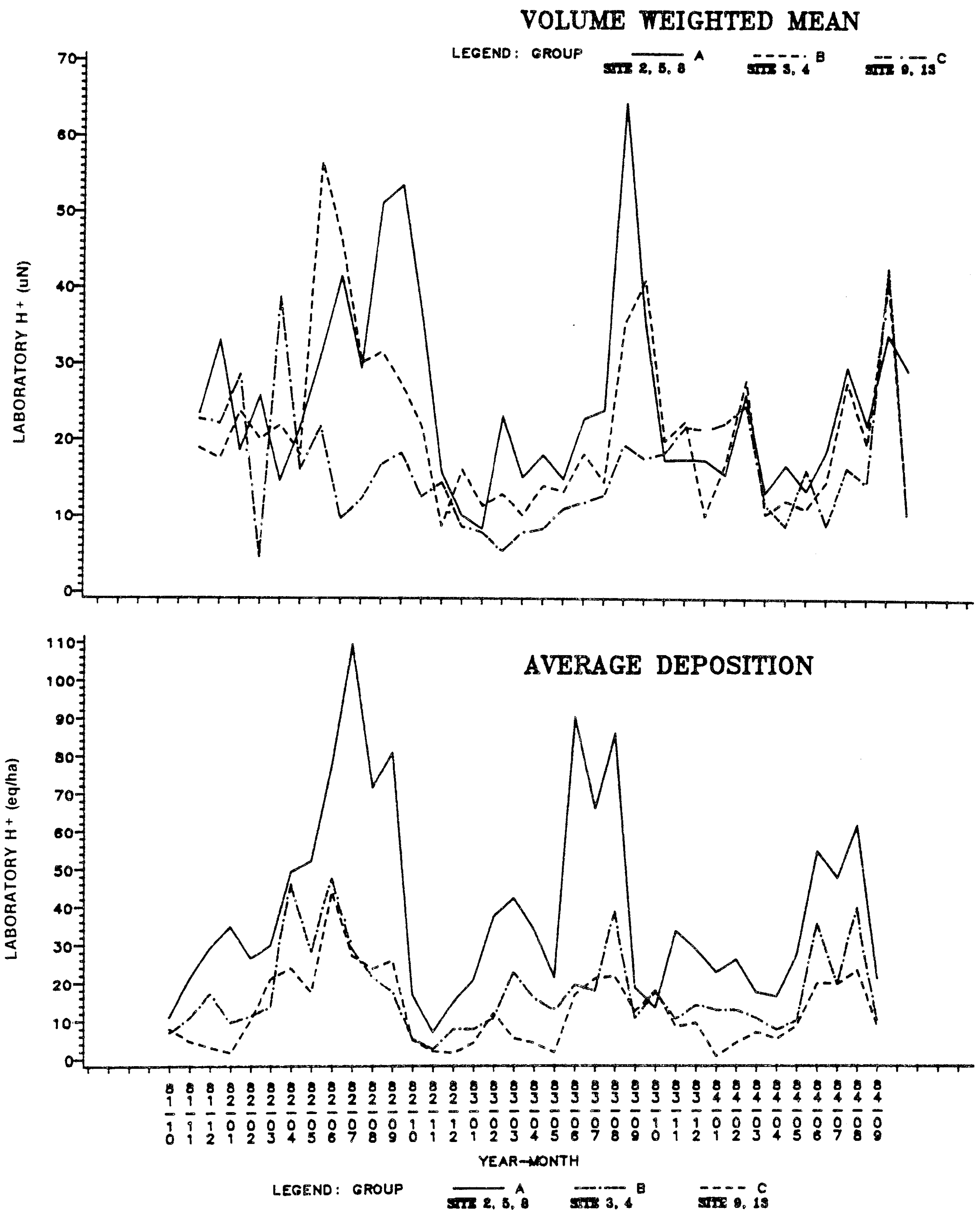

Figure 2.6-1
MONTHLY VWM CONCENTRATIONS AND
DEPOSITIONS OF LABORATORY H+

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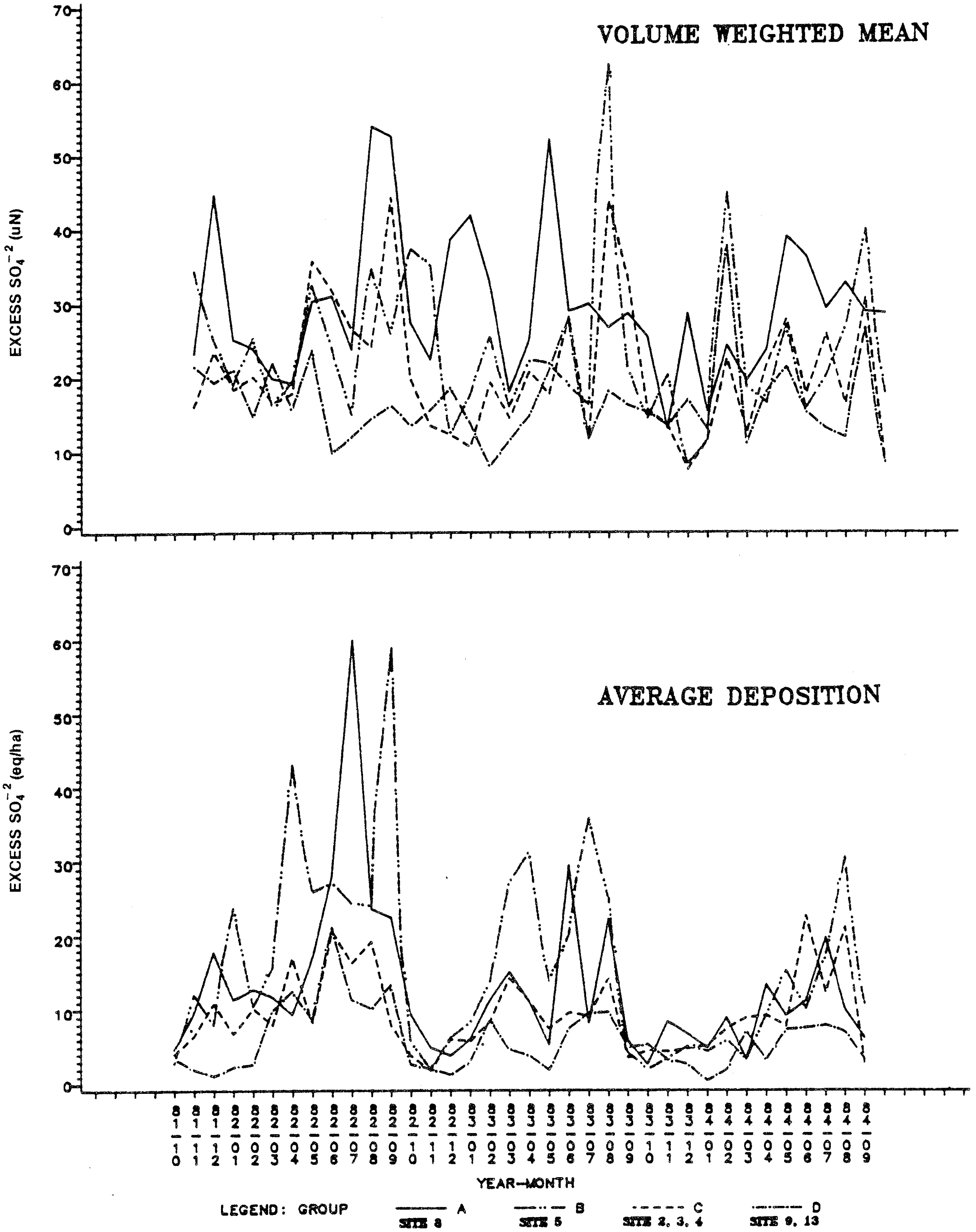

Figure 2.6-2
MONTHLY VWM CONCENTRATIONS AND DEPOSITIONS OF EXCESS $SO_4^{-2}$

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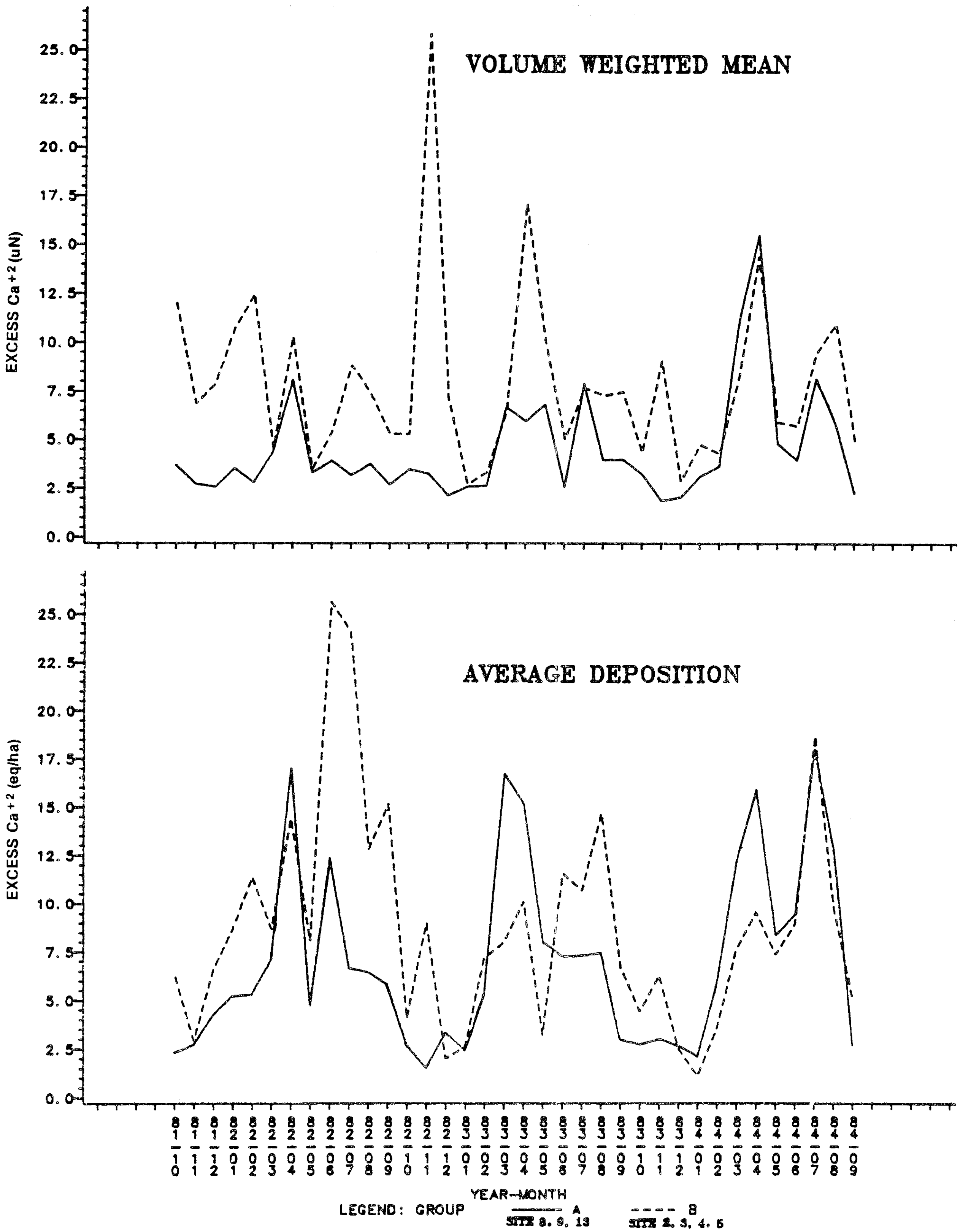

Figure 2.6-3
MONTHLY VWM CONCENTRATIONS AND DEPOSITIONS OF EXCESS Ca+2

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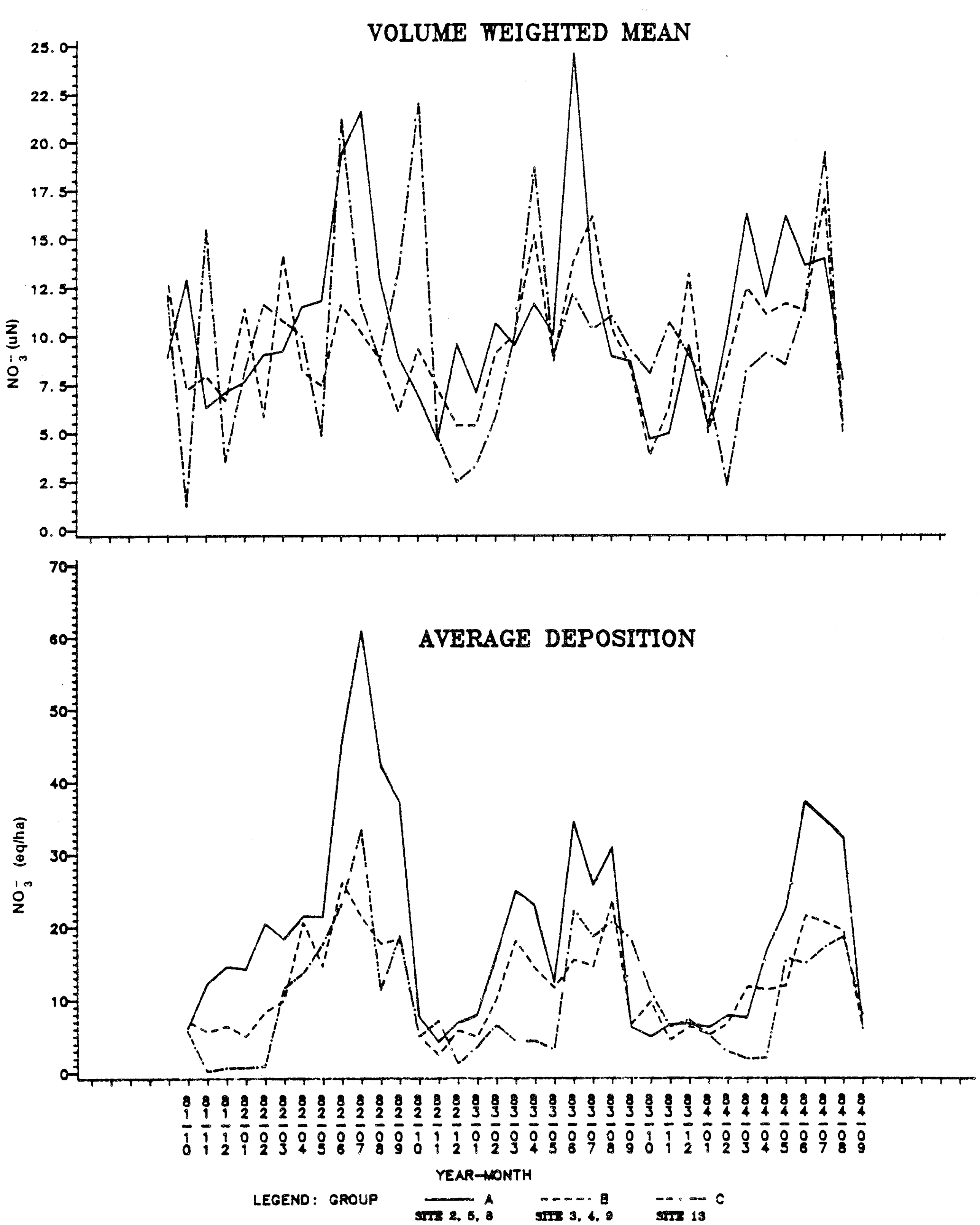

Figure 2.6-4
MONTHLY VWM CONCENTRATIONS AND DEPOSITIONS OF NO$_3^-$

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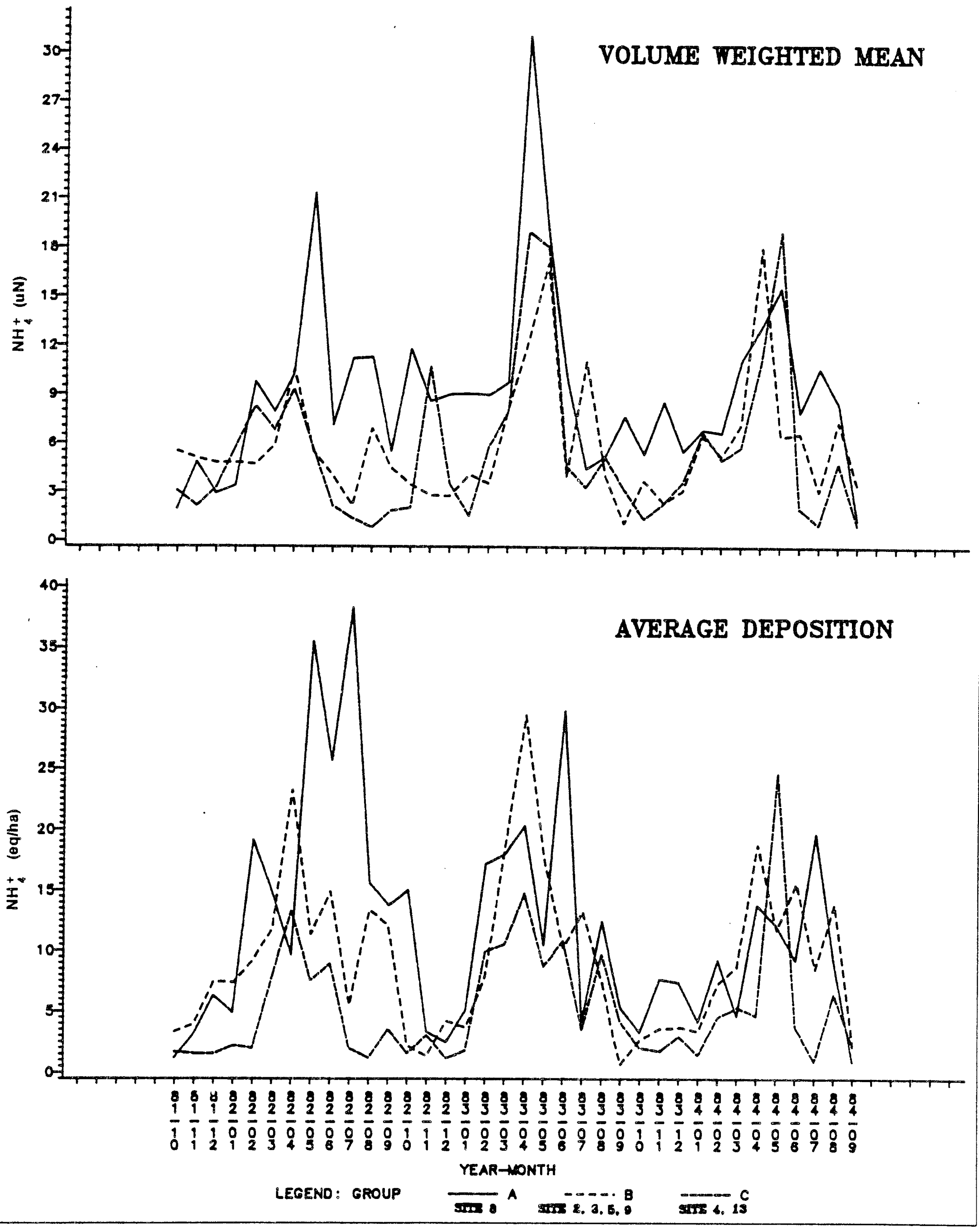

Figure 2.6-5
MONTHLY VWM CONCENTRATIONS AND DEPOSITIONS OF $NH_4^+$

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Results for deposition indicate seasonally variable atmospheric loadings for all ions. Differences across months and across site-groups are generally more distinct for deposition, especially $NO_3^-$, than for concentration. This is presumably due to the coincidence of north-south gradients in precipitation amount and concentration through the state. Monthly deposition of excess $Ca^{+2}$ also shows appreciable seasonality, but unlike the other ions, the distinction between site-groups is less clear than for concentration. This is expected, since the spatial concentration gradient for excess $Ca^{+2}$ runs counter to that for precipitation amount and most other ions.

### 2.6.2 COMPARISON OF PRECIPITATION DATA ACROSS SEASONS AND YEARS

To evaluate the statistical significance of site groups as a function of time, analyses of variance were performed by season for the 3-year monitoring period. Seasonal periods were considered appropriate units of time for two reasons. First, precipitation type and amount have historically differed across Florida from season to season. Summer rainfall is primarily convective and accounts for 60 to 78 percent of the 30-year mean annual rainfall at or near the seven precipitation monitoring stations used in this analysis. Winter precipitation, however, is typically associated with intrusion of cold fronts into the state. Second, monthly concentration and deposition data are suggestive of trends between seasons and years but have too few observations ($n = 4$ or 5 per site) to perform meaningful statistical analysis. Aggregated seasonal data sets contain approximately 25 observations per site, or multiples of 25 if sites are grouped, which is a valid sample size for analysis because differences between groups and/or seasons are sought at the 95-percent confidence level.

Volume-weighted geometric mean concentration and geometric mean deposition, along with associated 95-percent confidence intervals, for laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, excess $Ca^{+2}$, and $NH_4^+$ are shown in Figures 2.6-6 through 2.6-10. Results for laboratory $H^+$ concentration

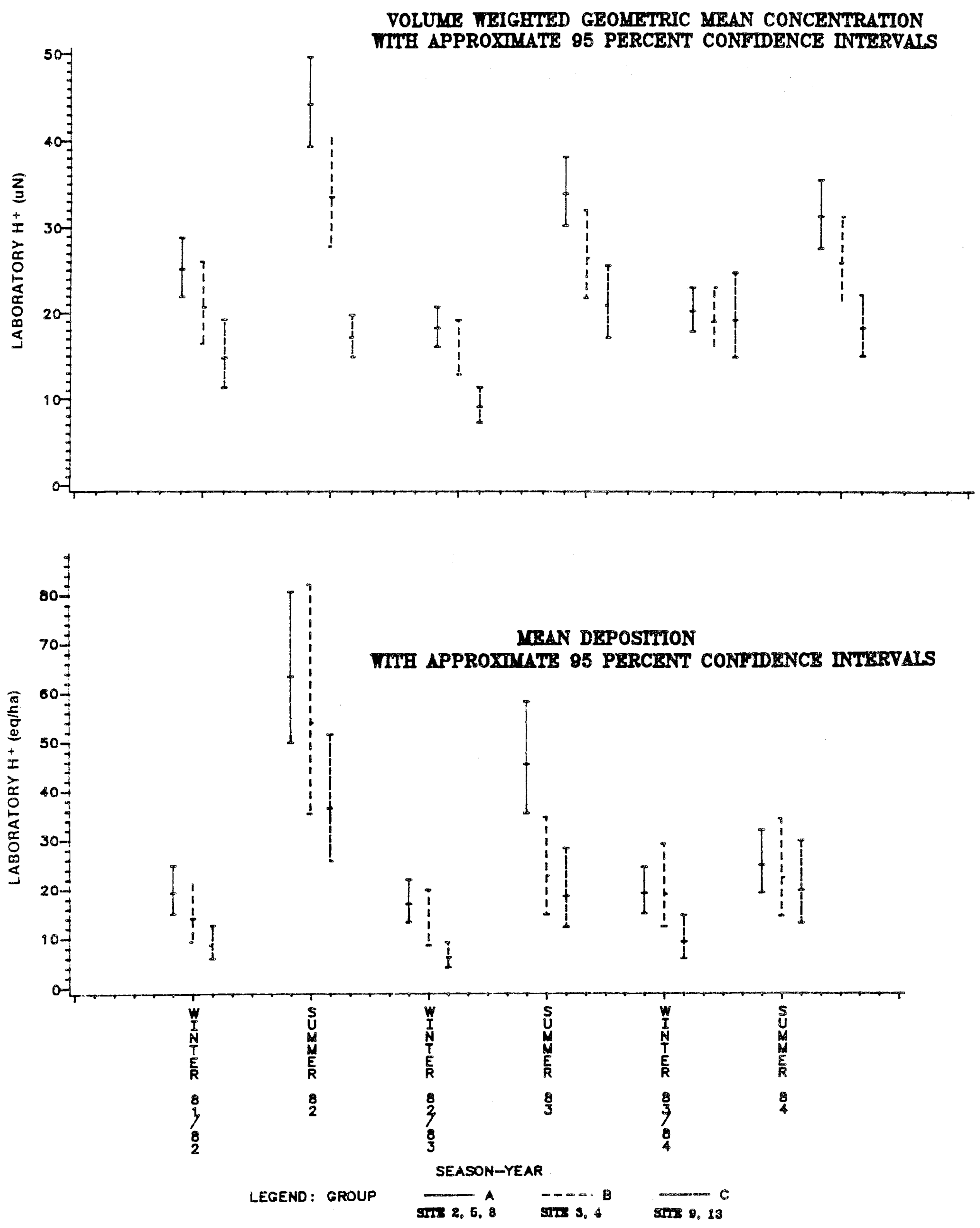

Figure 2.6-6
SEASONAL VWM CONCENTRATIONS AND
DEPOSITIONS OF LABORATORY H+

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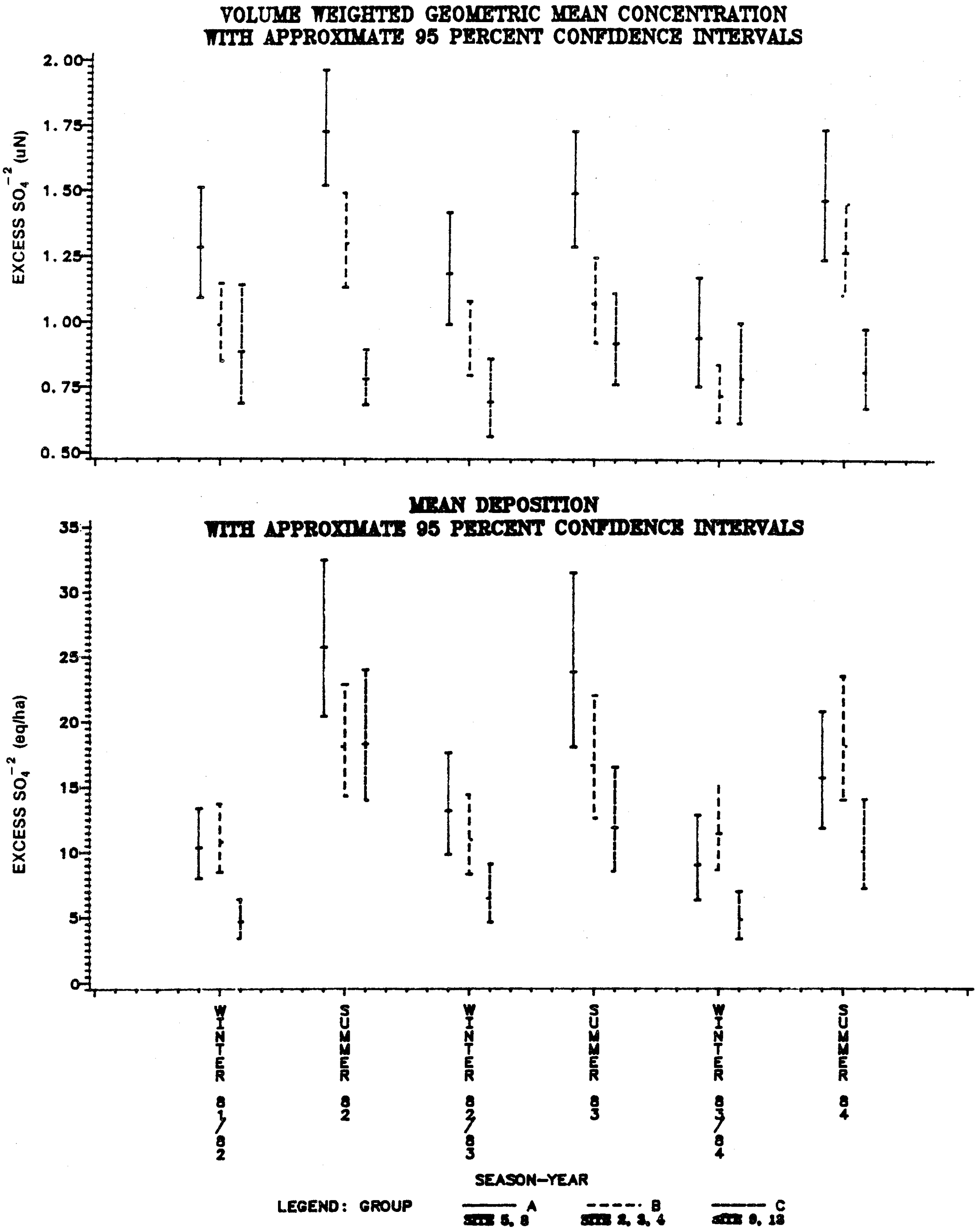

Figure 2.6-7
SEASONAL VWM CONCENTRATIONS AND DEPOSITIONS OF EXCESS $SO_4^{-2}$

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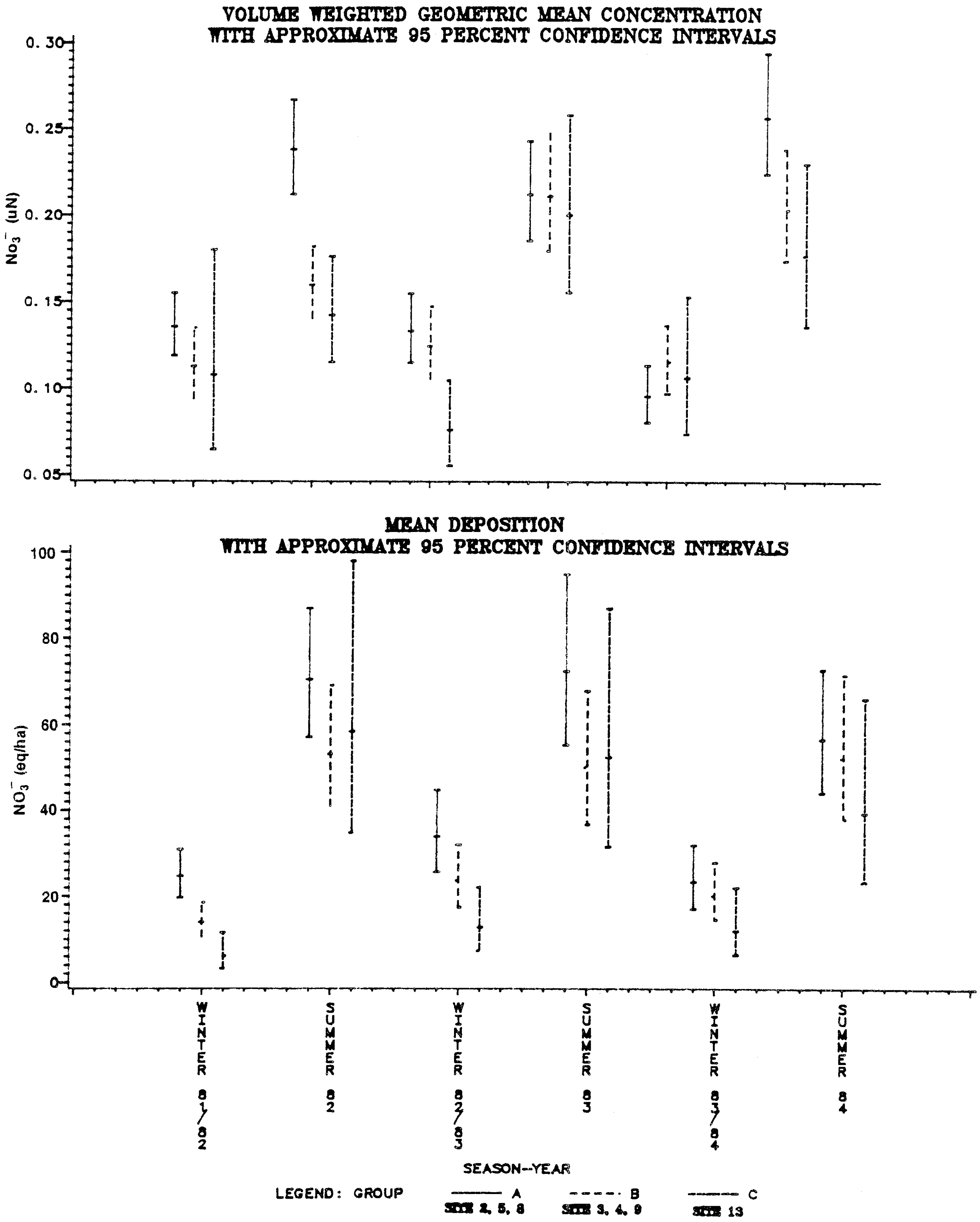

Figure 2.6-8
SEASONAL VWM CONCENTRATIONS AND
DEPOSITIONS OF $NO_3^-$

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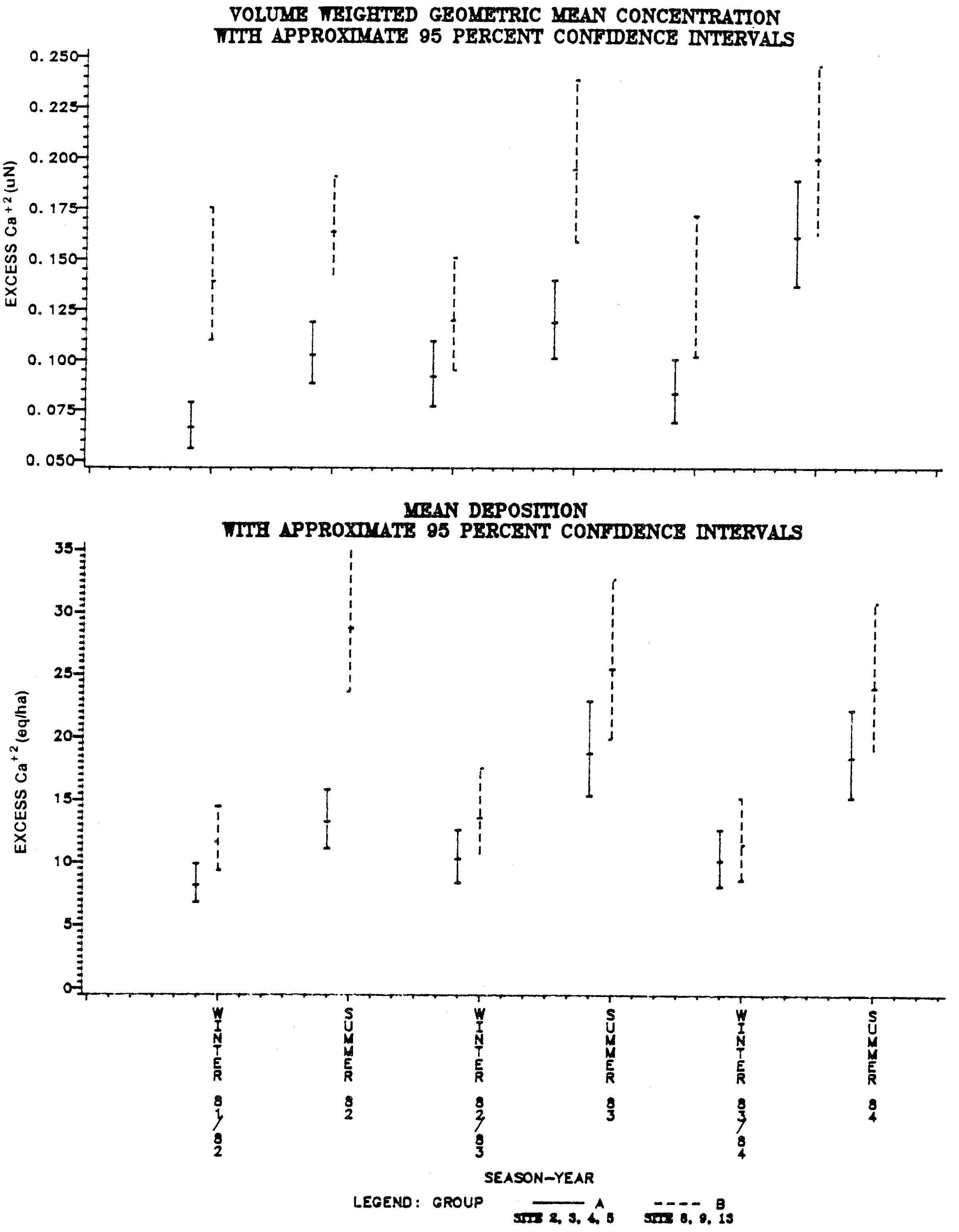

Figure 2.6-9
SEASONAL VWM CONCENTRATIONS AND DEPOSITIONS OF EXCESS $Ca^{+2}$

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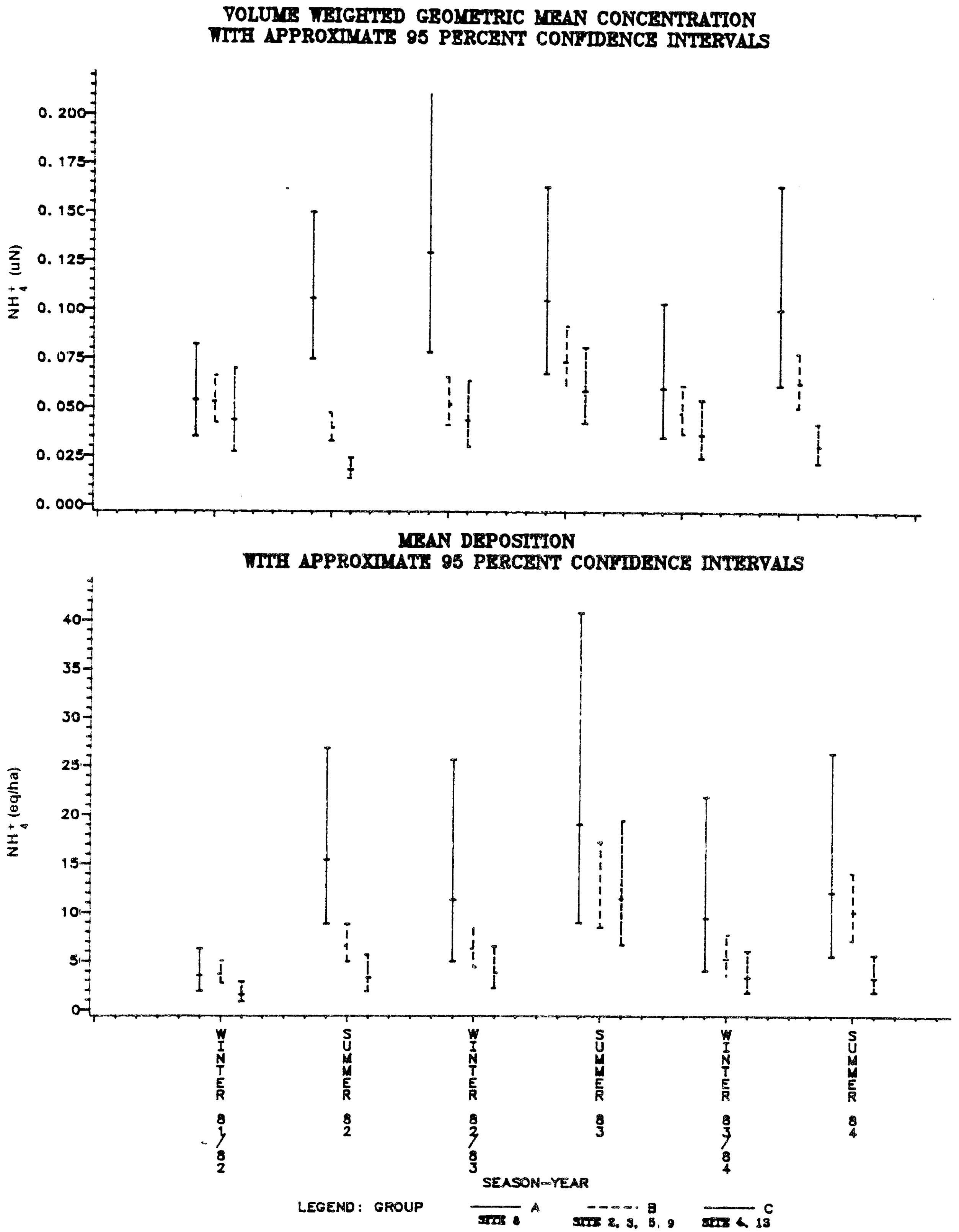

VOLUME WEIGHTED GEOMETRIC MEAN CONCENTRATION
WITH APPROXIMATE 95 PERCENT CONFIDENCE INTERVALS

MEAN DEPOSITION
WITH APPROXIMATE 95 PERCENT CONFIDENCE INTERVALS

Figure 2.6-10
SEASONAL VWM CONCENTRATIONS AND DEPOSITIONS OF $NH_4^+$

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show that site-groups invariably rank according to overall assignments [i.e., Site-Group A (Sites 2, 5, and 8) > Site-Group B (Sites 3 and 4) > Site-Group C (Sites 9 and 13)], but that differences between site-groups within a particular season may or may not be significant. Site-Group A, for example, differs significantly from Site-Group C for all seasons except winter 1983/1984, whereas Site-Group B differs from Site-Group A only during summer 1982 and from Site-Group C only during summer 1982 and winter 1982/1983. Winter 1983/1984 is the only period in which no two groups differ.

Comparison of laboratory $H^+$ means between successive seasons (e.g., winter 1981/1982 versus summer 1982) shows that winter values are often significantly lower than summer values. Winter-summer differences are invariably significant for Site-Group A (Sites 2, 5, and 8) and significant in 2 of 3 years for Site-Group B (Sites 3 and 4). Site-Group C (Sites 9 and 13) exhibits limited seasonal variation with a significant difference only for winter 1982/1983 versus summer 1983. Comparison of seasons across years (e.g., summer 1982 versus summer 1983) indicates that Site-Group A concentrations were higher in winter 1981/1982 than all other winters and higher in summer 1982 than all other seasons.

Results generally show fewer differences between site-groups for laboratory $H^+$ deposition than for concentration. Site-groups invariably rank according to overall means, but frequently show considerable overlap. All three site-groups show little variation in deposition across winters, but significant differences across summers. From summer 1982 to summer 1984, mean deposition decreased by nearly a factor of 2 for Site-Groups A and B. The third year of monitoring also differs from the first two in that no significant differences occur either across site-groups or across seasons.

Results generally indicate similar season-to-season and group-to-group patterns for excess $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ as for laboratory $H^+$. Winter-to-summer concentration fluctuations, although not always significant, are almost always greatest in the site-group with the highest concentration/deposition and differences between site-groups are typically greatest during the summer periods. It thus appears that the 3-year overall spatial site groupings (see Tables 2.5-1 and 2.5-2) are not consistently different over all seasons and all years. Winter periods show especially strong uniformity across groups and across years; summer periods appear responsible for the overall site groupings during the 3-year monitoring period.

Comparisons of annual data sets indicate that, for Site-Groups A and B, concentration and deposition of laboratory $H^+$ were significantly higher in 1981-1982 than in 1983-1984; the 1982-1983 period was not significantly different from either year. Results for Site-Group C, in contrast, show a non-significant decrease in laboratory $H^+$ concentration/deposition between 1981-1982 and 1983-1984, despite a significant decrease from summer 1982 to summer 1984. Data for excess $SO_4^{-2}$ indicate similar interannual comparisons as for laboratory $H^+$, whereas $NO_3^-$, excess $Ca^{+2}$, and $NH_4^+$ show no significant differences between years.

Overall results of the analysis of short-term precipitation chemistry variability indicate that seasonal trends in concentration/deposition are frequently significant for north Florida, but usually nonsignificant for south Florida. Summertime values for laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ are typically (but not always significantly) higher than corresponding winter values. Spatial gradients in precipitation chemistry also are relatively stronger during summer than winter. Over the 3-year monitoring period, annual concentration/deposition of laboratory $H^+$ and excess $SO_4^{-2}$ have decreased significantly in north Florida but remained relatively constant across south Florida. This reduction in acid deposition over north Florida appears to be due to a reduction in summertime rather than wintertime deposition. The underlying causes (e.g., meteorology, emissions) of this short-term trend are undetermined and therefore the likelihood and direction of future changes are unknown.

### 2.6.3 SEASONAL VARIABILITY OF AIR CHEMISTRY

Seasonal comparisons of ambient air concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ show distinct differences (Table 2.6-1). Summer concentrations of particulate $SO_4^{-2}$ and $HNO_3$ were higher than winter concentrations for all except the southernmost sites. In particular, the differential between summer and winter for particulate $SO_4^{-2}$ decreased from north to south suggesting that if $SO_2$ emissions are relatively constant over the seasons then transformation rates (i.e., from $SO_2$ to particulate $SO_4^{-2}$) at the southern sites are about the same during both seasons. For $SO_2$ and $NO_2$, winter concentrations were higher than summer concentrations by about the same amount for all sites except Site 8. Site 8 is in proximity (i.e., 50 km) of major $SO_2$ point sources and would be less influenced by differences in regional dispersion characteristics between summer and winter as well as transformation rates from $SO_2$ to particulate $SO_4^{-2}$. Results of statistical analysis of these seasonal differences indicate significant differences between summer and winter mean concentrations for $SO_2$ and $NO_2$ for all sites except Site 8 for $SO_2$. However, only certain sites exhibited statistically significant differences for particulate $SO_4^{-2}$ and $HNO_3$.

Statistical analysis of annual periods did not reveal any significant differences for any ambient parameter.

Table 2.6-1. Ratio* of Summer-To-Winter Mean Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ Concentration in Ambient Air (November 1982 to September 30, 1984)

| Site | Particulate $SO_4^{-2}$ | $SO_2$ | $HNO_3$ | $NO_2$ |
|---|---|---|---|---|
| 2 | 1.4 | 0.5 | 1.2 | 0.7 |
| 3 | 1.4 | 0.5 | 1.1 | 0.5 |
| 4 | 1.1 | 0.6 | 1.2 | 0.7 |
| 5 | 1.2 | 0.6 | 1.2 | 0.6 |
| 8 | 1.1 | 1.1 | 1.4 | 0.6 |
| 9 | 1.1 | 0.6 | 1.2 | 0.6 |
| 13 | 0.9 | 0.7 | 0.9 | 0.7 |
| 14† | 0.9 | 0.8 | 0.8 | 0.6 |

$$\text{*Summer-to-winter ratios} = \frac{\text{summer (April to September) concentrations}}{\text{winter (October to March) concentrations}}$$

†Through September 12, 1983.

Source: ESE, 1986.

## 2.7 CHEMICAL AND PHYSICAL RELATIONSHIPS

This subsection presents results of statistical analyses designed to infer relationships between laboratory $H^+$ and other ions in precipitation and between precipitation and air chemistry variables.

Multiple linear regression analyses were used to examine the relationships between laboratory $H^+$ (as the dependent variable) and excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$ (as independent variables) in precipitation. The relationships were derived for a subset of monitoring sites over a 3-year period, as well as seasons, to evaluate spatial-temporal variability of laboratory $H^+$ dependence on various ions. The relationship of ionic concentrations versus rainfall amount and of precipitation chemistry versus air chemistry (for samples taken concurrently) also were derived. Finally, ionic balances were computed for low-pH, high-pH, and intermediate-pH episodes to assess potential contributions of acids and bases to net precipitation acidity.

### 2.7.1 CHEMICAL RELATIONSHIPS OF LABORATORY $H^+$

Annual and seasonal multiple linear regressions of laboratory $H^+$ as a function of excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$ are shown in Tables 2.7-1 and 2.7-2. Results are shown for Sites 2, 5, 8, and 13 only, since these sites cover the full spatial extent of the network and represent the precipitation chemistry site-groups identified previously. Results for other north Florida sites , i.e., Sites 3 and 4, were similar to those for Sites 2 and 5, and results for Site 9 were similar to those for Site 13. Variables in Tables 2.7-1 and 2.7-2 were entered in order of decreasing importance to the overall prediction equation (i.e., most important first, and least important last). Partial-$R^2$ and total-$R^2$ values indicate the fraction of laboratory $H^+$ variability explained by each variable and the overall equation, respectively.

Annual regression equations for the years 1981/1982, 1982/1983, and 1983/1984 indicate that excess $SO_4^{-2}$ is the most important variable for

Table 2.7-1. Annual Prediction Equations for Laboratory $H^+$ Derived by Stepwise Multiple Linear Regression

| Site | Year* | Prediction Equation† and Partial $R^{2}$** | | | | | | Total $R^2$ |
|---|---|---|---|---|---|---|---|---|
| 2 | 1 | $H^+$ = | 0.7 | + 0.88($XS\text{-}SO_4^{-2}$) | − 0.74($NH_4^+$) | + 1.07($NO_3^-$) | − 0.63($XS\text{-}Ca^{+2}$) | |
| | | partial $R^2$ = | | 0.73 | 0.03 | 0.02 | 0.02 | = 0.80 |
| | 2 | $H^+$ = | 0.8 | + 0.94($XS\text{-}SO_4^{-2}$) | − 0.81($NH_4^+$) | + 0.92($NO_3^-$) | − 0.61($XS\text{-}Ca^{+2}$) | |
| | | partial $R^2$ = | | 0.88 | 0.01 | 0.01 | 0.01 | = 0.91 |
| | 3 | $H^+$ = | 3.4 | + 0.81($XS\text{-}SO_4^{-2}$) | − 0.78($XS\text{-}Ca^{+2}$) | + 0.84($NO_3^-$) | − 0.45($NH_4^+$) | |
| | | partial $R^2$ = | | 0.61 | 0.13 | 0.04 | 0.03 | = 0.81 |
| 5 | 1 | $H^+$ = | 0.5 | + 0.75($XS\text{-}SO_4^{-2}$) | + 1.42($NO_3^-$) | − 1.04($XS\text{-}Ca^{+2}$) | | |
| | | partial $R^2$ = | | 0.77 | 0.08 | 0.03 | | = 0.88 |
| | 2 | $H^+$ = | −0.4 | + 0.96($XS\text{-}SO_4^{-2}$) | − 1.32($XS\text{-}Ca^{+2}$) | + 1.12($NO_3^-$) | − 0.20($NH_4^+$) | |
| | | partial $R^2$ = | | 0.90 | 0.03 | 0.02 | 0.01 | = 0.96 |
| | 3 | $H^+$ = | 3.2 | + 0.89($XS\text{-}SO_4^{-2}$) | − 1.21($XS\text{-}Ca^{+2}$) | + 1.11($NO_3^-$) | − 0.37($NH_4^+$) | |
| | | partial $R^2$ = | | 0.71 | 0.09 | 0.09 | 0.01 | = 0.90 |
| 8 | 1 | $H^+$ = | −3.3 | + 0.85($XS\text{-}SO_4^{-2}$) | − 0.84($NH_4^+$) | + 0.88($NO_3^-$) | | |
| | | partial $R^2$ = | | 0.73 | 0.12 | 0.03 | | = 0.88 |
| | 2 | $H^+$ = | 1.6 | + 0.92($XS\text{-}SO_4^{-2}$) | − 0.94($NH_4^+$) | + 0.68($NO_3^-$) | − 0.46($XS\text{-}Ca^{+2}$) | |
| | | partial $R^2$ = | | 0.48 | 0.25 | 0.03 | 0.02 | = 0.78 |
| | 3 | $H^+$ = | 5.2 | + 1.00($XS\text{-}SO_4^{-2}$) | − 0.88($XS\text{-}Ca^{+2}$) | + 1.04($NH_4^+$) | − 0.56($NO_3^-$) | |
| | | partial $R^2$ = | | 0.45 | 0.21 | 0.07 | 0.04 | = 0.77 |
| 13 | 1 | $H^+$ = | −0.3 | + 1.00($XS\text{-}SO_4^{-2}$) | | | | |
| | | partial $R^2$ = | | 0.28 | | | | = 0.28 |

Table 2.7-1. Annual Prediction Equations for Laboratory $H^+$ Derived by Stepwise Multiple Linear Regression (Continued, Page 2 of 2)

| Site | Year* | Prediction Equation† and Partial $R^2$** | | | | | Total $R^2$ |
|---|---|---|---|---|---|---|---|
| | 2 | $H^+ =$ | $1.9 + 0.77(XS-SO_4^{-2})$ | $- 0.65(NH_4^+)$ | $- 0.21(XS-Ca^{+2})$ | $+ 0.45(NO_3^-)$ | |
| | | partial $R^2 =$ | 0.39 | 0.20 | 0.04 | 0.03 | = 0.67 |
| | 3 | $H^+ =$ | $1.9 + 0.88(NO_3^-)$ | $- 0.57(NH_4^+)$ | $+ 0.71(XS-SO_4^{-2})$ | | |
| | | partial $R^2 =$ | 0.39 | 0.06 | 0.05 | | = 0.50 |

*Year 1 = 1981-1982; Year 2 = 1982-1983; Year 3 = 1983-1984.

†Dependent variables listed in order of decreasing significance. Concentration of ions is in µN.

**Partial $R^2$ for each variable is shown below the applicable variable.

Notes: XS = Excess.
$R^2$ = Coefficient of determination.
Ideal Theoretical Equation for predicting laboratory $H^+$ in µN is:

$$H^+ = (XS-SO_4^{-2}) + (NO_3^-) + (XS-Cl^-) - (NH_4^+) - (XS-Ca^{+2})$$

Source: ESE, 1986.

Table 2.7-2. Seasonal Prediction Equations for Laboratory $H^+$ Derived by Stepwise Multiple Linear Regression

| Site | Season* | | Prediction Equation† and Partial $R^2$** | | | | | Total $R^2$ |
|---|---|---|---|---|---|---|---|---|
| 2 | Summer | $H^+$ = | 0.9 | + 0.91$(XS\text{-}SO_4^{-2})$ | - 0.74$(NH_4^+)$ | + 1.01 $(NO_3^-)$ | - 0.53$(XS\text{-}Ca^{+2})$ | |
| | | partial $R^2$ = | | 0.73 | 0.03 | 0.02 | 0.01 | = 0.79 |
| | Winter | $H^+$ = | 2.3 | + 0.76$(XS\text{-}SO_4^{-2})$ | - 0.60$(XS\text{-}Ca^{+2})$ | + 0.88$(NO_3^-)$ | - 0.87$(NH_4^+)$ | |
| | | partial $R^2$ = | | 0.63 | 0.05 | 0.04 | 0.03 | = 0.75 |
| 5 | Summer | $H^+$ = | 0.3 | + 0.86$(XS\text{-}SO_4^{-2})$ | + 1.35$(NO_3^-)$ | - 1.26$(XS\text{-}Ca^{+2})$ | - 0.23$(NH_4^+)$ | |
| | | partial $R^2$ = | | 0.78 | 0.05 | 0.08 | <0.01 | = 0.91 |
| | Winter | $H^+$ = | 3.0 | + 0.86$(XS\text{-}SO_4^{-2})$ | + 0.67$(NO_3^-)$ | - 0.8$(XS\text{-}Ca^{+2})$ | | |
| | | partial $R^2$ = | | 0.86 | 0.01 | 0.02 | | = 0.89 |
| 8 | Summer | $H^+$ = | -0.1 | + 1.01$(XS\text{-}SO_4^{-2})$ | - 0.88$(NH_4^+)$ | - 0.63$(XS\text{-}Ca^{+2})$ | - 0.72$(NO_3^-)$ | |
| | | partial $R^2$ = | | 0.52 | 0.20 | 0.07 | 0.05 | = 0.84 |
| | Winter | $H^+$ = | 4.4 | + 0.81$(XS\text{-}SO_4^{-2})$ | - 0.66$(NH_4^+)$ | | | |
| | | partial $R^2$ = | | 0.46 | 0.11 | | | = 0.57 |
| 13 | Summer | $H^+$ = | 1.2 | + 0.85$(XS\text{-}SO_4^{-2})$ | - 0.59$(NH_4^+)$ | + 0.49$(NO_3^-)$ | - 0.16$(XS\text{-}Ca^{+2})$ | |
| | | partial $R^2$ = | | 0.42 | 0.09 | 0.02 | 0.01 | = 0.54 |
| | Winter | $H^+$ = | 2.7 | + 1.22$(XS\text{-}SO_4^{-2})$ | - 1.09$(NH_4^+)$ | | | |
| | | partial $R^2$ = | | 0.17 | 0.09 | | | = 0.26 |

*Season: Summer = April through September; Winter = October through March

†Dependent variables listed in order of decreasing significance. Concentration of ions is in µN.

**Partial $R^2$ for each variable is shown below the applicable variable.

Notes: XS = Excess.

Ideal Theoretical Equation tested for predicting laboratory $H^+$ in µN is:

$$H^+ = (XS\text{-}SO_4^{-2}) = (NO_3^-) = (XS\text{-}Cl^-) - (NH_4^+) - (XS\text{-}Ca^{+2})$$

Source: ESE, 1986.

predicting laboratory $H^+$ for all combinations of sites and years except one (Site 13, year 1983/1984). In general, the second most important variable is a base cation (i.e., excess $Ca^{+2}$ or $NH_4^+$), and $NO_3^-$ typically ranks third or fourth in overall importance. Multiple $R^2$ values range from 0.28 to 0.96, indicating that 28 to 96 percent of the variability of laboratory $H^+$ is explained by the prediction equation. The low $R^2$ value at Site 13 (0.28) may be due to the relatively low overall variability of laboratory $H^+$ in south Florida. A relatively high proportion of Site 13 samples exhibited laboratory pH values $\geq 5.0$. Above pH 5.0, small amounts of unidentified ions or ions not included in the model (e.g., organic acids) may play a large role in the determination of precipitation acidity (Galloway et al., 1982).

Comparisons of prediction models for the three annual periods shows that the overall importance of excess $Ca^{+2}$ to prediction equations has increased from 1981/1982 to 1983/1984 and that intercept values also have increased for the same period. The partial-$R^2$ values for excess $Ca^{+2}$ in prediction models increased from the first two annual periods to the third annual period for Sites 2, 5, and 8 which appears to be in general agreement with the slightly higher excess $Ca^{+2}$ concentrations observed during the third year of the study. At Sites 2 and 8, for example, excess $Ca^{+2}$ was entered last or not at all in prediction equations for Year 1 and Year 2, but it was second in the equations for Year 3. Increases in the model intercept from <1.0 μN to between 1.9 and 5.2 μN suggest that a significant portion of the mean laboratory $H^+$ concentration was not accounted for by the variables in the 1983/1984 prediction equation.

Comparison of prediction equations across seasons shows that excess $SO_4^{-2}$ was the most important predictor of laboratory $H^+$ for all site-season combinations. Multiple $R^2$ values and equation intercepts were invariably higher and lower, respectively, during the summer than in winter. This observation indicates that summertime equations accounted for more of the overall variability of laboratory $H^+$ as well as a greater portion of its concentration. Given statewide mean laboratory $H^+$ concentrations during wintertime of approximately 15 μN, the winter prediction equations in Table 2.7-2 suggest that approximately 20 percent of the observed laboratory $H^+$ could not be explained by excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$.

## 2.7.2 PRECIPITATION CHEMISTRY VERSUS RAINFALL AMOUNT

The relationship between analyte concentration and the size of precipitation events was evaluated by simple linear regression of the logarithmic transform of the following equation.

$$[x] = P^a$$

where: $[x]$ = analyte concentration (μN),
$P$ = precipitation amount (cm), and
$a$ = constant.

This equation is similar in form to that examined previously by Hicks *et al*. (1981), Barrie and Neustradler (1983), and Edgerton (1981) for northeastern United States, Canadian, and Florida precipitation, respectively. It is also similar to the equation derived by McNaughton (1983) for application in precipitation scavenging models. This analysis was performed using data from Sites 5 and 9 only, because these sites were operated on a daily sampling schedule throughout the 3-year period.

Annual concentration versus rainfall curves for laboratory $H^+$ and excess $Ca^{+2}$ at Gainesville are depicted in Figure 2.7-1. Predicted concentrations of laboratory $H^+$ approach 100 uN (pH 4.00) for the smallest rainfall events analyzed (approximately 0.04 cm), but decrease by a factor of 5 (to 20 μN) for events of 0.5 cm or larger. Excess $Ca^{+2}$ concentrations decrease from nearly 50 uN to approximately 3 uN within 0.5 cm of rainfall.

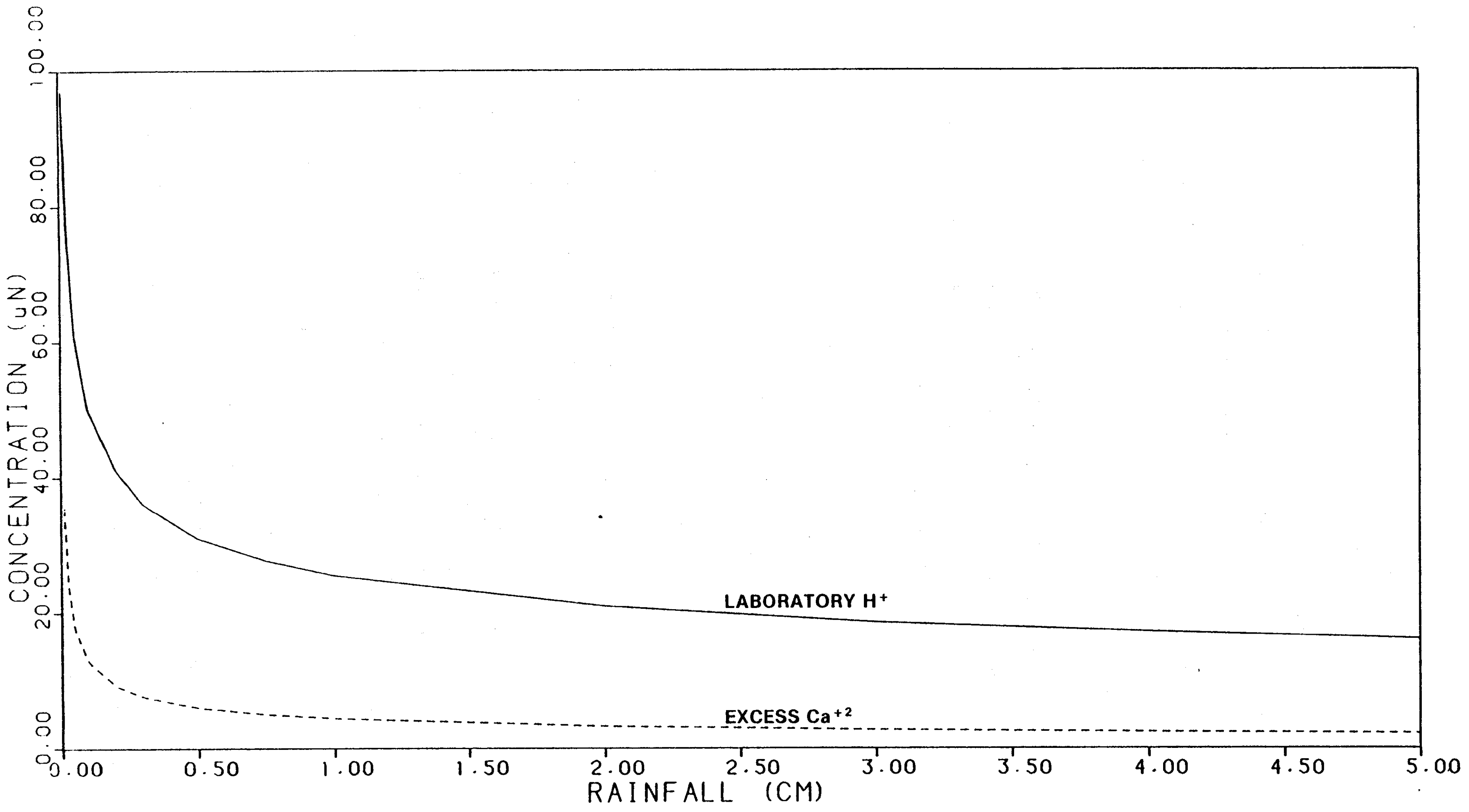

Figure 2.7-1
RELATIONSHIP BETWEEN LABORATORY $H^+$ AND $Ca^{+2}$ CONCENTRATIONS AND RAINFALL AMOUNT FOR GAINESVILLE PRECIPITATION

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Results of the analysis (see Table 2.7-3) showed that analyte concentrations, except for $NH_4^+$, decayed fairly rapidly with increasing precipitation amounts. The most rapid decay rate was invariably for excess $Ca^{+2}$ (a = -0.44 to -0.76), followed by $NO_3^-$, and then either excess $SO_4^{-2}$ or laboratory $H^+$. The rapid decay of excess $Ca^{+2}$ relative to excess $SO_4^{-2}$ was similar to that observed by Tanaka and Winchester (1980) for Tallahassee precipitation and is expected behavior for large aerosols. The rapid decay of $NO_3^-$ relative to excess $SO_4^{-2}$ in turn suggested that precipitation scavenging of these species could have been governed by different physicochemical processes. Uptake rates of $HNO_3$ and $SO_2$ by raindrops, for example, could be diffusion-limited and solubility-limited, respectively (Durham *et al.*, 1981).

Comparison of coefficients between seasons showed somewhat slower concentration decreases with rainfall amount in summer at Site 5, but faster decreases in summer for Site 9. This suggests that differences in precipitation chemistry between Site 5 and Site 9 could be the result of seasonal differences in precipitation scavenging efficiencies and/or atmospheric concentrations of particulates and gases rather than differences in precipitation amounts.

### 2.7.3 POTENTIAL ACIDS AND BASES IN PRECIPITATION

The contribution of acid anions (i.e., excess $SO_4^{-2}$ and $NO_3^-$) and base cations (i.e., excess $Ca^{+2}$ and $NH_4^+$) was calculated by normalizing concentrations to laboratory $H^+$ (i.e., as a percent of $H^+$ concentration). The resulting values indicate maximum percentage contribution of an acidic or basic species to the net precipitation acidity. Results of this calculation are shown for three pH ranges and for all precipitation in Table 2.7-4. The pH ranges used in the potential acid/base calculations were <4.3, 4.3 to 4.9, and >4.9. The low-pH range was selected because it represents precipitation samples with laboratory $H^+$ values at least twice the VWM concentrations for Sites 2, 5, 9, and 13. The high-pH range was chosen because it represents samples with

Table 2.7-3. Relationship Between Concentration and Rainfall Amount*

| Site | Season† | Laboratory $H^+$ | Excess $SO_4^{-2}$ | $NO_3^-$ | $NH_4^+$ | Excess $Ca^{+2}$ |
|---|---|---|---|---|---|---|
| 5 | Summer | -0.28 ± 0.10 | -0.23 ± 0.10 | -0.37 ± 0.07 | NS | -0.44 ± 0.12 |
|  | Winter | -0.33 ± 0.10 | -0.36 ± 0.13 | -0.43 ± 0.12 | NS | -0.76 ± 0.14 |
|  | Annual | -0.29 ± 0.08 | -0.28 ± 0.08 | -0.34 ± 0.08 | -0.16 ± 0.12 | -0.46 ± 0.09 |
| 9 | Summer | -0.33 ± 0.13 | -0.38 ± 0.13 | -0.38 ± 0.15 | NS | -0.51 ± 0.15 |
|  | Winter | 0.25 ± 0.08 | -0.27 ± 0.17 | -0.28 ± 0.22 | NS | -0.57 ± 0.18 |
|  | Annual | -0.15 ± 0.13 | -0.31 ± 0.09 | -0.29 ± 0.11 | NS | -0.68 ± 0.10 |

*The equation tested is:

$$[x] = P^a$$

where: [x] = analyte concentration (μN),
P = precipitation amount (cm), and
a = coefficient listed.

†Summer = April through September
Winter = October through March

Notes: NS = no significant relationship.

Source: ESE, 1986.

Table 2.7-4. Potential Acids and Bases for Low-pH, Intermediate-pH, and High-pH Precipitation Samples as the Percent of $H^+$ Concentration (μN)

| Site | pH Range | % of Total Rainfall | Potential Acids* | | | Potential Bases† | | | Net Acidity |
|---|---|---|---|---|---|---|---|---|---|
| | | | $XS\text{-}SO_4^{-2}$ | $NO_3^-$ | Total | $NH_4^+$ | $XS\text{-}Ca^{+2}$ | Total | (Total Acids) - (Total Bases) |
| 2 | <4.3 | 12 | 80 | 33 | 113 | 18 | 8 | 26 | 87 |
| | 4.3-4.9 | 49 | 89 | 47 | 136 | 26 | 17 | 43 | 93 |
| | >4.9 | 39 | 129 | 63 | 192 | 41 | 49 | 90 | 102 |
| | overall | 100 | 90 | 43 | 133 | 24 | 18 | 42 | 91 |
| 5 | <4.3 | 12 | 80 | 33 | 113 | 18 | 11 | 29 | 84 |
| | 4.3-4.9 | 67 | 86 | 42 | 128 | 25 | 19 | 44 | 84 |
| | >4.9 | 21 | 117 | 72 | 189 | 37 | 49 | 86 | 103 |
| | overall | 100 | 92 | 47 | 139 | 27 | 24 | 51 | 88 |
| 9 | <4.3 | 2 | 99 | 49 | 148 | 19 | 27 | 46 | 102 |
| | 4.3-4.9 | 39 | 96 | 58 | 154 | 29 | 27 | 56 | 98 |
| | >4.9 | 59 | 159 | 88 | 247 | 51 | 82 | 133 | 114 |
| | overall | 100 | 113 | 65 | 178 | 34 | 43 | 77 | 101 |
| 13 | <4.3 | 1 | 81 | 45 | 126 | 15 | 25 | 40 | 86 |
| | 4.3-4.9 | 35 | 90 | 71 | 161 | 24 | 50 | 74 | 87 |
| | >4.9 | 64 | 183 | 126 | 309 | 115 | 136 | 251 | 58 |
| | overall | 100 | 107 | 74 | 181 | 44 | 64 | 108 | 73 |

*$XS\text{-}SO_4^{-2}$ assumed to be $H_2SO_4$; $NO_3^-$ assumed to be $HNO_3$.
†$NH_4^+$ assumed to be $NH_3$; $Ca^{+2}$ assumed to be calcium carbonate ($CaCO_3$).

Notes: All potential acids and bases normalized to laboratory $H^+$ concentration; i.e., analyte/laboratory $H^+$.
All concentrations used in calculations were in μN.
XS = excess.

Source: ESE, 1986.

laboratory $H^+$ values approaching those reported for remote global precipitation (Galloway et al., 1982).

Potential contributions of all acids/bases appeared to increase from low-pH episodes to high-pH episodes at all sites. Total acid anion concentrations for all pH levels exceeded 100 percent of laboratory $H^+$ at all sites; however, the net precipitation acidity (i.e., acids minus bases) was well below 100 percent of laboratory $H^+$ at three of four sites. Explanations for this observation could include a bias in chemical analyses; the presence of an additional acid(s) in precipitation; and the possibility that $NH_4^+$ and/or excess $Ca^{+2}$ were not behaving exclusively as bases (or base counterions). Note, however, that if the latter explanation is true, it cannot be due to interactions between $NH_4^+$/excess $Ca^{+2}$ and excess $SO_4^{-2}/NO_3^-$ since these ions were implicitly taken into account in the subtraction of bases from acids.

Net acidity (i.e., acids minus bases) and normalized concentrations of $NO_3^-$ generally increased with pH. Above pH 4.9, the measured acids and bases were able to account fully for laboratory $H^+$, except in the case of Site 13. At Site 13, total potential acids and total potential bases were both greater than 100 percent, indicating that laboratory $H^+$ was a relatively minor component of precipitation chemistry in south Florida.

Comparison of the potential contribution of excess $SO_4^{-2}$ and $NO_3^-$ shows an increase: (1) with increasing pH, and (2) from north Florida (Sites 2 and 5) to south Florida (Sites 9 and 13).

At Sites 2 and 5, the ratio of excess $SO_4^{-2}$ to $NO_3^-$ for low-pH episodes was approximately 2.4, whereas for Sites 9 and 13, it was approximately 2.0. For high-pH episodes, in contrast, the ratio of excess $SO_4^{-2}$ to $NO_3^-$ ranged from 2.0 at Site 2 to 1.4 at Site 13. Given the relative frequencies of low-pH and high-pH episodes in north and south Florida, this finding suggests that the overall contribution of excess $SO_4^{-2}$ to precipitation acidity decreased from north Florida to south Florida. Previous analyses of Florida precipitation over annual periods have indicated similar decreases in excess-$SO_4^{-2}$:$NO_3^-$ ratios from north Florida to south Florida (Brezonik et al., 1981; ESE, 1983b; ESE, 1984).

### 2.7.4 AIR CHEMISTRY INTERRELATIONSHIPS

Seasonal concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ for a 2-year period were used to calculate molar oxidation and sulfur/nitrogen ratios for Florida (Table 2.7-5). The results for molar oxidation ratios, particulate $SO_4^{-2}$/(particulate $SO_4^{-2}$ + $SO_2$) and $HNO_3$/($HNO_3$ + $NO_2$), show a definite seasonal variability. For sulfur, summer oxidation ratios are approximately 50 percent higher than winter ratios at most sites. Seasonal differences in sulfur oxidation ratios have also been observed at the Hubbard Brook Experimental Forest in New Hampshire. These ratios were observed to range from about 0.75 for August/September to about 0.25 for November/December (Saltzman et al., 1983). In general, seasonal variability is uniform over the state with the exception of Site 8 and Site 13. As indicated previously, Site 8 is near an area of relatively high $SO_2$ emissions and, contrary to other sites, exhibited higher $SO_2$ concentrations in the summer than winter. This suggests that transformation rates for nearby $SO_2$ sources may be a limiting factor at this site and supports a nonlinear relationship between $SO_2$ emissions and particulate $SO_4^{-2}$ concentrations over relatively small ($\leq$50 km) distances. Site 13, located in the extreme southern portion of Florida, demonstrates that the difference between summer and winter seasons at this subtropical site are reduced from its more northern counterparts and suggests similar transformation rates over an annual period at this site.

Nitrogen oxidation ratios also exhibited a seasonal variability similar to that for sulfur. Summer nitrogen oxidation ratios were, for the most part, about 100 percent higher than winter. Again, Site 13 exhibited about the same difference between summer and winter oxidation ratios for nitrogen as that observed for sulfur. The summer and winter oxidation

Table 2.7-5. Seasonal Oxidation and Sulfur/Nitrogen Ratios

| | Oxidation Ratio* | | | | Sulfur/Nitrogen Ratio (Molar) | |
|---|---|---|---|---|---|---|
| | Sulfur | | Nitrogen | | | |
| Site | Summer | Winter | Summer | Winter | Summer | Winter |
| 2 | 0.65 | 0.41 | 0.12 | 0.07 | 1.34 | 1.06 |
| 3 | 0.69 | 0.44 | 0.22 | 0.12 | 2.52 | 1.67 |
| 4 | 0.63 | 0.45 | 0.11 | 0.06 | 1.19 | 1.00 |
| 5 | 0.57 | 0.42 | 0.11 | 0.06 | 1.08 | 0.86 |
| 8 | 0.39 | 0.40 | 0.10 | 0.05 | 1.36 | 0.82 |
| 9 | 0.57 | 0.38 | 0.17 | 0.10 | 1.59 | 1.45 |
| 13 | 0.63 | 0.56 | 0.16 | 0.15 | 1.67 | 1.57 |

*Oxidation ratios are:

1. Particulate $SO_4^{-2}$/(Particulate $SO_4^{-2}$ + $SO_2$) as sulfur, and
2. $HNO_3$/($HNO_3$ + $NO_2$) as nitrogen.

Source: ESE, 1986.

ratios at Site 3 were approximately a factor of 2 higher than the ratios for the northern Florida sites. At Site 3, $NO_2$ concentrations were approximately a factor of 2 lower than other northern sites which may account for this difference. The reasons for the generally lower $NO_2$ concentrations at Site 3 are not known.

Sulfur oxidation ratios are approximately a factor of 5 higher than corresponding nitrogen oxidation ratios suggesting that $HNO_3$ is removed at greater rates by dry and wet deposition processes than particulate $SO_4^{-2}$. This observation is consistent with experimental and empirical evidence which indicates that $HNO_3$ is removed much more efficiently than particulate $SO_4^{-2}$ (Hicks, 1985; Barrie and Hales, 1984; and Huebert, 1983). Sulfur/nitrogen ratios exhibit a similar seasonal trend as oxidations although no uniform spatial pattern is apparent. Similar to the results observed for the oxidation ratios, the difference between summer and winter are lower at Sites 9 and 13.

### 2.7.5 RELATIONSHIPS BETWEEN PRECIPITATION AND AIR CHEMISTRY

Attempts to derive scavenging ratios from contemporaneous precipitation and air chemistry samples generally produced unsatisfactory results. Multiple linear regressions of excess $SO_4^{-2}$ concentrations versus rainfall amount, particulate $SO_4^{-2}$, and $SO_2$ explained only 26 to 46 percent of the variability of excess $SO_4^{-2}$ in precipitation. Similar regressions for $NO_3^-$ concentrations versus rainfall amount, $HNO_3$, and $NO_2$ explained only 24 to 56 percent of the variability of $NO_3^-$ in precipitation.

Rather than imply weak relationships between air and precipitation chemistry, these results suggest that the sampling design used in this study does not lend itself to the investigation of precipitation scavenging ratios; this could be due, for example, to incompatible time periods for sample collection. Precipitation events (especially thunderstorms) typically have lifetimes ranging from minutes to a few hours, whereas air samples were collected over continuous 24-hour periods. Air quality at the time of precipitation thus may bear little resemblance to that reflected by the air sample. Similarly, although air quality measurements at 10 m are useful for dry-deposition calculations, they may not accurately reflect the quality of air entering precipitation systems (i.e., at cloud-base altitude of approximately 1,000 m).

## 2.8 RELATIONSHIPS OF PRECIPITATION AND AIR CHEMISTRY WITH OBSERVED METEOROLOGICAL CONDITIONS

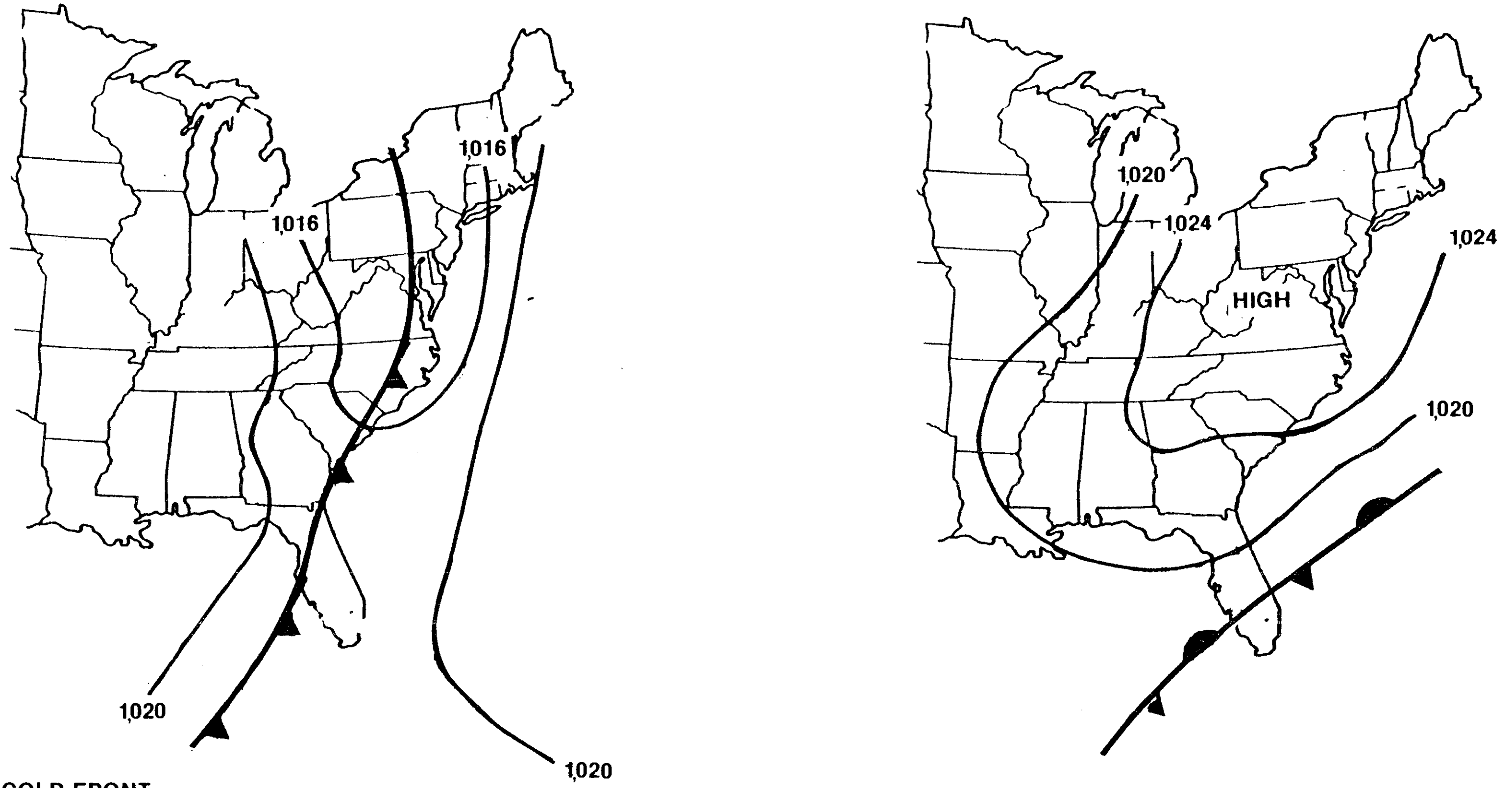
In Subsections 2.5 and 2.6, considerable spatial and temporal variability in observed precipitation chemistry for Florida was reported. Specifically, statistically significant spatial differences were observed in the precipitation chemistry and ambient air quality from north Florida to south Florida, and temporal differences were observed between seasons. Some insight in the cause for such observed spatial and temporal differences may be gained through an evaluation of precipitation chemistry and ambient air quality and coincident synoptic-scale (i.e., large-scale) meteorological conditions.

For the northeastern United States, differences in synoptic-scale meteorology have been associated with differences in precipitation chemistry and ambient air quality. Raynor and Hayes (1982) found that deposition of $H^+$, $SO_4^{-2}$, and $NO_3^-$ was greatest during warm-front events, but that concentrations of these species were highest during convective storms (thunderstorms). Results of the Sulfate Regional Experiment (SURE) showed that the highest ambient $SO_4^{-2}$ concentrations in the northeast and midwest United States were associated with maritime tropical air masses and the lowest were associated with continental polar and transition air masses (EPRI, 1983). The presence of a transient high pressure over the midwest to northeast United States was found by King and Vukovich (1982) to be highly correlated with elevated pollution levels and deteriorating horizontal visibility. The clockwise flow caused by continental high-pressure systems can transport pollutants from the eastern United States to the Gulf coast and southeast United States, whereas the flow around maritime high-pressure systems can transport pollutants to the midwest and northeast from the southeast United States (Wolff et al., 1981).

Although these same synoptic-scale meteorological features that occur over the northeast and midwest United States can influence Florida, the magnitude and extent of their influence is significantly different. For example, the synoptic-scale meteorology which can cause transport of air pollutants from source regions in the midwest to the northeast United States will cause different regimes of transport for Florida (e.g., continental high pressure). In order to evaluate the possible influence of synoptic-scale meteorology on observed precipitation chemistry and ambient air quality in Florida, empirical relationships between precipitation/air chemistry and synoptic-scale meteorological conditions across Florida were developed and are presented in this section.

Synoptic-scale meteorological classifications have been made to segregate observed precipitation chemistry and ambient air quality (Raynor and Hayes, 1982; EPRI, 1983). Such classification schemes have also been used in long-range transport (LRT) model assessments (EPRI, 1984). The classification schemes can generally be divided into three categories: air mass type [i.e., continental polar (warm and cold) and maritime tropical], pressure system type (i.e., polar high, Bermuda high, polar low, Gulf low), and frontal type (i.e., warm, cold, and stationary) (EPRI, 1984). A classification scheme consisting of six distinct conditions was selected for this analysis and is described below:

1. Cold Front--A cold front that has traversed all or part of the state (see Figure 2.8-1). This is most common from October through March and the source of about 18 percent of statewide precipitation. Precipitation in a cold front generally occurs preceding or along this system. Cold fronts are usually oriented northeast to southwest across the state with wind directions generally from southeast to southwest ahead of the front and west to north behind the front (see Figure 2.8-1).
2. Stationary Front--The remains of a cold front that has weakened and stalled across the state (usually northern or central portions of Florida, see Figure 2.8-1). This meteorological condition occurs occasionally, usually in the months of September, October, March, and April and is associated with



COLD FRONT
DECEMBER 16, 1982
(RAINFALL ALONG FRONT FROM 0.59 INCH
TO TRACE OVER FLORIDA)

STATIONARY FRONT
OCTOBER 16, 1983
(TRACE TO 1.62 INCHES OF RAINFALL
OVER PENINSULA FLORIDA)

NOTE: ISOBARS GIVEN IN MILLIBARS.

Figure 2.8-1
EXAMPLE OF COLD FRONT AND STATIONARY FRONT OVER FLORIDA

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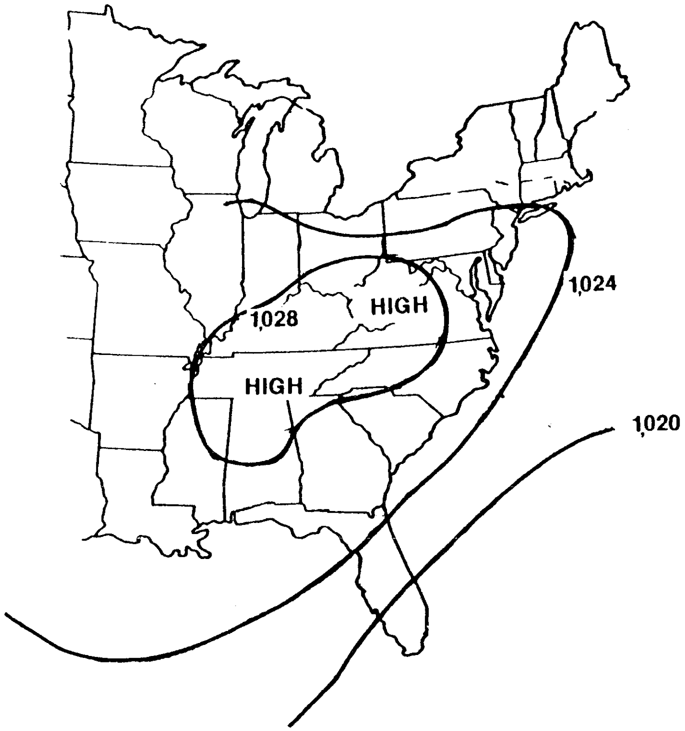
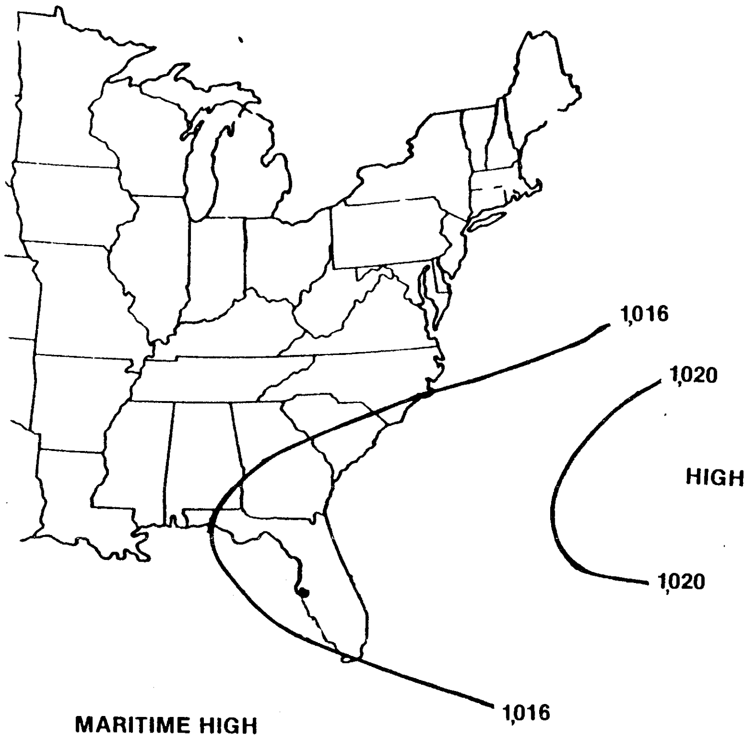
moderate precipitation across the panhandle and northern peninsula but little precipitation (i.e., <10 percent) elsewhere in the state. The orientation and winds associated with this system is similar to that of a cold front. This system contributes less than 10 percent of statewide precipitation.

3. Continental High--A high-pressure system typically centered over midsection of the eastern United States and traveling toward the east or southeast slowly in summer, rapidly in winter. Fronts are absent from the state. The anti-cyclonic (i.e., clockwise) flow produces wind from the north-northeast direction over much of the panhandle and northern peninsula and northeast to east over the southern peninsula. Precipitation is generally higher in southern peninsula of Florida than either the panhandle or northern peninsula of the state (see Figure 2.8-2). Statewide, precipitation from these systems amount to about 20 percent of the total.
4. Maritime High--High-pressure system over Atlantic Ocean that usually resulted from a continental high that traveled over eastern United States (i.e., Bermuda high in summer). Fronts are absent from the state. The anti-cyclonic flow produces wind from the southeast clockwise through southwest directions in Florida. Little or no precipitation in winter, significant convective precipitation (thunderstorms) in summer. Precipitation is higher in the panhandle and northern peninsula portions of Florida than the southern peninsula (see Figure 2.8-2). These systems contribute about 25 percent of Florida's statewide precipitation; the most of any other meteorological system.
5. Gulf Low--Low-pressure system spawned in Gulf of Mexico usually without a trailing cold front. This feature is generally more common in winter than summer; however, summer systems are usually tropical in nature (e.g., tropical storms and hurricanes). Winds over Florida are largely dependent on the



CONTINENTAL HIGH
NOVEMBER 6, 1982
(RAINFALL OVER SOUTHERN PENINSULA OF FLORIDA
FROM TRACE TO 0.65 INCH)



MARITIME HIGH
JUNE 29, 1983
(RAINFALL OVER NORTHERN AND SOUTHERN FLORIDA
FROM TRACE TO OVER 1 INCH)

NOTE: ISOBARS GIVEN IN MILLIBARS.

Figure 2.8-2
EXAMPLE OF CONTINENTAL HIGH AND MARITIME HIGH PRESSURE AREAS

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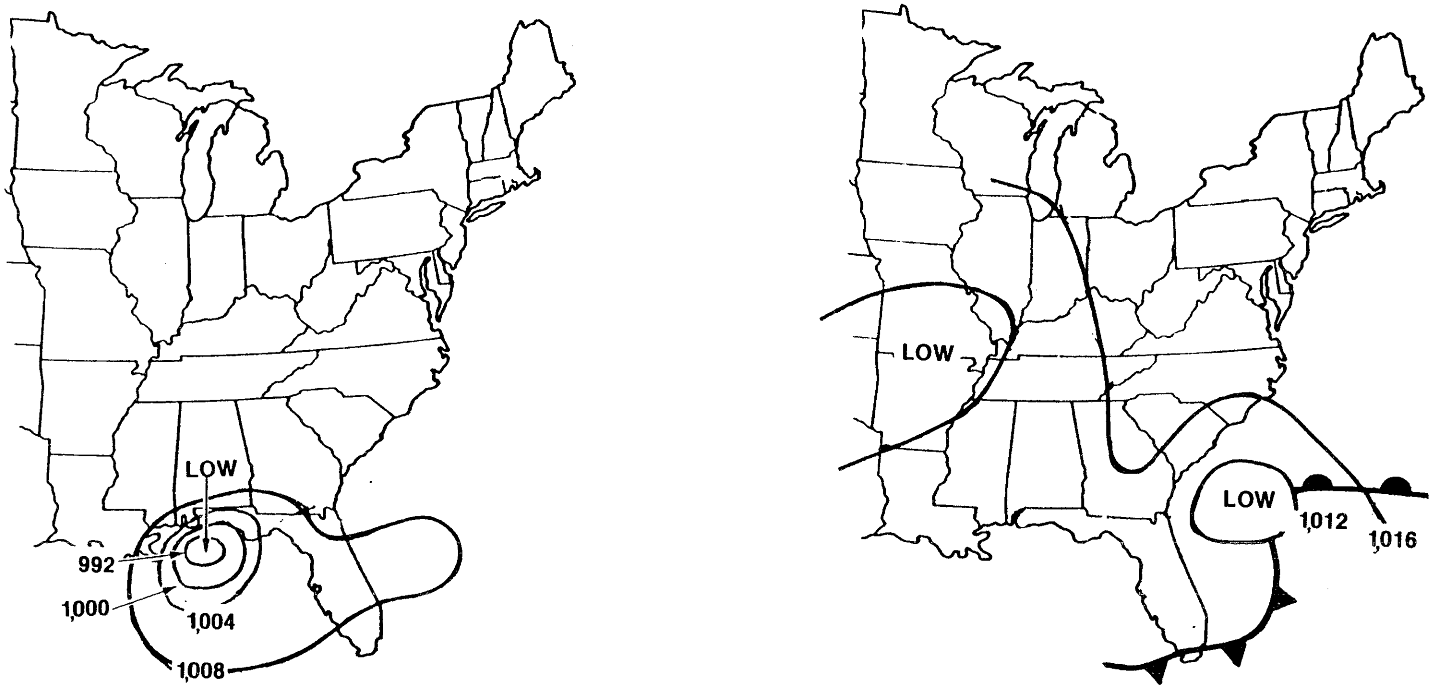
location of this system relative to land; south of this system winds are generally from the southwest to southeast while north of this system winds are generally from the northeast to northwest. Precipitation from this system is generally about 18 percent of statewide precipitation (see Figure 2.8-3).

6. Continental-Atlantic Low--Low-pressure system located over Atlantic Coast (usually over water) to northeast and east of Florida. This feature is occasionally a Gulf low that has traversed Florida, but is more often spawned off the east coast of the United States as a result of the passage of a frontal system. Winds are generally from the northwest to northeast over the peninsula of state. Precipitation associated with these systems is generally about 12 percent of statewide precipitation (see Figure 2.8-3).

The meteorological classifications selected for analysis were combined with daily precipitation chemistry data from Sites 2, 5, 9, and 13 over the period from October 1, 1982, through September 30, 1983. These sites were selected because they also were used as receptors for air mass trajectory analysis (see Subsection 3.3.3) and provide a broad geographic coverage of the state. In addition, the period of analysis (i.e., October 1, 1982, through September 30, 1983) also coincides with the period that trajectory analysis was performed. Therefore, results of the meteorological classification and trajectory analysis can be compared directly for these sites. The analysis of air chemistry versus meteorology was conducted with data from all monitoring sites for the period of December 1982 through September 1984.

Positions of high-pressure systems, low-pressure systems, and fronts within and around Florida were reviewed at 6-hour time intervals using microfilm weather data obtained from the National Weather Service (NWS). Results of the 6-hour analyses were then used to produce 24-hour meteorological classifications corresponding approximately to the time of



GULF LOW
FEBRUARY 28, 1983
(RAINFALL OVER ALL
FLORIDA FROM 2.2 INCHES TO TRACE)

CONTINENTAL-ATLANTIC LOW
JANUARY 22, 1983
(RAINFALL OVER ALL FLORIDA
FROM TRACE TO 0.42 INCH)

NOTE: ISOBARS GIVEN IN MILLIBARS.

Figure 2.8-3
EXAMPLE OF GULF LOW AND CONTINENTAL-ATLANTIC LOW PRESSURE AREAS

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precipitation and air sampling periods (i.e., 8 a.m. to 8 a.m. for precipitation; midnight to midnight for air). Finally, precipitation and air chemistry data were sorted by weather classifications, and mean concentrations and wet deposition were calculated for each classification.

## 2.8.1 PRECIPITATION CHEMISTRY

VWM concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ are listed by meteorological class in Table 2.8-1. Concentration results show that cold fronts and Gulf lows are similar and that these classifications invariably account for the lowest laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ values. A majority of sites exhibit lowest VWM concentrations for cold-front precipitation.

Meteorological classifications associated with high VWM concentrations, in contrast, vary from site to site. At Site 2, continental highs exhibit concentration of all species that are roughly a factor of 2 higher than concentrations of any other classification. VWM concentrations during continental highs also are relatively higher at Site 5, but among the lowest observed at Sites 9 and 13. This finding indicates that synoptic-scale meteorology can have a markedly variable influence on spatial patterns of statewide precipitation chemistry. In the case of continental highs, the distinction between north Florida precipitation and south Florida precipitation may be due to variable residence times over land and water. This effect is evaluated further in the trajectory analysis section (Subsection 3.3.3).

Precipitation chemistry at Site 5 shows the highest VWM concentrations for all meteorological classifications and also the greatest variability in concentrations across meteorological classifications. Site 13, in contrast, typically exhibits lowest VWM concentrations (except during maritime highs) and the lowest class-to-class variability. This finding is in general agreement with results of the temporal variability analyses (Subsection 2.6), which showed minimal differences in south Florida precipitation chemistry from season to season and year to year.

Over all sites and meteorological classes, continental-Atlantic lows exhibit the greatest VWM concentrations at Site 5. Laboratory $H^+$ and excess $SO_4^{-2}$ concentrations for these events are roughly 150 percent of

Table 2.8-1. VWM Concentrations* for Laboratory $H^+$, Excess $SO_4^{-2}$, and $NO_3^-$ and Mean Rainfall by Meteorological Class for the Period September 1982 Through September 1983.

| | | Meteorological Class | | | | | |
|---|---|---|---|---|---|---|---|
| Site | Analyte | Stationary Front | Cold Front | Continental High | Maritime High | Continental-Atlantic Low | Gulf Low |
| 2 | Laboratory $H^+$ | 15.3 | 8.7 | 33.6 | 16.1 | NSP | 13.6 |
| | Excess $SO_4^{-2}$ | 16.7 | 9.8 | 33.2 | 15.7 | NSP | 14.0 |
| | $NO_3^-$ | 9.2 | 4.6 | 13.9 | 8.2 | NSP | 7.5 |
| | Rainfall (cm/event) | 2.64 | 1.61 | 1.70 | 2.11 | NSP | 1.49 |
| | Number of events | 7 | 10 | 16 | 34 | 1 | 15 |
| 5 | Laboratory $H^+$ | 37.5 | 18.4 | 35.1 | 36.8 | 50.9 | 21.2 |
| | Excess $SO_4^{-2}$ | 30.3 | 17.6 | 29.4 | 29.4 | 45.5 | 19.1 |
| | $NO_3^-$ | 16.6 | 8.4 | 16.2 | 15.5 | 19.3 | 8.6 |
| | Rainfall (cm/event) | 1.18 | 2.55 | 0.96 | 1.51 | 2.82 | 1.58 |
| | Number of events | 5 | 15 | 10 | 27 | 9 | 14 |
| 9 | Laboratory $H^+$ | 34.7 | 11.8 | 9.7 | 15.4 | 16.9 | 13.6 |
| | Excess $SO_4^{-2}$ | 33.2 | 14.9 | 11.1 | 14.7 | 21.6 | 15.3 |
| | $NO_3^-$ | 7.3 | 7.1 | 3.3 | 4.0 | 10.2 | 8.5 |
| | Rainfall (cm/event) | 0.71 | 1.96 | 1.83 | 0.89 | 1.53 | 1.48 |
| | Number of events | 14 | 15 | 16 | 20 | 12 | 16 |
| 13 | Laboratory $H^+$ | 15.4 | 6.4 | 9.3 | 17.1 | 9.3 | 4.8 |
| | Excess $SO_4^{-2}$ | 11.8 | 10.3 | 11.2 | 23.9 | 9.9 | 10.8 |
| | $NO_3^-$ | 11.9 | 6.3 | 7.0 | 17.1 | 6.1 | 5.4 |
| | Rainfall (cm/event) | 0.78 | 0.96 | 1.86 | 0.78 | 2.09 | 3.28 |
| | Number of events | 3 | 16 | 23 | 21 | 10 | 9 |

* All concentrations are µN.

cm/event = Centimeters per event.

NSP = No significant precipitation (i.e., <1 percent of total)

Source: ESE, 1986.

those in the next highest classes and roughly 250 percent of those in the lowest classes (i.e., cold front, Gulf low). On the other hand, differences in $NO_3^-$ concentrations between classes are not as great. Continental-Atlantic lows thus exhibit the highest concentrations of laboratory $H^+$, excess $SO_4^{-2}$ and $NO_3^-$ as well as the highest excess $SO_4^{-2}:NO_3^-$ ratio (i.e., 2.36).

The contrast between continental-Atlantic lows and Gulf lows at Site 5 is noteworthy because these classifications also suggest differences in potential source regions. Given the counterclockwise circulation around low-pressure systems, the likely direction of transport around Gulf lows (with respect to Site 5) is from the south, whereas the likely direction of transport around continental-Atlantic lows is from the north.

The percentage of total deposition by site and meteorological classification for laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ is presented in Table 2.8-2. These results generally show that the effects of each meteorological class vary from site to site. At Site 2, maritime highs contributed nearly half of the annual precipitation and slightly over 40 percent of the laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ deposition. Continental highs, in contrast, contributed 17 percent of rainfall but approximately 30 percent of deposition. Strikingly, continental-Atlantic lows were an insignificant source of rainfall and deposition, indicating that the spatial variability of rainfall itself may strongly influence spatial deposition trends.

At Site 5, continental-Atlantic lows and maritime highs each accounted for roughly 30 percent of annual deposition. Maritime-high rainfall also was approximately 30 percent, but continental-Atlantic-low rainfall was only 18 percent. This finding underscores the episodic nature of atmospheric depositions and shows that a small number of events ($n = 10$ for continental-Atlantic lows at Site 5) can have a considerable influence on precipitation chemistry. This effect is also seen for maritime-high precipitation at Site 13.

Table 2.8-2. Percent of Total Deposition of Laboratory $H^+$, Excess $SO_4^{-2}$, and $NO_3^-$; Total Rainfall; and Number of Events by Meteorological Class for the Period September 1982 Through September 1983

| | | Meteorological Class | | | | | | Total Deposition Rainfall Amount and Events* |
|---|---|---|---|---|---|---|---|---|
| Site | Analyte | Stationary Front | Cold Front | Continental High | Maritime High | Continental-Atlantic Low | Gulf Low | |
| 2 | Laboratory $H^+$ | 10 | 5 | 31 | 42 | NSP | 11 | 301 |
| | Excess $SO_4^{-2}$ | 11 | 6 | 30 | 42 | NSP | 11 | 303 |
| | $NO_3^-$ | 13 | 5 | 26 | 43 | NSP | 12 | 147 |
| | Rainfall | 12 | 10 | 17 | 47 | NSP | 14 | 178 |
| | Number of Events | 7 | 10 | 16 | 34 | 1 | 15 | 83 |
| 5 | Laboratory $H^+$ | 5 | 16 | 7 | 33 | 29 | 10 | 327 |
| | Excess $SO_4^{-2}$ | 5 | 17 | 7 | 31 | 30 | 11 | 276 |
| | $NO_3^-$ | 6 | 18 | 9 | 36 | 28 | 11 | 139 |
| | Rainfall | 4 | 27 | 7 | 29 | 18 | 16 | 131 |
| | Number of Events | 5 | 15 | 10 | 27 | 9 | 14 | 80 |
| 9 | Laboratory $H^+$ | 18 | 18 | 15 | 15 | 16 | 18 | 172 |
| | Excess $SO_4^{-2}$ | 15 | 20 | 15 | 13 | 18 | 18 | 186 |
| | $NO_3^-$ | 8 | 25 | 11 | 9 | 22 | 25 | 104 |
| | Rainfall | 8 | 23 | 23 | 14 | 14 | 19 | 119 |
| | Number of Events | 14 | 15 | 16 | 20 | 12 | 16 | 93 |
| 13 | Laboratory $H^+$ | 4 | 8 | 34 | 24 | 17 | 12 | 146 |
| | Excess $SO_4^{-2}$ | 2 | 10 | 26 | 26 | 14 | 21 | 177 |
| | $NO_3^-$ | 4 | 10 | 30 | 28 | 13 | 16 | 114 |
| | Rainfall | 2 | 12 | 33 | 13 | 16 | 23 | 134 |
| | Number of Events | 3 | 16 | 23 | 21 | 10 | 9 | 82 |

*Total deposition in kg/ha-yr; rainfall amount in cm.

NOTE: NSP = No significant precipitation (i.e., <1 percent of annual total).

Source: ESE, 1986.

The opposite effect generally occurs in the case of cold-front and Gulf-low precipitation. Over the four monitoring sites, cold fronts accounted for an average of 18 percent of annual precipitation, but only 12 percent of laboratory $H^+$ deposition.

Table 2.8-3 presents deposition per event of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ for each site and meteorological classification. These results are similar to that observed for total deposition which indicated variable influences of meteorological classes at each site. For Site 2, stationary fronts and continental highs contributed the highest event deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$. In contrast, continental-Atlantic lows and maritime contributed the highest per event deposition at Site 5. Except for a few instances, per event deposition at Sites 9 and 13 were similar over four to five meteorological classes.

## 2.8.2 AIR CHEMISTRY VERSUS METEOROLOGY

Geometric mean concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ are shown by meteorological class in Tables 2.8-4 and 2.8-5. Results for $SO_4^{-2}$ indicate relatively strong variability of concentrations with meteorological class in north Florida (i.e., Sites 2 through 5), but reduced variability in south Florida. Similar to precipitation chemistry, air chemistry variability is lowest at Site 13. Synoptic-scale meteorology, therefore, appears to have little influence on particulate $SO_4^{-2}$ concentrations in extreme south Florida.

The variability of particulate $SO_4^{-2}$ and $HNO_3$ concentrations across site classes generally follows the pattern exhibited in the analysis of precipitation chemistry. At Site 2, concentrations are highest for continental-Atlantic lows, stationary fronts, and continental highs and lowest for Gulf lows and cold fronts. The relatively high values for continental-Atlantic lows are of interest, since they suggest that, if it had rained at Site 2 during the continental-Atlantic lows, the resulting concentrations of $SO_4^{-2}$ and $NO_3^-$ might have been relatively high. Due to

Table 2.8-3. Laboratory $H^+$, Excess $SO_4^{-2}$, and $NO_3^-$ Deposition per Event* for Sites 2, 5, 9, and 13 by Meteorological Class (October 1, 1982, Through September 30, 1983)

| | | Meteorological Class | | | | | |
|---|---|---|---|---|---|---|---|
| Site | Analyte | Stationary Front | Cold Front | Continental High | Maritime High | Continental-Atlantic Low | Gulf Low |
| 2 | Laboratory $H^+$ | 4.3 | 1.5 | 5.8 | 3.7 | NSP | 2.2 |
| | Excess $SO_4^{-2}$ | 4.8 | 1.8 | 5.7 | 3.7 | NSP | 2.2 |
| | $NO_3^-$ | 2.7 | 0.7 | 2.4 | 1.9 | NSP | 1.2 |
| 5 | Laboratory $H^+$ | 3.3 | 3.5 | 2.3 | 5.0 | 10.5 | 2.3 |
| | Excess $SO_4^{-2}$ | 2.8 | 3.1 | 1.9 | 3.2 | 9.2 | 2.2 |
| | $NO_3^-$ | 1.7 | 1.7 | 1.3 | 1.9 | 4.3 | 1.1 |
| 9 | Laboratory $H^+$ | 2.2 | 2.1 | 1.6 | 1.3 | 2.3 | 1.9 |
| | Excess $SO_4^{-2}$ | 2.0 | 2.5 | 1.7 | 1.2 | 2.8 | 2.1 |
| | $NO_3^-$ | 0.6 | 1.7 | 0.7 | 0.5 | 1.9 | 1.6 |
| 13 | Laboratory $H^+$ | 1.9 | 0.7 | 2.2 | 1.7 | 2.5 | 1.9 |
| | Excess $SO_4^{-2}$ | 1.2 | 1.1 | 2.0 | 2.2 | 2.8 | 4.1 |
| | $NO_3^-$ | 1.5 | 0.7 | 1.5 | 1.5 | 1.8 | 2.0 |

*Deposition in equivalents per hour per event (eq/hr/event).

Note: NSP = No significant precipitation.

Source: ESE, 1986.

Table 2.8-4. Geometric Mean Particulate $SO_4^{-2}$ and $HNO_3$ Concentrations* by Meteorological Class

| | | Meteorological Class | | | | | |
|---|---|---|---|---|---|---|---|
| Site | Analyte | Stationary Front (n = 9) | Cold Front (n = 33) | Continental High (n = 84) | Maritime High (n = 60) | Continental-Atlantic Low (n = 37) | Gulf Low (n = 11) |
| 2 | $SO_4^{-2}$ | 5.3 | 3.7 | 4.6 | 3.9 | 5.9 | 3.2 |
| | $HNO_3$ | 1.1 | 0.7 | 0.9 | 0.9 | 1.3 | 0.7 |
| 3 | $SO_4^{-2}$ | 6.0 | 3.5 | 4.5 | 3.6 | 5.5 | 3.6 |
| | $HNO_3$ | 1.2 | 0.7 | 0.9 | 0.9 | 1.1 | 0.7 |
| 4 | $SO_4^{-2}$ | 4.0 | 3.8 | 4.3 | 3.4 | 5.6 | 3.8 |
| | $HNO_3$ | 0.5 | 0.6 | 0.7 | 0.6 | 1.1 | 0.7 |
| 5 | $SO_4^{-2}$ | 5.7 | 4.1 | 4.0 | 3.8 | 5.5 | 3.0 |
| | $HNO_3$ | 1.4 | 0.9 | 1.0 | 1.0 | 1.2 | 1.0 |
| 8 | $SO_4^{-2}$ | 3.3 | 3.6 | 4.0 | 3.5 | 4.8 | 3.5 |
| | $HNO_3$ | 0.7 | 0.7 | 0.8 | 0.8 | 1.0 | 0.8 |
| 9 | $SO_4^{-2}$ | 2.9 | 2.7 | 3.4 | 2.9 | 4.3 | 2.4 |
| | $HNO_3$ | 0.6 | 0.6 | 0.7 | 0.7 | 0.8 | 0.6 |
| 13 | $SO_4^{-2}$ | 2.4 | 2.4 | 3.0 | 2.7 | 3.4 | 2.2 |
| | $HNO_3$ | 0.7 | 0.5 | 0.5 | 0.5 | 0.6 | 0.4 |

* All concentrations in $\mu g/m^3$.

Source: ESE, 1986.

Table 2.8-5. Geometric Mean $SO_2$ and $NO_2$ Concentrations* by Meteorological Class

| Site | Analyte | Meteorological Class: Stationary Front (n = 9) | Cold Front (n = 33) | Continental High (n = 84) | Maritime High (n = 60) | Continental-Atlantic Low (n = 37) | Gulf Low (n = 11) |
|---|---|---|---|---|---|---|---|
| 2 | $SO_2$ | 1.8 | 2.0 | 2.2 | 1.2 | 2.9 | 1.9 |
| | $NO_2$ | 5.9 | 6.5 | 8.0 | 6.1 | 7.9 | 5.6 |
| 3 | $SO_2$ | 1.1 | 1.7 | 2.2 | 1.4 | 2.8 | 1.4 |
| | $NO_2$ | 3.2 | 3.4 | 3.9 | 2.7 | 4.0 | 4.3 |
| 4 | $SO_2$ | 0.7 | 2.2 | 2.2 | 1.1 | 2.8 | 1.4 |
| | $NO_2$ | 2.0 | 6.1 | 7.1 | 5.6 | 7.2 | 5.3 |
| 5 | $SO_2$ | 2.9 | 2.1 | 2.5 | 1.4 | 2.7 | 1.9 |
| | $NO_2$ | 9.3 | 6.4 | 11.8 | 8.1 | 7.7 | 10.8 |
| 8 | $SO_2$ | 1.5 | 3.4 | 2.8 | 3.0 | 2.9 | 4.5 |
| | $NO_2$ | 5.9 | 9.6 | 10.9 | 6.0 | 10.0 | 10.2 |
| 9 | $SO_2$ | 1.2 | 2.0 | 2.3 | 1.2 | 2.4 | 1.7 |
| | $NO_2$ | 2.9 | 4.2 | 5.3 | 3.7 | 3.9 | 4.2 |
| 13 | $SO_2$ | 1.3 | 1.1 | 1.3 | 1.0 | 0.9 | 1.1 |
| | $NO_2$ | 2.6 | 2.0 | 2.6 | 2.5 | 1.4 | 2.4 |

* All concentrations in $\mu g/m^3$.

Source: ESE, 1986.

the limited nature of the database (i.e., 1 year), it cannot be determined whether the lack of continental-Atlantic-low precipitation was unusual. However, by definition, this synoptic situation would not be expected to give rise to widespread precipitation in the panhandle.

Also noteworthy is the overall ranking of particulate $SO_4^{-2}$ and $HNO_3$ concentrations during maritime highs. Contrary to results for the precipitation chemistry, particulate $SO_4^{-2}$ and $HNO_3$ rank among the lowest during maritime highs. This result suggests that maritime-high precipitation may be unusually efficient in removing atmospheric pollutants.

Geometric mean concentrations of $SO_2$ (Table 2.8-5) are relatively low (i.e., 1 to 3 $\mu g/m^3$) statewide for all meteorological classes, but generally follow patterns described for particulate $SO_4^{-2}$ and $HNO_3$. Concentrations are highest during meteorological conditions conducive to transport from the north (e.g., continental high) and lowest during those conducive to transport from the south (e.g., maritime high). The major exception to this behavior is at Site 8, where Gulf lows, maritime highs, and cold fronts produce the highest values. This is generally consistent with results of the spatial variability analyses (Subsection 2.5), which showed $SO_2$ concentrations to be locally influenced at Site 8.

$NO_2$ concentrations (Table 2.8-5) also showed considerable variability from class to class; however, the statewide pattern differs from that of particulate $SO_4^{-2}$, $HNO_3$, and $SO_2$. $NO_2$ concentrations for each meteorological class are highest at Sites 5 or 8 and are lower at Sites 13 and 3. As noted in Subsection 2.5, this observation shows that $NO_2$ concentration patterns are subject to considerable local influence.

## 2.9 SUMMARY OF ACID DEPOSITION IN FLORIDA

Precipitation and ambient air chemistry data measured over a 3-1/2-year period (i.e., July 1, 1981, through December 31, 1984) are analyzed and presented in this report in order to address key research questions relating to acidic deposition in Florida. The key research questions related to acid deposition monitoring (refer to Table 1.2-1) were the basis for the data presentations and analyses contained in Subsections 2.3 through 2.8 and are specifically addressed in the subsections that follow.

### 2.9.1 DATA QUALITY

A prime objective of the acid deposition monitoring program focused on determining the overall quality and uncertainty in the database. Specifically, a goal of this report was to address the question:

- How do field collection and analytical methods influence the observed wet-only acid deposition levels and related chemical species in Florida?

Seven corollaries are inherent in this question and were addressed in the analyses presented in Subsection 2.4. The answers to these seven related questions are summarized below.

- What is the overall quality of field measurements? (Refer to Subsection 2.4.1.)

Field measurement data quality was assessed through LIS solution measurements and bimonthly audit sample analyses. Over a 3-year period, mean pH measurements of unknown samples were within approximately ±5 percent (expressed as $H^+$), with over 80 percent of the individual LIS observations were within ±15 percent or ±0.065 pH unit. For the less acidic (higher pH) LIS solutions, individual measurements were less accurate, with approximately 70 percent of the individual observations within ±15 percent. Overall, however, about 93 percent of all LIS observations and over 95 percent of audit samples were within ±0.1 pH unit. These data suggest that the measurement of field pH in precipitation samples was at least within ±0.1 pH unit for individual precipitation samples, and VWM field pH was within ±5 percent of the actual VWM value.

- What is the accuracy of laboratory data? (Refer to Subsection 2.4.2.)

Results from unknown and EPA reference samples and spiked precipitation samples indicate a mean accuracy of ±5 percent for all measurements. Laboratory analyses of $SO_4^{-2}$ and $NO_3^-$ in precipitation were within ±3 and ±2 percent, respectively. Accuracy of $SO_4^{-2}$, $SO_2$, $NO_3^-$, and $NO_2$ in ambient air as determined through EPA and unknown reference samples was, on the average, within ±5 percent of the actual value. Individual measurements for these parameters were found to be within ±15 percent of actual value over 98 percent of the time. These data suggest that VWM laboratory concentrations of the major analytes measured in precipitation samples (i.e., $H^+$, $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$, $NH_4^+$, $NO_3^-$, $SO_4^{-2}$, and $Cl^-$) and mean ambient air concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ are within ±5 percent of the true value in the sample.

- What is the precision of laboratory data? (Refer to Subsection 2.4.2.)

Analyte precision, determined through replicate analysis of precipitation and ambient air samples, was uniformly less than 10 percent. Laboratory precision of $SO_4^{-2}$, $Cl^-$, and $NO_3^-$ in precipitation samples was better than ±5 percent, whereas precision of ambient air samples was within ±2 percent.

- What are the effects of contamination from buckets, filters, and overall sample handling? (Refer to Subsection 2.4.3.)

Potential sample contamination, determined through analysis of dynamic and filter blanks, was 2 percent or less of wet deposition at any site for $Ca^{+2}$, $Na^{+}$, $NH_4^{+}$, and $Cl^{-}$ and less than 1.0 percent of wet deposition for $SO_4^{-2}$, $NO_3^{-}$, and $H^{+}$. Only the minor ions $Mg^{+2}$ and $K^{+}$ had contamination potentials greater than 5 percent of wet deposition.

Sample contamination as suggested by these results thus appears to have minimal influence on the reported trends and patterns of chemistry.

- What is the variability in, and differences between, the following (refer to Subsection 2.4.4):
  1. Precipitation amounts collected in collocated rain gages and wet-fall buckets,
  2. Precipitation amounts collected in collocated rain gages versus wet-fall buckets,
  3. W/W collocated monitoring,
  4. D/W collocated monitoring, and
  5. D/D collocated monitoring.

Collocated sampling was performed at up to four sites during the course of monitoring and provided data from which variability and differences between different monitoring frequencies (i.e., weekly and daily) could be determined. Differences between collocated sampling were observed and generally varied by the type of collocated sampling (i.e., W/W, D/D, and D/W) and the specific analyte measured.

Over a 3-year period, the mean recovery in rainfall amount collected by all wet-fall buckets compared to all Belfort rain gages was 101.5 ±1.8 percent. The precision of the Belfort rain gages, as measured by collocated rain gages, was 1.14 ±0.86 percent. Precision between collocated wet-fall bucket measurements of rainfall amount was 1.9 percent for W/W measurements, 2.1 percent for D/D measurements, and 1.4 percent for D/W measurements.

In general, collocated differences between analyte concentrations increased from W/W to D/D to D/W with differences between D/W collocated samples about a factor of 1.5 to 2 greater than W/W differences. The magnitude of such differences was analyte-specific. For example, mean absolute differences in $NO_3^-$ and $SO_4^{-2}$ concentrations were within 15 percent for all collocated sampling, whereas mean absolute differences for $NH_4^+$ ranged from 25 percent for W/W sampling to 39 percent for D/W sampling. However, the differences between collocated measurements for the same type of collocated monitoring was often quite different for individual sites and analytes, suggesting that influences may be caused by the individual site characteristics. Such observed differences in collocated measurements, i.e., overall precision, were only partially accounted for by laboratory precision. Direct comparisons between mean percent differences in laboratory measurements and collocated measurements indicate that laboratory measurements could only contribute from about 10 to 25 percent, depending on the analyte, of the differences observed between collocated monitors.

Statistical analyses suggest that analyte concentrations from collocated measurements were not significantly different for most parameters, especially those of prime importance: laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, and excess $Ca^{+2}$. For example, the CV for $SO_4^{-2}$ ranged from 7.7 to 25 percent for collocated measurements, whereas the CV in the observed data from collocated sites was 88 percent.

Taken together these results suggest that there are differences, in observed concentrations, depending on the sampling frequency as well as the individual locations. The variability caused by these combined influences, compared with the overall measurement, is small, suggesting that the observed differences in precipitation chemistry between individual samples and sites is not a result of collection or analytical methods.

- What are the differences between field and laboratory pH? (Refer to Subsection 2.4.5.)

Field pH was significantly lower than laboratory pH in all cases. Differences between field and laboratory averaged 24.0 percent for all sites operated over the 3-year period, with a range of 11.9 percent at Site 5 to 37.3 percent at Site 9. Several chemical explanations for differences between field and laboratory pH have been hypothesized, including slow dissolution of basic particulate material, decomposition of organic acids, ammonia ($NH_3$) absorption, $SO_2$ outgassing, and loss of $H^+$ to bucket walls. Although organic acids were found in Florida precipitation (see Subsection 2.3.1.6), the amount of organic acids could, at most, only explain about 25 to 33 percent of the difference in field and laboratory pH. The potential influences of the other mechanisms are unknown.

- What is the overall uncertainty in the data? (Refer to Subsection 2.4.4.)

The overall uncertainty in data is a result of three major effects: errors in laboratory measurement, sample contamination from sample media, and the influence of sample collection and handling. Each of these can be categorized as having an effect on observed precipitation chemistry in the following order: sample contamination < laboratory error << sample collection and handling.

The results clearly demonstrated that sample contamination and laboratory error combined were generally less than 10 percent of total deposition. The influence of sample collection and handling (as measured by collocation) appears to contribute much more variability than laboratory operations. Yet, when compared to the overall variability in precipitation measurements, this effect is small suggesting that the monitoring data collected are reasonably representative of actual concentration and deposition fields in Florida precipitation.

### 2.9.2 SPATIAL PATTERNS OF DEPOSITION AND CONCENTRATION

Concentration and deposition patterns of wet-only precipitation chemistry data were analyzed over a 3-year period and are presented in Subsection 2.5 in order to address the key research question:

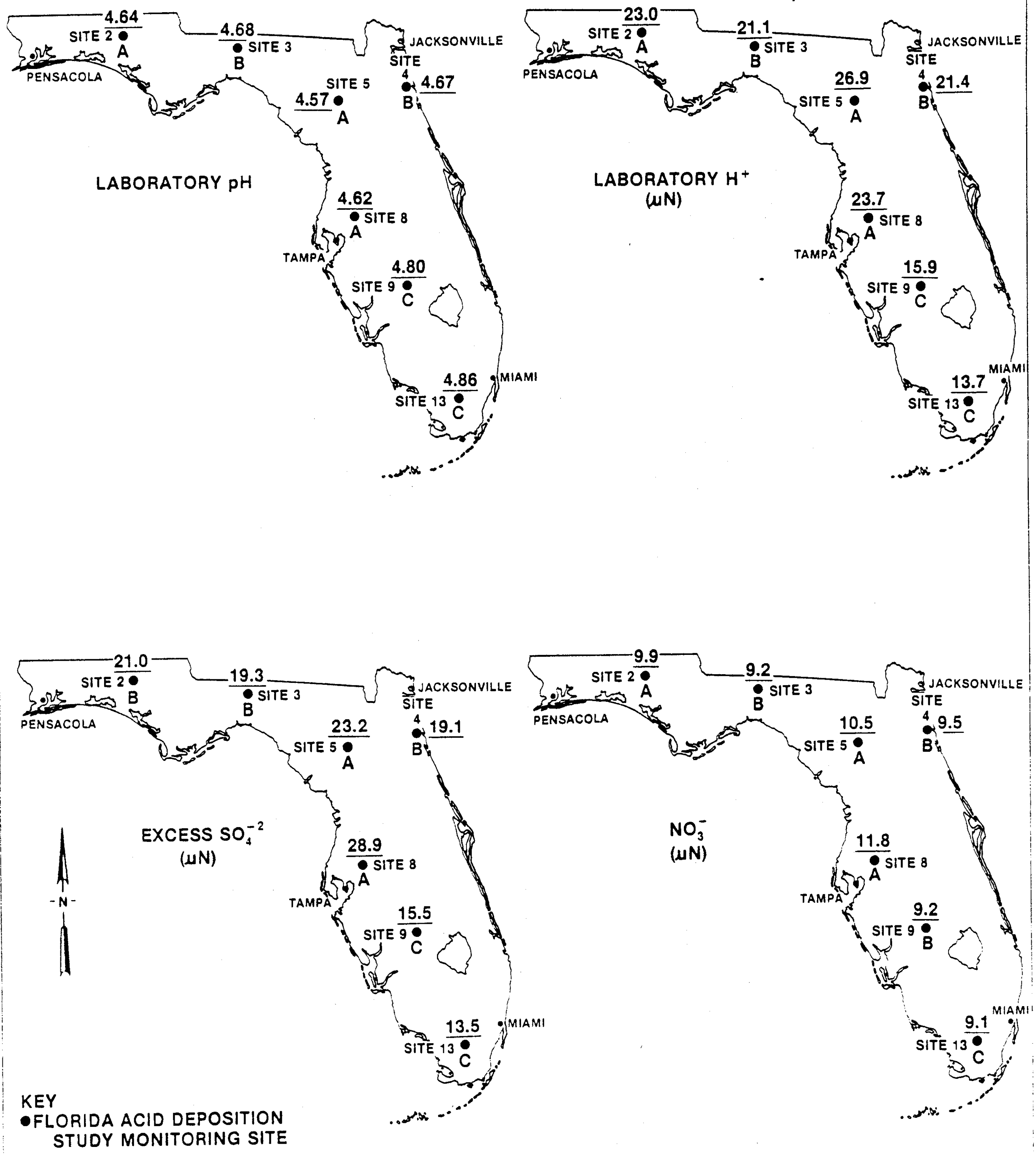
- What are the current spatial patterns of wet-only acidic deposition and major chemical species in Florida?

Associated with this question are three related questions:

- What are the statistically significant patterns in concentration fields? (Refer to Subsection 2.5.1.)
- What are the statistically significant patterns in deposition fields? (Refer to Subsection 2.5.2.)
- What are the spatial patterns in air chemistry? (Refer to Subsection 2.5.3.)

Over the 3-year period, distinct spatial patterns in concentrations emerged but were different depending on the analyte evaluated. In general, a north-south gradient in concentrations of the major acidic species (i.e., laboratory $H^+$, $SO_4^{-2}$, and $NO_3^-$) was observed in concentration fields of wet-only precipitation (Figure 2.9-1). However, this pattern was not uniform across the state since concentrations of $H^+$ and excess $SO_4^{-2}$ were highest at the north-central Florida sites (5 and 8). These sites were statistically distinct from other sites and highest in concentrations of excess $SO_4^{-2}$; when combined with Site 2, they were statistically distinct and highest in concentrations of laboratory $H^+$ and $NO_3^-$.

For laboratory $H^+$ and excess $SO_4^{-2}$, sites located in the panhandle (Sites 2 and 3) and northern peninsula (Sites 4, 5, and 8) of Florida were approximately 55 percent higher in concentration than southern peninsula sites (Sites 9 and 13). This statistical grouping strongly



NOTE: A, B, AND C DENOTES SIGNIFICANTLY DIFFERENT SITE-GROUPS.

Figure 2.9-1
3-YEAR VWM CONCENTRATIONS AND STATISTICALLY SIGNIFICANT SITE-GROUPS FOR pH, $H^+$, $SO_4^{-2}$, AND $NO_3^-$

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supports a general north-south decrease in acidity observed in previous study reports and by other researchers (ESE, 1983b, 1984, and 1985; Brezonik et al., 1980).

Unlike observed concentrations and patterns of $H^+$ and excess $SO_4^{-2}$, the $NO_3^-$ concentration at the highest statistically different sites (Sites 5 and 8) were only about 20 percent higher than the observed $NO_3^-$ concentrations at all other sites. This finding suggests that $NO_3^-$ plays only a minor role in the spatial variability of laboratory $H^+$ across Florida.

The pattern in laboratory $H^+$ concentrations is sufficiently distinct to suggest that local influences exert some effect on observed laboratory $H^+$ concentrations. Such influences may be attributed in part to excess $Ca^{+2}$ and $NH_4^+$ concentrations in rainfall. Concentrations of excess $Ca^{+2}$ at Sites 8, 9, and 13 were 59 percent higher and statistically different from all other sites. This pattern is in general agreement with the $Ca^{+2}$ content of Florida soils. Concentrations of $NH_4^+$ at Site 8 were approximately 67 percent higher than at Sites 2, 3, 5, and 9 and 106 percent higher than at Sites 4 and 13.

Deposition patterns of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ generally followed concentration patterns. Since rainfall was found to be significantly different and higher at Sites 2, 3, 4, and 5 than Sites 8, 9, and 13, the amount of rainfall generally had a similar and complementary pattern to the observed concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$. The highest depositions observed for Sites 2, 5, and 8 formed a homogeneous group that was statistically different and higher in deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ than all other sites. Total deposition of these presumably acidic species, when combined, suggests a strong north-south gradient.

As shown in Figure 2.9-2, a northern transect across Florida's panhandle and northern peninsula indicates relatively uniform wet deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ across all sites. Conversely, a north-south transect through Florida's peninsula (see Figure 2.9-3) indicates a large reduction in laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ deposition between Sites 5 and 14.

Deposition patterns of excess $Ca^{+2}$ and $NH_4^+$ were similar to the concentration patterns observed. The highest statistically different deposition of excess $Ca^+$ was found to be at Sites 8, 9, and 13; the highest $NH_4^+$ deposition was at Site 8. The effect of rainfall amount would tend to depress the differences in deposition for these analytes.

Ambient air concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ over a 2-year period suggest statistically distinct spatial patterns. Concentrations of particulate $SO_4^{-2}$ and $HNO_3$ decrease by approximately 40 percent and 30 percent, respectively, across the state (Figure 2.9-4), suggesting a north-south gradient in these potential precursors of excess $SO_4^{-2}$ and $NO_3^-$ in precipitation. Ambient $SO_2$ and $NO_2$ concentrations also suggest a north-south gradient but superimposed with local influences (i.e., sources). This observation is generally supported by intersite correlations which indicated that concentrations of $SO_2$ and $NO_2$ at selected sites were less dependent on observed concentrations at adjacent sites than particulate $SO_4^{-2}$ and $HNO_3$ concentrations. The latter appear to vary more uniformly across the state. In addition, the results of interparameter correlations indicate stronger relationships between particulate $SO_4^{-2}$ and $HNO_3$ than their nonoxidized forms. However, ambient air concentrations in the southern peninsula of Florida appear to have greater independence between all parameters measured.

When coupled with the information concerning concentrations and depositions of laboratory $H^+$, $SO_4^{-2}$, and $NO_3^-$ observed over the eastern United States, the data obtained from this study's network suggest that

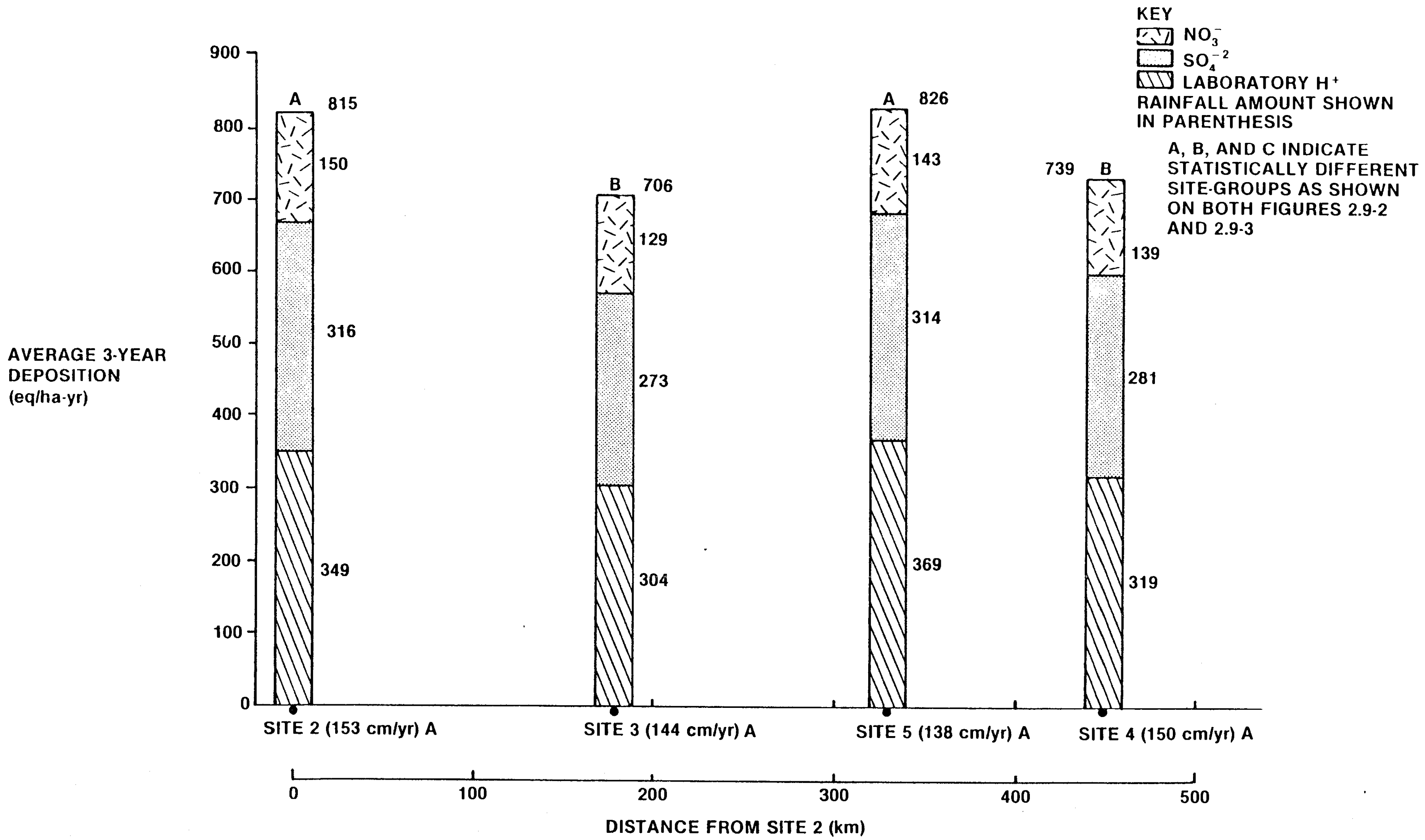

Figure 2.9-2
3-YEAR AVERAGE DEPOSITION OF LABORATORY $H^+$, EXCESS $SO_4^{-2}$, AND $NO_3^-$ FOR SITES 2, 3, 4, AND 5 (NORTHERN TRANSECT) AS A FUNCTION OF DISTANCE FROM SITE 2

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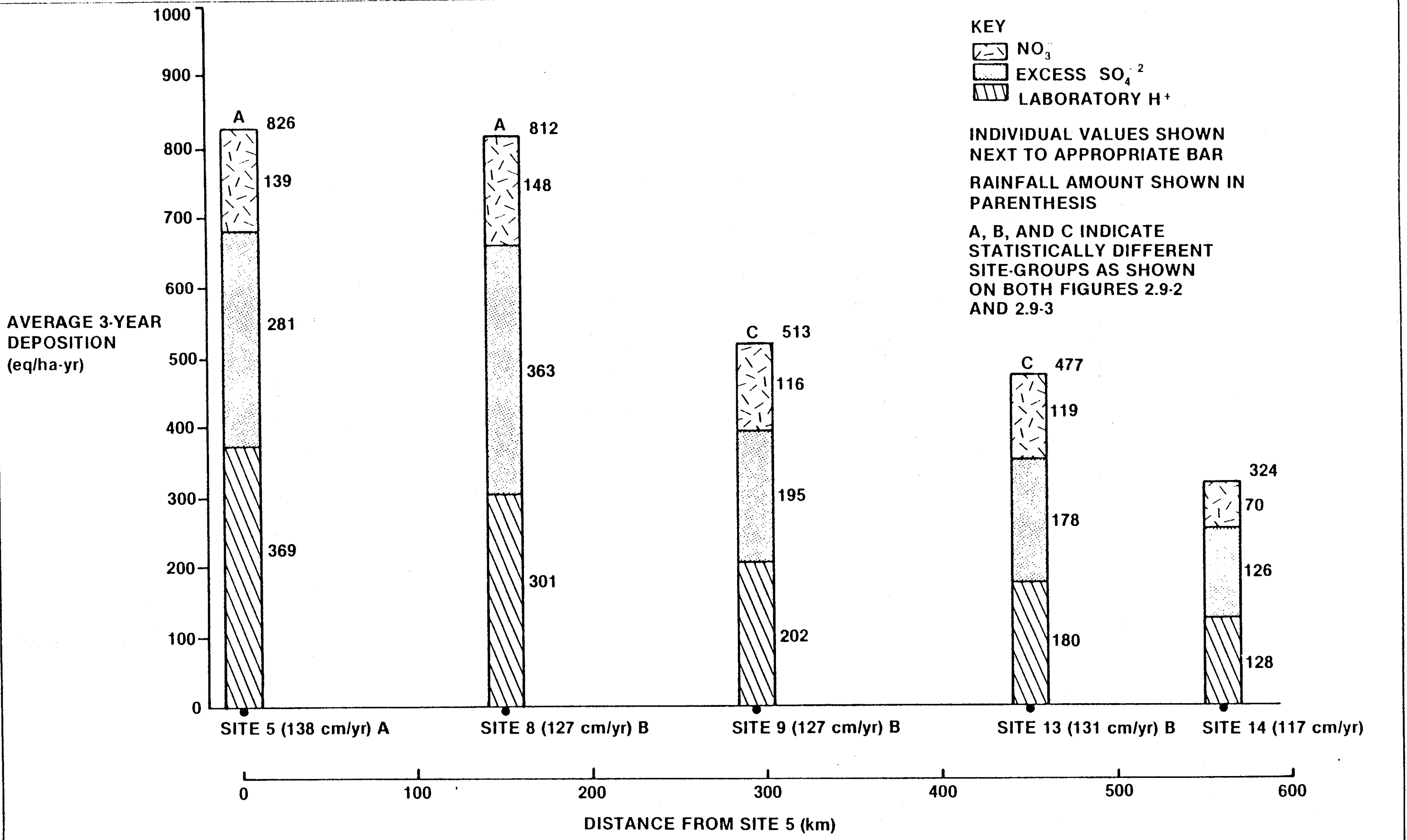

Figure 2.9-3
3-YEAR AVERAGE DEPOSITION OF LABORATORY $H^+$, EXCESS $SO_4^{-2}$, AND $NO_3^-$ FOR SITES 5, 8, 9, 13, AND 14 (NORTH-SOUTH TRANSECT) AS A FUNCTION OF DISTANCE FROM SITE 5

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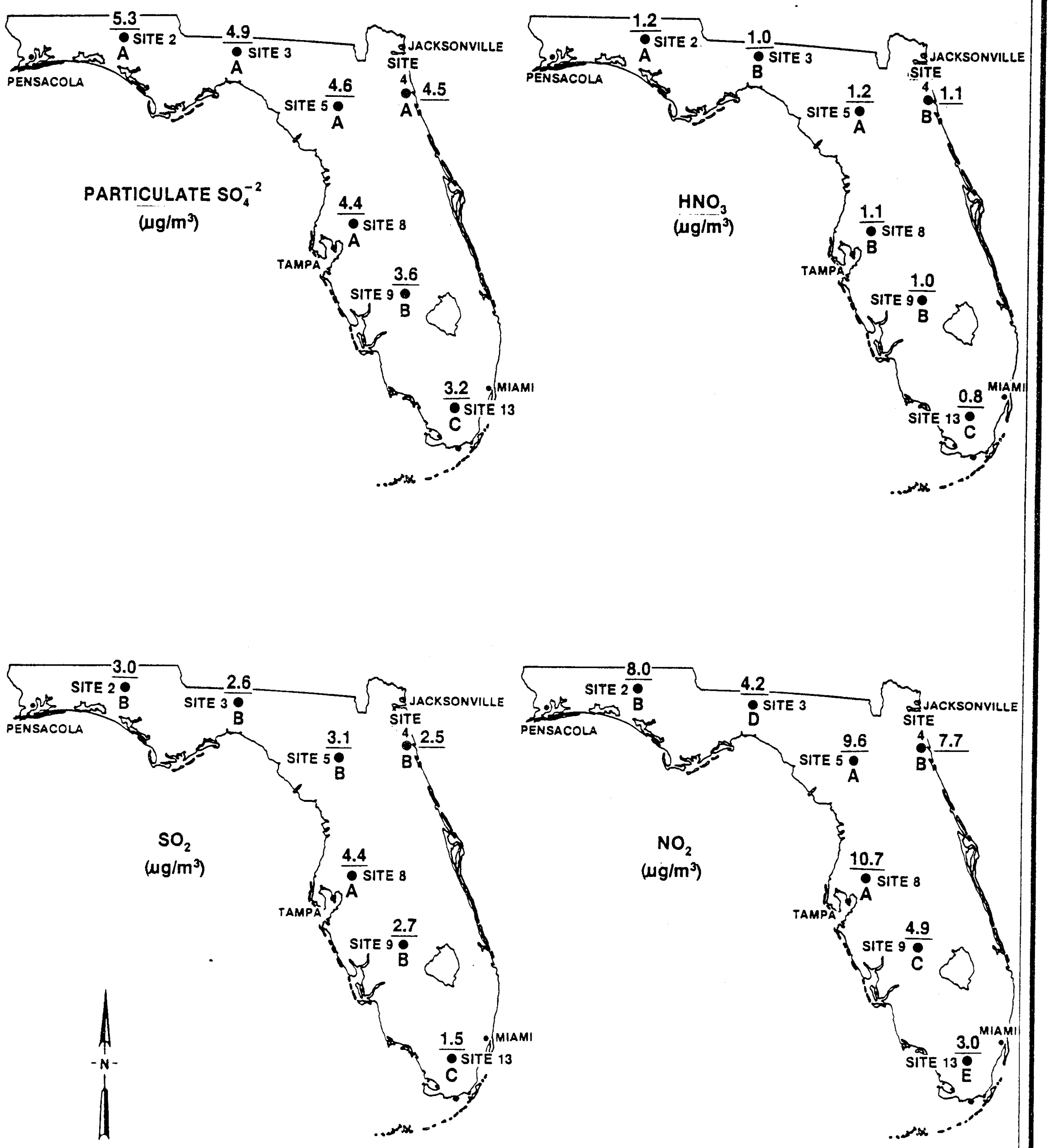

NOTE: A, B, C, D, AND E DENOTE STATISTICALLY DIFFERENT SITE-GROUPS.

Figure 2.9-4
AMBIENT AIR CONCENTRATIONS OF PARTICULATE $SO_4^{-2}$, $HNO_3$, $SO_2$, AND $NO_2$ OVER 2-YEAR PERIOD

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precipitation chemistry in Florida may be part of a phenomenon that is continental in scale. However, the observed spatial patterns for Florida clearly suggest the possibility of localized influences (i.e., rainfall amount) in precipitation chemistry since the highest concentrations and depositions of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ were observed in the north to central portions of the state (i.e., Sites 5 and 8).

### 2.9.3 TOTAL DEPOSITION

Estimates of total deposition were made by adding wet depositions observed from the monitoring network to dry depositions calculated using ambient air concentrations and assumed deposition velocities to address the question:

- What are the likely current values of total deposition in Florida?

The results (Figure 2.9-5) indicate that about one-third of the sulfur deposited in Florida may be in the dry form. In contrast, about two-thirds of the nitrogen was calculated to come from dry deposition. For sulfur, the total deposition ranged from 640 eq/ha-yr at Site 8 to 306 eq/ha-yr at Site 13. Total deposition of nitrogen was estimated to range from 438 eq/ha-yr at Site 8 to 243 eq/ha-yr at Site 13. Because of uncertainties associated with using an assumed deposition velocity, the accuracy of these estimates is unknown.

### 2.9.4 SEASONAL AND NEAR-TERM TRENDS OF WET-ONLY ACIDIC DEPOSITION AND MAJOR CHEMICAL SPECIES

Analyses of seasonal and diurnal trends over a 3-year period are presented in Subsection 2.6 in order to evaluate whether temporal differences in concentration and deposition fields exist across Florida. These analyses focus on the key research question:

- What are the monthly, seasonal, and near-term trends of wet-only acidic deposition and major chemical species in Florida?

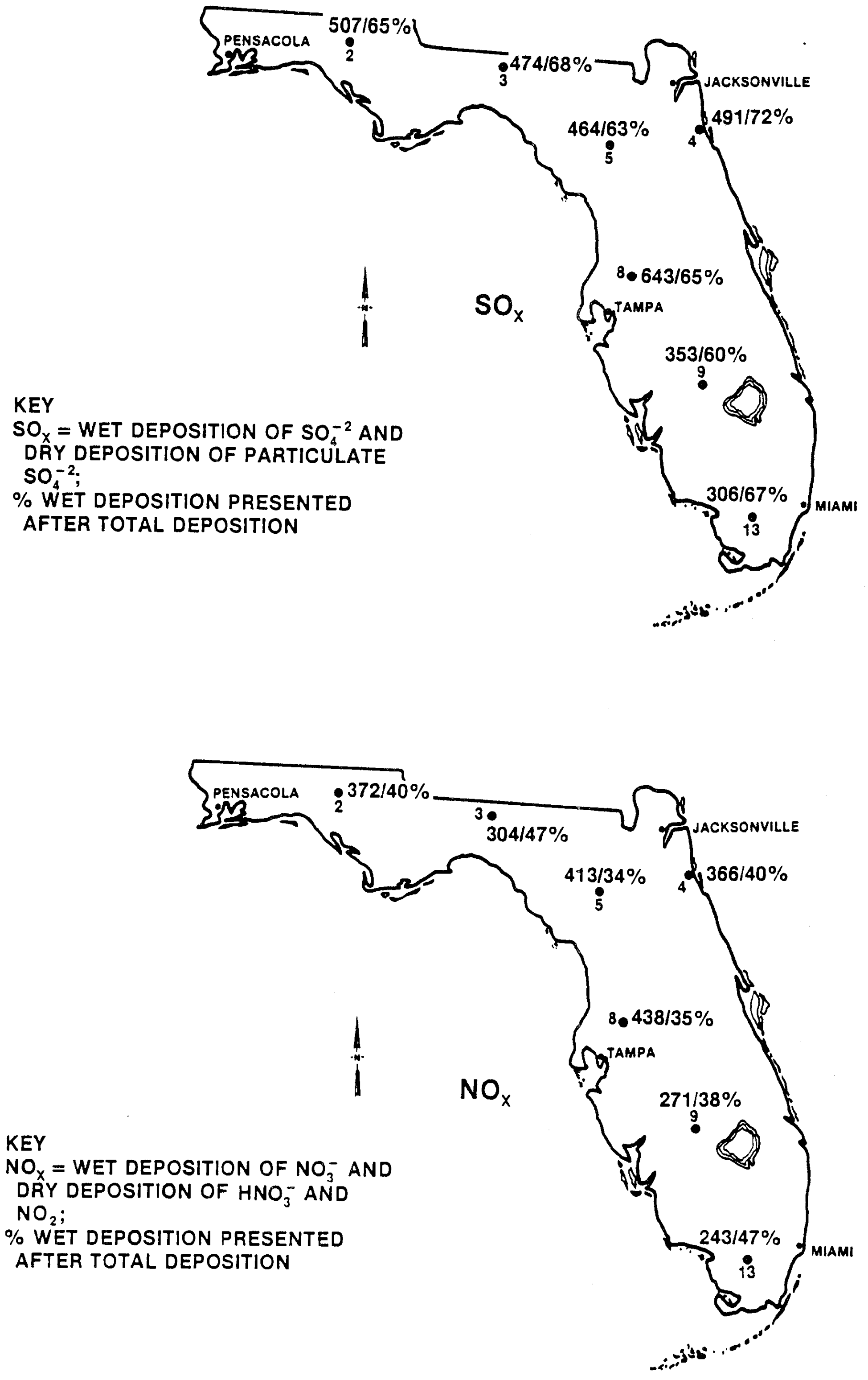

Figure 2.9-5
TOTAL ESTIMATED DEPOSITION (eq/ha) OF $SO_X$ AND $NO_X$ FOR OCTOBER 1982 THROUGH SEPTEMBER 1983

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The analysis, however, appropriately centered on a statistical analysis of temporal differences in precipitation chemistry by sites or groups of sites. Thus, a corollary question addressed was:

- What are the statistically different temporal relationships in precipitation chemistry by site, by group, and by season? (Refer to Subsection 2.6.2.)

Differences in seasonal concentrations and depositions were observed over the 3-year period. Summer-to-winter ratios of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ concentrations were approximately 2.0; summer-to-winter deposition ratios were 2.0 or greater. Summer-to-winter rainfall ratios ranged from approximately 1.0 at Sites 2 and 3 to 1.5 or greater at Sites 4, 5, 8, 9, and 13.

Statistical analysis between summer and winter concentrations within site-groups often found significant differences between summer and winter concentrations of laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, excess $Ca^+$, and $NH_4^+$. The statistical differences between summer and winter concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ are strongest between site-groups located in the panhandle and northern peninsula (Sites 2, 3, 4, 5, and 8) than those sites located in the southern peninsula. In general, fewer statistical differences between site-groups were observed for deposition than concentration. Summer concentration and deposition patterns across site-groups varied considerably more than the corresponding winter patterns and, for north-central sites, showed a significant decrease between the first and third years of the study.

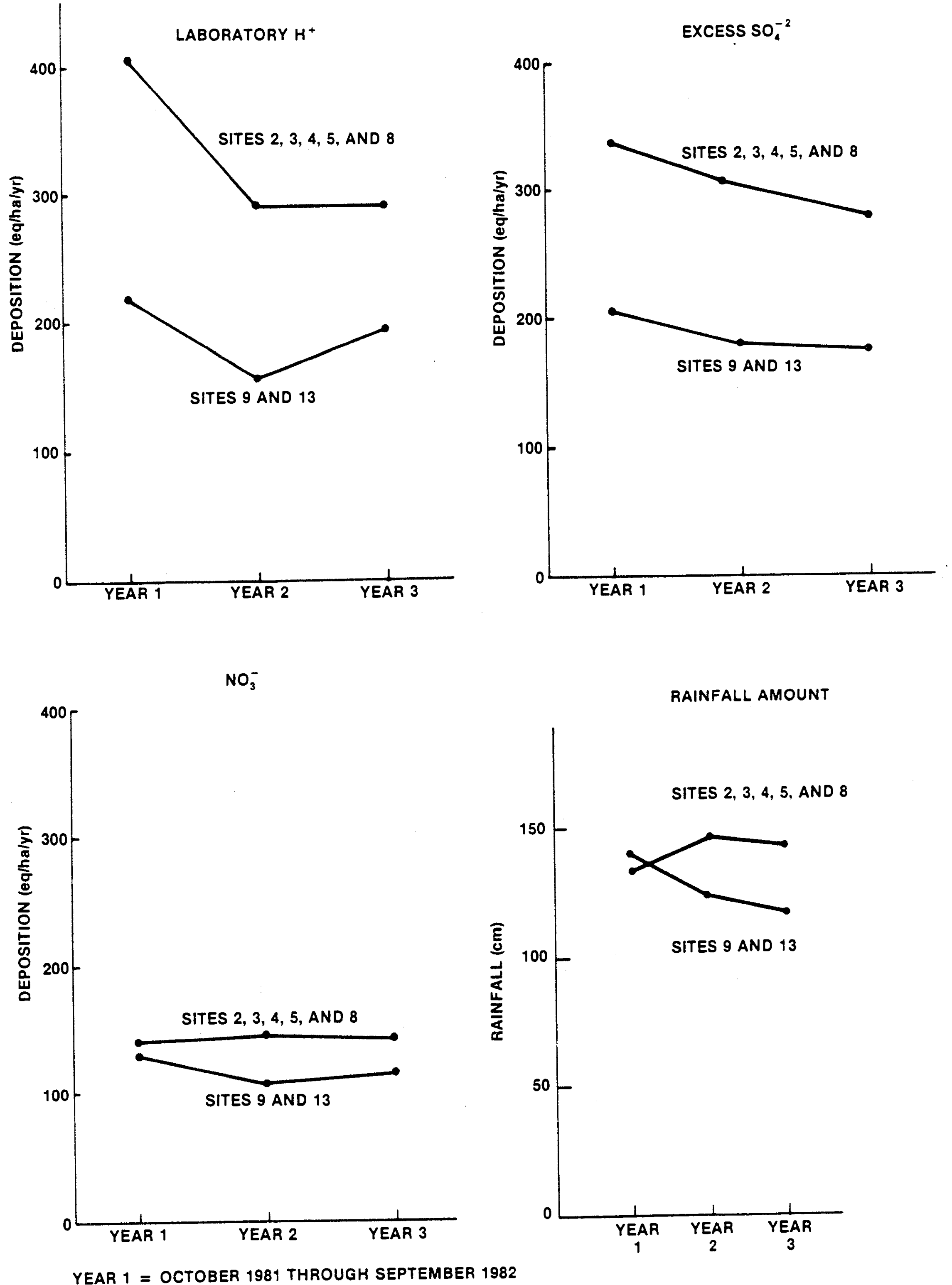
Comparison of annual periods suggests decreases in both concentration and deposition of laboratory $H^+$ and excess $SO_4^{-2}$; decreases were especially apparent for the panhandle and northern peninsula sites. Laboratory $H^+$ and excess $SO_4^{-2}$ concentrations decreased by 36 percent and 19 percent, respectively, from the first to the third year for the panhandle and northern peninsula sites. However, the southern peninsula sites experienced only a 12 percent and 7 percent decrease in deposition of laboratory $H^+$ and excess $SO_4^{-2}$, respectively, from the first to third years.

Concentrations of $NO_3$ decreased only at Sites 2 and 3 over the 3-year period; Sites 4 and 9 increased in concentration, and Sites 5, 8, and 13 remained about the same.

The trends in deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ over the 3-year period were similar to trends observed for concentration (Figure 2.9-6). Deposition of laboratory $H^+$ decreased by about 28 percent over the 3-year period for the panhandle and northern peninsula sites; for the southern peninsula sites, laboratory $H^+$ decreased 27 percent between the first and second years but increased by 24 percent between the second and third years. Excess $SO_4^{-2}$ deposition generally decreased uniformly between the first and third year, with observed decreases of 16 percent for the panhandle and northern peninsula sites and 14 percent for the southern peninsula sites. Deposition of $NO_3^-$ remained relatively constant over the 3-year period for both the panhandle and northern peninsula sites and the southern peninsula sites.

The amount of rainfall during the 3-year period actually increased by 8 percent for the panhandle and northern peninsula sites, while for the southern peninsula sites, rainfall decreased by 16 percent. This latter result suggests that rainfall amount as opposed to concentration played a more important role in observed variability of deposition in southern Florida than the rest of the state.

Statistical differences were found in both concentration and deposition of laboratory $H^+$ and excess $SO_4^{-2}$ between the first and third annual periods. No significant differences were observed between annual periods for $NO_3^-$, excess $Ca^{+2}$, or $NH_4^+$.



YEAR 1 = OCTOBER 1981 THROUGH SEPTEMBER 1982
YEAR 2 = OCTOBER 1982 THROUGH SEPTEMBER 1983
YEAR 3 = OCTOBER 1983 THROUGH SEPTEMBER 1984

Figure 2.9-6
ANNUAL DEPOSITION OF LABORATORY $H^+$, EXCESS $SO_4^{-2}$, AND $NO_3^-$, AND RAINFALL AMOUNT FOR PANHANDLE AND NORTHERN PENINSULA SITES (2, 3, 4, 5, AND 8) AND SOUTHERN PENINSULA SITES (9 AND 13)

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In summary, the following observations are apparent from an analysis of the temporal variability in 3 years of precipitation chemistry data:

1. Concentration and deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ are seasonally dependent in Florida, with the highest concentrations and depositions occurring in summer;
2. Rainfall amount appears to influence this seasonal variability;
3. A statistically significant decrease in laboratory $H^+$ and excess $SO_4^{-2}$ was observed over time; this observation was strongest for the panhandle and northern peninsula portions of the state; and
4. The variability in $NO_3^-$ over the 3-year period was low and not significant.

## 2.9.5 CHEMICAL AND PHYSICAL RELATIONSHIPS OF ACIDITY IN PRECIPITATION

The monitoring data collected over the 3-year period allowed an evaluation of certain chemical and physical relationships in wet-only precipitation. The results of these evaluations, which are presented in Subsection 2.7, focused on addressing the key research question:

- What are the chemical and physical relationships between the acidity of Florida's rainfall and (1) the major cations and anions in rainfall, (2) rainfall amount, and (3) ambient air concentrations?

The paragraphs that follow address each inherent part of this key research question:

- What are the chemical and physical relationships between laboratory $H^+$ and the major cations and anions found in precipitation? (Refer to Subsection 2.7.1.)

Results of multi-variate regression analysis indicated that between 28 and 96 percent of the variability in laboratory $H^+$ concentrations could be explained by an equation of the form:

$$[H^+] = A[\text{excess } SO_4^{-2}] + B[NO_3^-] + C[\text{excess } Cl^-] - D[NH_4^+]$$
$$E - [\text{excess } Ca^{+2}] + F$$

where: [ ] = Concentration (μN), and
A through F = Constants.

The relationships were strongest for the northern sites and explained from 77 to 96 percent of the variability in laboratory $H^+$ concentrations. The lowest amount of variability in laboratory $H^+$ concentrations was explained at the southernmost site evaluated, with $R^2$ values between 28 and 67 percent. Excess $SO_4^{-2}$ was found to be the most important variable in the regression equation, by explaining from 45 to 90 percent of the variability in $H^+$ concentration at the northern sites. Only 5 to 28 percent of the laboratory $H^+$ variability was explained by excess $SO_4^{-2}$ at the southernmost site. The second most important variable was a cation (i.e., $Ca^{+2}$ or $NH_4^+$) but explained no more than 25 percent of the laboratory $H^+$ variability. $NO_3^-$ typically ranked third or fourth in importance. Over the 3-year period, the importance of excess $SO_4^{-2}$ remained about the same, but the importance of excess $Ca^{+2}$ increased, especially from the first to the second year. This increase in importance of excess $Ca^{+2}$ may partially account for the lower laboratory $H^+$ depositions observed from the first through third year. Increases in the model intercept (i.e., constant F in preceding equation) suggested that a significant portion (from 14 to 22 percent) of the laboratory $H^+$ concentration is not accounted by the variables in the third-year regression equations. Regression equations for the summer and winter indicated that more of the variability in $H^+$ concentrations could be explained in summer than winter; however, excess $SO_4^{-2}$ was important for both seasons.

- What are the relationships between precipitation chemistry and rainfall amount? (Refer to Subsection 2.7.2.)

Relationships between analyte concentration and rainfall amount were developed for two sites (Sites 5 and 9) for annual as well as seasonal time periods. Statistically significant relationships, in an inverse or exponential form, were found for laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, and excess $Ca^{+2}$. Concentration was found to decay rapidly with increasing precipitation amount. The general order of magnitude of each analyte decay rate was:

$$\text{Excess } Ca^{+2} > NO_3^- > \text{Excess } SO_4^{-2} \approx \text{Laboratory } H^+$$

The rapid decay rate of excess $Ca^{+2}$ is expected since these ions initially start as supermicron aerosols and are more easily scavenged than ions starting as gases or submicron aerosols (i.e., $NO_3^-$ and excess $SO_4^{-2}$). As a result, the influence of $Ca^{+2}$ is more likely to be more local. Differences between $NO_3^-$ and excess $SO_4^{-2}$ decay rates suggest that precipitation scavenging of these species may be governed by different physiochemical processes.

- What are the potential acids and bases in Florida's precipitation? (Refer to Subsection 2.7.3.)

The acids and bases potentially contributing to net acidity were found to vary as a function of site location and the pH range of the rainfall event. For Sites 2, 5, 9, and 13, the potential contribution of excess $SO_4^{-2}$ as $H_2SO_4$ was 68, 66, 63, and 59 percent, respectively, of the total potential acids; this result suggests that $SO_4^{-2}$ becomes less important as a contributor to total potential acidity from north to south. Conversely, $NO_3^-$ (as the potential acid $HNO_3$) became increasingly important from north to south with potential contribution of total acidity of 32 percent, 34 percent, 37 percent, and 41 percent for Sites 2, 5, 9, and 13, respectively.

Potential bases $NH_4^+$ and excess $Ca^{+2}$ increased as a percentage of total potential acidity from north to south. These bases were 31 percent, 36 percent, 43 percent, and 60 percent of the total potential acids for Sites 2, 5, 9, and 13, respectively. $NH_4^+$ was slightly higher in importance as a base than excess $Ca^{+2}$ for the northern sites (2 and 5) whereas excess $Ca^{+2}$ was more important as a base for the southern sites (9 and 13).

The net precipitation acidity (i.e., acids - bases) was below the observed laboratory $H^+$ at three of the four sites. Explanations for this result include a bias in chemical analysis, the presence of additional acids in precipitation, or the possibility that $NH_4^+$ and/or excess $Ca^{+2}$ are not acting exclusively as bases (or base counterions).

Contributions of all potential acids/bases as a percent of $H^+$ concentration increased from low-pH events (i.e., <pH 4.3) to high-pH events (>pH 4.9) at all sites. Except at Site 13, measured acids and bases were able to fully account for laboratory $H^+$; however, at lower pHs, from 102 to only 84 percent of the laboratory $H^+$ could be accounted for.

- What are the interrelationships in air chemistry? (Refer to Subsection 2.7.4.)

Calculated oxidation ratios for $SO_x$ ranged from about 0.60 in summer to about 0.44 in the winter. For $NO_x$, oxidation ratios were about 0.14 in the summer and 0.09 in the winter. These results indicate substantial seasonal variability in oxidation rates. Since both $SO_x$ and $NO_x$ are emitted principally in the gaseous, unoxidized form [i.e., $SO_2$, nitric oxide (NO), and $NO_2$] and since most studies indicate that oxidation rates of $NO_x$ are at least as high as oxidation rates of $SO_2$, they also suggest that $HNO_3^-$ is removed more efficiently than particulate $SO_4^{-2}$.

The sulfur and nitrogen oxidation ratios for the southern Florida site (13) was less influenced by the seasons, suggesting that oxidation rates remain relatively the same year round in the subtropical environment of the Florida Everglades.

- What are the relationships between precipitation and air chemistry? (Refer to Subsection 2.7.5.)

Exponential relationships between excess $SO_4^{-2}$ and $NO_3^-$ in precipitation and their ambient air counterparts (particulate $SO_4^{-2}$ and $SO_2$, and $HNO_3$ and $NO_2$, respectively) were evaluated for seven sites. Rainfall amount was also included in the relationships evaluated. The exponential relationships explained from 26 to 46 percent of the variability in excess $SO_4^{-2}$ concentrations in rainfall and from 24 to 56 percent of the variability in $NO_3^-$ concentrations. However, these results are confounded by the possible temporal differences between the air sampling (i.e., 24 hours) and the rainfall event.

### 2.9.6 RELATIONSHIPS OF PRECIPITATION AND AIR CHEMISTRY WITH OBSERVED METEOROLOGICAL CONDITIONS

Precipitation chemistry and ambient air monitoring data from four sites (Sites 2, 5, 9, and 13) were sorted by six synoptic-scale meteorological conditions that occur in Florida in order to evaluate the influence of such conditions on observed precipitation and ambient air chemistry. The six synoptic-scale meteorological conditions consisted of cold front, stationary front, continental high, maritime high, Gulf low, and continental-Atlantic low. The purpose of this analysis was to provide insight on potential transport mechanisms into Florida that would be treated in greater detail through trajectory analysis (see Subsection 3.3.3).

The relationships between monitoring data and meteorological classifications are presented in Section 2.8 and addressed the key research question:

- What are the relationships between observed precipitation and air chemistry and meteorological conditions in Florida?

The two corollaries of this question are addressed in the following paragraphs.

- How does precipitation chemistry vary as a function of synoptic meteorological conditions? (Refer to Subsection 2.8.1.)

VWM concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ were sorted by the six synoptic-scale meteorological classifications. The lowest concentrations were observed under cold frontal and Gulf-low conditions. Concentrations under these conditions were about 50 to 75 percent lower than the highest concentrations observed for other meteorological classifications. During these meteorological conditions, much of the transport into Florida is from the south to southwest, areas of low acid precursor emissions.

Meteorological classifications associated with the highest concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$, in contrast, varied from site to site. This finding indicated that synoptic-scale meteorology can have a markedly variable influence on spatial patterns of statewide precipitation chemistry. The general order of decreasing concentrations of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ was:

Panhandle (Site 2): Continental High > Stationary Front ≃ Maritime High > Cold Front ≃ Gulf Low

Northern Peninsula (Site 5): Continental-Atlantic Low > Maritime High ≃ Continental High ≃ Stationary Front > Cold Front ≃ Gulf Low

Southern Peninsula (Site 9): Stationary Front > Maritime High ≃ Continental-Atlantic Low ≃ Gulf Low ≃ Cold Front > Continental High

South Florida (Site 13): Maritime High > Stationary Front > Continental High ≃ Continental-Atlantic Low > Cold Front ≃ Gulf Low

Precipitation chemistry at the northern peninsula site exhibited the highest concentrations for all meteorological classifications and also the greatest variability in concentrations across meteorological classifications. In contrast, Site 13 in the extreme southern peninsula of Florida typically exhibited the lowest concentrations and the least concentration differences between meteorological classes, suggesting that synoptic conditions have less influence on precipitation chemistry in southern Florida.

Deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ by meteorological classification generally indicated unique effects of synoptic-scale conditions from site to site. Especially important was the amount of rainfall that occurred. For example, 70 percent of total deposition at the panhandle site occurred under maritime (40 percent) and continental high (30 percent) conditions. However, maritime highs contributed nearly half of the annual precipitation at the panhandle site, and continental highs contributed only 17 percent of the annual rainfall. At the northern peninsula site, maritime highs and continental-Atlantic lows each accounted for about 30 percent of the annual deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$. Rainfall, however, during maritime highs was about twice that observed during continental-Atlantic lows.

Deposition on an event basis demonstrated the episodic nature of precipitation chemistry in Florida. This conclusion is exhibited by the general order of decreasing deposition by event:

Panhandle (Site 2): Continental High > Stationary Front > Maritime High > Gulf Low > Cold Front
Northern Peninsula (Site 5): Continental-Atlantic Low >> Maritime High > Cold Front ≃ Stationary Front > Continental High ≃ Gulf Low

| | |
|---|---|
| Southern Peninsula (Site 9): | Continental-Atlantic Low ≃ Cold Front > Stationary Front ≃ Gulf Low > Continental High > Maritime High |
| South Florida (Site 13): | Continental High > Maritime High > Gulf Low ≃ Continental-Atlantic Low > Cold Front > Stationary Front |

These results generally show that the effects of each meteorological class vary from site to site. At Site 2, maritime highs contributed nearly half of the annual precipitation and slightly over 40 percent of the laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ deposition. Continental highs, in contrast, contributed 17 percent of rainfall but approximately 30 percent of deposition. Strikingly, continental-Atlantic lows were an insignificant source of rainfall and deposition, indicating that the spatial variability of rainfall itself may strongly influence spatial deposition trends.

- How does ambient air chemistry vary as a function of synoptic meteorological conditions? (Refer to Subsection 2.8.2.)

Ambient air concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ were classified by the six synoptic-scale meteorological conditions. Results indicated considerable variability of concentrations with synoptic-scale conditions in the panhandle and northern peninsula of Florida but reduced variability in the southern peninsula, especially extreme south Florida. This observation was similar to that observed for precipitation chemistry and suggests that synoptic-scale meteorology has little influence on either the observed ambient air concentrations or on precipitation chemistry in extreme south Florida.

Concentrations varied by a factor of 2 across meteorological class. The highest particulate $SO_4^{-2}$ and $HNO_3$ concentrations were generally observed under continental-Atlantic low, stationary front, and continental high conditions. Concentrations of particulate $SO_4^{-2}$ and $HNO_3$ during maritime highs were among the lowest; a result in contrast to that observed for deposition. This result suggests that convective storms associated with this synoptic-scale system may be efficient in depositing these atmospheric pollutants.

Annual average concentrations of $SO_2$ and $NO_2$ appeared to be affected generally by local sources. However, for specific episodes, concentrations were highest during meteorological conditions conducive to transport from the north and lowest during conditions conducive to transport from the south.

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# 3.0 RELATIONSHIPS OF SOURCES TO ACID DEPOSITION IN FLORIDA

## 3.1 INTRODUCTION AND OBJECTIVES

### 3.1.1 INTRODUCTION AND OBJECTIVES

The primary objective of the Source Attribution Program is to assess the contribution of Florida's current anthropogenic emission sources to current levels of acidic deposition in Florida and in neighboring states.

Extensive literature research was performed first to determine available techniques to meet this objective. Specifically, this research led to the following activities:

1. Identifying and evaluating existing source attribution methods used in estimating acidic deposition,
2. Selecting an atmospheric deposition models/methods for analysis, and
3. Assessing and obtaining the necessary emissions, meteorology, and air quality databases required for the models.

Findings of these efforts (ESE, 1985) indicated that none of currently available LRT models or analyses methods was technically superior to any other. Each model performed consistently within its basic framework and limitations. Since none of the models was specifically developed for or applied in the southeastern United States, the efforts focused on examining model components for potential suitability and applicability to Florida. Emphasis was placed on using models or methods that had previously been applied and available in the modeling community. In addition, the models were evaluated for: (1) flexibility in use of model components to allow modifications to address specific physical and chemical processes in Florida, and (2) potential for long- and short-term computations of $SO_2$ and $SO_4^{-2}$ concentrations and depositions.

Based on these investigations, two methods were selected to assess source-receptor relationships: a source-oriented approach using an LRT model to simulate concentration and deposition fields, and a mass-balance approach using air mass trajectory calculations coupled with air quality monitoring data. Two approaches were selected because these alternative yet similar techniques would provide a range in estimating the potential source contribution to acid deposition in Florida.

These models were used in the Source Attribution Program to:

1. Estimate relative contributions of selected source areas to regionally located receptors;
2. Provide relative temporal and spatial estimates of concentration/deposition fields at unmonitored locations;
3. Assist in the interpretation of monitoring data in developing/verifying acidic transformation or deposition rates.

From the literature review performed (ESE, 1985), concentration and deposition fields simulated using LRT models should be considered preliminary and should not be used as the basis for the development of regulatory policies. The state of the art in LRT modeling has not progressed sufficiently to accurately predict concentration and deposition fields over the model domain (i.e., the eastern United States). Inherent limitations in simulating the complex physical and chemical processes in the atmosphere exist and have not been overcome through rigorous verification and validation. In addition to the uncertainties in the techniques used to simulate the physical and chemical processes, there are also uncertainties in the databases needed for model input. Also, the LRT modeling analyses performed to date have not been applied specifically to the southeastern United States or to Florida. Thus, any LRT model application to Florida is a research effort that requires considerable investigation into identifying and modifying model components pertinent to Florida application; identifying, acquiring, and processing national databases for use in model application; and identifying and applying analytical methods to assess model performance by comparing simulated to observed data.

The mass-balance technique is used to assess the relative contribution of in-state and out-of-state sources of acid precursors to the observed precipitation acidity in Florida. In this technique, estimates of sources, sinks, import, and export of $SO_x$ and $NO_x$ are combined to form a mass-balance model for Florida. Sources and sinks of $SO_x$ and $NO_x$ are estimated using the emission inventory developed for the LRT model and acid deposition monitoring, respectively. The import term is developed from air mass trajectories coupled with ambient air monitoring data, whereas export is calculated by difference (i.e., the mass-balance term).

Mass balance is not, however, without significant limitations in providing an assessment of potential source contribution of acid precursors in Florida. Because a mass-balance model focuses on the state as a whole, it is not possible to accurately assign emissions to interstate source regions as an LRT model is designed to do. In addition, a mass-balance model cannot account for physical and chemical processes which could distribute, both spatially and temporally, wet and dry deposition of acid precursors. Rather, the mass-balance technique can provide a somewhat quantitative estimate of in-state and out-of-state source contributions. Such an estimate would, however, have inherent errors each of which would be associated with a model component. Specifically, errors would occur in:

1. Calculation and assignment of trajectories as either in-state or out-of-state;
2. Observed ambient air concentrations;
3. Estimates of anthropogenic and biogenic emissions; and
4. Statewide estimates of wet and dry deposition.

Nonetheless, the mass-balance technique will provide information concerning the likely range of source contributions to Florida.

The remainder of this section is organized as follows. The modeling approach is summarized in Subsections 3.1.2 and 3.1.3. A relatively detailed overview of the modeling methods is presented in Subsection 3.2, and the modeling results are presented in Subsection 3.3.

### 3.1.2 SUMMARY OF LRT MODELING

#### 3.1.2.1 Model Components

LRT models can estimate concentrations and depositions due to a specific source or set of sources. The function of the LRT is to translate emissions from sources to concentrations and depositions using mathematical formulas to represent the physical and chemical processes that occur in the atmosphere. The main features of a LRT model can be defined in terms of the following components:

1. Emissions,
2. Transport and dilution processes,
3. Chemical transformation, and
4. Removal processes due to wet and dry deposition.

Although the components are treated individually, the model must combine the individual components into an integrated system for the temporal and spatial scales considered in the analysis.

The treatment of transport and dilution that have been developed to date can generally be classified into one of three categories:

1. Lagrangian,
2. Eulerian, or
3. Statistical.

Lagrangian, or trajectory, models use moving frames of reference based on individual air parcels or puffs which are transported according to observed or calculated wind fields. Concentration and deposition fields are accumulated and translated to each grid. Eulerian, or grid, models divide the model domain into a 2- or 3- dimensional array of cells with advection and dilution of materials simulated in each cell by a set of mathematical expressions. Statistical trajectory models produce a large number of air trajectories that are calculated with climatological wind frequency data or with a long series of wind analyses. The climatological, or ensemble, trajectories are analyzed statistically to determine average pollutant contributions and horizontal diffusion.

In a given model, turbulence may be represented by a well-mixed volume, semi-empirical diffusion coefficients, eddy diffusivities, Lagrangian statistics, or more complex turbulence algorithms. The well-mixed volume approach does not consider turbulence, except in an implicit manner. The most common parameters in current pollutant transport models are semi-empirical diffusion coefficients determined from field studies which provide measurements to estimate plume dispersion. Most Eulerian models use the eddy diffusivity formulation which is based on theoretical, physical, and numerical studies. Some models have applied Lagrangian statistics generated from field data to simulate turbulent effects in the atmosphere; however, problems occur because most field data are obtained in a Eulerian framework.

Reaction mechanisms are incorporated in LRT models to simulate physical/chemical transformation of acid precursors by such mechanisms as photochemical oxidation, in-cloud oxidation, and gas-to-particle conversion. Not all of these processes, however, are explicitly treated in all models. In many models, chemical processes are limited to the conversion of $SO_2$ to $SO_4^{-2}$. Other acidic precursors (e.g., $NO_2$) are either not considered or not considered simultaneously with $SO_2$. Since other precursors are not included in the analysis, the model simulations will account for only a portion of the total deposition that is likely to occur.

The removal mechanisms incorporated in the models reduce the mass of airborne pollutants by either wet or dry deposition. Wet deposition is the removal of pollutants by precipitation via below- and in-cloud scavenging processes. Dry deposition is the removal of pollutants by transfer from the air to exposed surfaces. Parameterizations of removal mechanisms used in LRT models vary widely. Since calculations of dilution and physical and chemical processes are made in moving frames of references in Lagrangian models, the models are capable of treating these processes only as simplified first-order decay rates. Consequently, Lagrangian models typically account for complex chemical and physical mechanisms in the atmosphere as simple linear processes. Eulerian models, on the other hand, are well-suited to use complex precipitation scavenging, cloud dynamics, and dry deposition because the model divides the atmosphere into a 2- or 3-dimensional array of cells. For each cell, components such as physical removal processes are simulated by a set of mathematical expressions and treatment of nonlinear chemistry can be incorporated.

### 3.1.2.2 Historical Assessments and Evaluations

In recent years, there have been several major assessments concerning the adequacy of LRT modeling of acidic deposition or precursors [United States-Canada Work Group 2, 1982; National Academy of Sciences (NAS), 1983; EPRI, 1984]. These studies have generally been performed by groups of national experts with relevant experience and specialities to assess the validity of modeling assumptions and parameterizations, including the emission, meteorology, and air quality data used in validating model performance.

The Regional Modeling Subgroup (United States-Canada Work Group 2, 1982) concluded that, after a review of eight LRT models, it was not possible to recommend a "best" model because of the uncertainties in the emissions and precipitation data and in the measurement data used for evaluation. The results showed that, although monthly concentration and deposition are often moderately correlated to measured values, the accuracy and uncertainties of these estimates must be more thoroughly quantified.

The NAS findings (1983) indicated that although theoretical models have provided results that are qualitatively consistent with field observations, current models have not provided results that give confidence in transforming emissions from specific sources to specific sensitive receptors. The models are developed using simplifying assumptions to provide practical and economical means of calculating regional-scale concentrations and depositions. Because measured data are not available to adequately validate or verify model results, there is also little confidence in using the models in predicting responses to the atmospheric processes to alternative control strategies. Therefore, given the lack of knowledge of the basic physical and chemical processes of the atmosphere in the context of LRT modeling and the insufficiency of databases to support model input and evaluation, the NAS advised caution in projecting changes in deposition patterns that result from emission changes in precuror gases.

A report prepared for EPRI (1984) evaluated not only model performance but also the model code, documentation, and basis of assumptions. From an initial list of 42 models, 3 models were chosen as representative of models now in use. Each of the three models that were examined in detail was found to have some computer coding errors, generally minor, which were readily changed without significant changes in model performance. These models were based on simplified assumptions that distorted the physical reality of the system and, in some instances, violated fundamental physical constraints. Detailed diagnostic evaluations of the model components showed expected sensitivities to atmospheric transport, chemical reactions, and deposition but emphasized the need for substantial improvement in scientific understanding and representation of aqueous-phase chemistry and dry deposition.

### 3.1.2.3 LRT Model Limitiation

The meteorological and chemical processes occurring in the atmospheric boundary layer are complex, and are simulated in models by mathematical expressions that are simplified and, in most instances, incomplete in describing the entire process. Several studies which compare model simulations and ambient measurements of $SO_2$ and $SO_4^{-2}$ concentrations and $SO_4^{-2}$ deposition (EPRI, 1984; NCAR, 1983; EPA, 1983; United States-Canada Work Group 2, 1982; Bhumralkar et al., 1980) suggested that discrepancies between observed data and model simulations could be due to a number of factors. These factors which limit the model performance can be summarized as follows:

1. Natural sulfur emissions and compounds, particularly those from outside the model grid boundary, are neglected. As a result, the model may underpredict concentrations and depositions, particularly dry deposition, which is assumed to occur in the lowest layers of the atmosphere.
2. Transport of pollutants above the mixing layer is not treated. Pollutants can be drawn upward by penetrative convective cloud activity (venting) or by rising motions produced by converging air masses. These pollutants can subsequently reenter the lower atmosphere by turbulent entrainment, air mass subsidence, or in precipitating systems. By not accounting for this process, model simulations can overpredict or underpredict observed values.
3. Emission, meteorological, and monitoring data used are generally not avaliable for coincident time periods and are deficient in the temporal and spatial coverage for the model domain. As a result, because the model input of observed data must be interpolated both spatially and temporally, the degree of confidence in model output is greatly reduced.
4. The initial mixing of pollutant emissions generally occurs within an entire grid cell. Because emissions tend to be subgrid-scale phenomena (i.e., source is smaller than grid cell volume), the initial dispersion of a pollutant depends strongly on the state of the mixing layer. During the day, when the mixing layer is turbulent, plume dispersion is much greater than at night when the atmosphere becomes stably stratified.
5. Dispersion, terrain effects, frontal and convective processes, and clouds are treated either in a very simplified manner or not at all.
6. There has been little verification or validation of model simulations with measured data. Even if the model is validated

to the fullest extent possible, its validation is dependent on existing databases. Thus, validation of a model should be an evolutionary process by which the model is tested against measurement data as they become available.

7. Insufficient knowledge of fundamental physical/chemical processes can limit model performance. A key example of this is the linearity issue. It is currently unknown whether, or on what spatial scales, the atmospheric $SO_2$-oxidant system departs from perfect elasticity (i.e., changes in deposition proportional to changes in emissions). Thus, each modeler has considerable latitude in structuring the model.
8. Model documentation frequently is not sufficient to fully convey to the user the scientific principals of each model component on which the overall model is based. As a result, modifications to a model code are difficult, particularly if errors in computer code remain undiscovered.

All of these factors apply to any model execution and evaluation performed in Florida. Because Florida defines the terrestrial boundary of the southeastern United States, the complexities are compounded since the quantity and quality of observational (e.g., meteorological) data in and around Florida are limited. As a result, attempts to use these data in LRT models will introduce uncertainties, particularly when the data are interpolated to more refined temporal and spatial scales.

One important aspect in which LRT models are deficient is treatment of local-scale factors, particularly the land-breeze and sea-breeze phenomena. Recent reviews [Nuclear Regulatory Commission (NRC), 1982; NRC, 1983] indicate that because the factors controlling transport and diffusion in coastal regions are localized, dispersion conditions are highly complex and site-specific and cannot be reduced to a simplified formula. Although the general atmospheric processes occurring as land and sea breezes are reasonably well understood, a rigorous validation of existing modeling techniques has not been performed. The validation efforts conducted thus far have used data of unknown quality and provide, at best, an incomplete representation of the coastal atmosphere. Several types of models developed for addressing this phenomena (e.g., Gaussian, numerical) either cannot provide a rigorous description of atmospheric mechanisms in coastal regions or require substantial resources (e.g., computer) to perform simulations. Because of these complexities in attempting to address this phenomenon on a localized scale, no attempt has been made to account for this effect on the scales required by LRT models.

To improve the methods and assumptions of LRT modeling, NAPAP is undertaking research efforts that attempt to understand the atmospheric link between emissions of precursor pollutants and deposition. The research is guided by specific objectives to improve understanding of:

1. Vertical and horizontal transport of acid substances and their precursors,
2. Major chemical transformations that produce acid substances in the atmosphere,
3. Precipitation scavenging processes and aqueous-phase transformations, and
4. Dry deposition of acidifying substances to various surfaces and under diverse atmospheric conditions.

Field studies have and will be performed that can provide both a database for developing and testing mathematical source/receptor models and an independent database for evaluating the performance of the mathematical models. Thus, with the continued improvements and development to predictive and interpretative models, there will be more confidence in model results which identify which sources and/or source regions are most likely to affect specific receptor regions and which pollutants cause acid deposition in those regions.

### 3.1.3 SUMMARY OF MASS-BALANCE MODELING

#### 3.1.3.1 Model Components

The purpose of developing a mass-balance model was to construct a semiquantitative tool for assessing the relative contribution of in-state and out-of-state sources of acid precursors to the observed acidity in Florida. This model is based on atmospheric trajectory analysis, information on wet/dry deposition, ambient air concentrations, and emissions data for the period September 14, 1982, to September 13, 1983. The specific tasks in constructing the mass-balance model were:

1. Development of a 5-year climatology of backward trajectories using the NOAA-Atmospheric Transport and Deposition (ATAD) model for four regions within Florida, represented by the following monitoring locations:
    a. Florida panhandle--Caryville (Site 2)
    b. Northern Florida peninsula--Gainesville (Site 5)
    c. Central Florida peninsula--Archbold (Site 9)
    d. Southern Florida peninsula--Florida Everglades (Site 13)
2. Assess relationships between trajectory data and precipitation/air monitoring data for Caryville, Gainesville, Archbold, and Everglades for the Phase III monitoring period (i.e., September 14, 1982, to September 13, 1983).
3. Estimate import of $SO_x$ and $NO_x$ to/from Florida using trajectory and air chemistry data for the period of September 14, 1982, to September 13, 1983.

#### 3.1.3.2 Previous Applications

The computation of atmospheric trajectories has been a useful tool for decades (e.g., Petterssen, 1940). Estimates of the movement of warm and cool air masses are necessary for weather prediction, and the application of trajectory analysis to the transport of pollutants is a logical extension of the technique. The use of trajectory analysis in pollution-related studies has become commonplace in recent years. Trajectories have been used to estimate gas and particle deposition velocities to the open ocean (Prahm et al., 1976), to track air parcel motion in remote areas of the world such as Hawaii and Alaska (Miller, 1981a and 1981b), to examine the evolution of haze episodes in the southwestern United States (Macias et al., 1981), and to evaluate potential sources of aerosols in the northeastern United States (Galvin et al., 1978; Samson, 1980).

One of the earliest attempts to relate trajectory and precipitation chemistry data was performed by Cogbill and Likens (1974), who compared manually computed 500-millibar (mb) trajectories from weather charts with daily precipitation pH values at Ithaca, New York. Results showed that high pH values were associated with trajectories originating from the north, east, and southeast, while lower pH values were associated with trajectories from the west and southwest. Using computerized trajectories, Munn et al. (1984) have recently analyzed a long-term database of weekly precipitation pH at Hubbard Brook, New Hampshire, with similar results; however, the difference in temporal scales between trajectory calculations and measurement can be a significant limitation. To date, trajectory analysis has been used to interpret precipitation chemistry in Scandinavia (Dovland et al., 1976), eastern Canada (Kurtz and Scheider, 1981), the northeastern United States (Miller and Galloway, 1978), Bermuda (Miller and Harris, 1985), and Amsterdam Island (Galloway and Gaudry, 1984).

Edgerton (1981) developed the only mass-balance model of direct relevance to Florida. In his model, Edgerton used a steady-state assumption along with anthropogenic and biogenic emissions estimates and 40-year average meteorological data to construct a sulfur mass-balance model for the year 1980. The results of the model suggest that in-state sources of sulfur may contribute a large portion (71 to 81 percent) of the sulfur (as $SO_4^{-2}$) in statewide precipitation. Imported sulfur from both continental and maritime regions also was found to play a significant role in Florida's atmospheric sulfur budget; sea salt and biogenic sources were considered to have minor roles.

## 3.2 METHODS OVERVIEW

### 3.2.1 INTRODUCTION

As discussed earlier, acid deposition modeling performed to date has generally not included detailed simulations of concentration and deposition fields for Florida. To meet the objectives of the Source Attribution Program, two techniques selected to assess acidic deposition in Florida included LRT modeling and mass-balance approach. Use and testing of these techniques require input data for specific time periods. For LRT modeling, the time period selected was from September 15, 1982, to September 15, 1983.

### 3.2.2 EMISSION INVENTORY

Based on previous results (ESE, 1984), emissions during 1980 from the fossil-fuel steam-electric generators in Florida accounted for approximately 80 and 86 percent of the $SO_2$ and $NO_x$ emissions, respectively, from point sources. Because of the magnitude of these electric utility emissions relative to all other emissions in Florida (i.e., approximately 68 percent of $SO_2$ and 32 percent of $NO_x$), an intensive effort was made to collect utility $SO_2$ and $NO_x$ emission data for September 15, 1982, to September 15, 1983. The purpose for obtaining these data was to establish a detailed utility emission inventory for use in LRT modeling. Also, since LRT modeling requires emissions from outside of Florida, point- and area-source data were collected for the eastern United States, with emphasis on the southeastern United States.

#### 3.2.2.1 Collection and Processing Procedures

#### Florida Utilities

Stack, operating, and emissions data were requested from 13 electric utilities with 121 fossil-fuel steam-electric generating units at 39 plants. The data requested from each utility included:

1. General stack and operating data,
2. Daily $SO_2$ and $NO_x$ emission data, and
3. Hourly $SO_2$ and $NO_x$ emission data and hourly operating load data (e.g., percent of maximum operating capacity) for specific case study periods.

Forms were completed by the utility companies for the period from September 15, 1982, through September 15, 1983 (see examples of forms in ESE, 1983a). Most of the utilities responded to this request by providing the data on these forms or on their own forms which had similar formats. In some cases, the information was sent on computer tape and processed to correspond to the format requested.

General stack and operating data were requested for each stack, with boiler operation data prepared for 50, 75, and 100 percent of maximum load. If the combustion gases from one or more boilers were vented through one stack, the operating conditions were requested for the total stack output. Each utility was requested to provide $SO_2$ and $NO_x$ emission data calculated using procedures specified by DER and the Federal Energy Regulatory Commission (FERC) for annual operating reports [i.e., $SO_2$ and $NO_x$ emissions based on fuel-use data and AP-42 procedures (EPA, 1983)].

After initial review for completeness, the utility data were placed in computer data files in the formats requested. To ensure completeness, monthly emissions were calculated by computer from daily estimates and compared to monthly estimates submitted separately by utilities. Any missing data were obtained from utilities prior to quality control review of the entire data files.

### Florida Nonutility Sources

The Florida nonutility emissions included point- and area-source emissions. For the point-source emissions, the 1981 Air Permit Inventory System (APIS) data were utilized and modified in an attempt to update the inventory for the period September 15, 1982, through September 15, 1983. Based on results of the 1980 emission inventory, emission data for sources with actual emissions greater than 1,000 tons per year (tons/yr) were identified. The following procedures were used to update emissions data for those sources:

1. Requests were made to the regional DER offices to obtain the 1982 and 1983 annual operating reports, which present estimated actual emissions for each point source within a plant and fuel usage. (No seasonal data were available).
2. Emission data available from air dispersion modeling analyses performed (e.g., prevention of significant deterioration permit applications) in Florida were reviewed to obtain emission estimates.

3. Emissions and stack data collected from the first two steps were used to update the APIS data to account for changes in stack, operating, and emission data that reflected estimated actual emissions for September 15, 1982, through September 15, 1983. Although both estimated actual and maximum allowable emissions were updated, only actual emissions were used in the LRT modeling effort.

The area-source information, presented for each county in the state, consisted of four general source categories: fuel consumption, solid waste, transportation, and miscellaneous. The fuel consumption and solid waste categories are further classified into residential, commercial-institutional, and industrial use. The transportation category is classified into gasoline- and diesel-powered land vehicles, aircraft, and vessels. In this study, the miscellaneous category consists only of agricultural burning.

### Non-Florida Sources

Emissions information obtained from governmental and research organizations was reviewed in an attempt to define non-Florida point-source and area-source emission data. A portion of this emission information included comprehensive data compilations of point and area sources for much of the eastern United States. Specifically, the following emission inventories were evaluated:

1. MAP3S 1978 emission inventory,
2. SURE 1978 and 1979 emission inventories,
3. NAPAP 1980 emission inventory, and
4. EPRI 1982 emission inventory.

In addition, state agencies were contacted to obtain point- and area-source emission inventories which were available on National Emission Data System (NEDS) forms.

The MAP3S and SURE databases were compiled several years prior to the study period and were not considered for use. The MAP3S data were compiled to represent 1978 emissions, and SURE data were developed for 1978 and 1979. The NAPAP data, were developed to represent 1980 emissions. This data development is part of the NAPAP program, established by Congress in 1980, to coordinate and expand research relevant to the problems posed by acidic deposition in and around the United States. The NAPAP data are readily available from EPA, although minimal documentation is provided and data are supplied on tape with formats that require processing (i.e., reformatting) for general use. The EPRI database was developed to provide an emission inventory for 1982 for the contiguous United States and southeastern Canada. The data for the United States were based on NEDS and state agency inventories for point sources and NEDS inventory for area sources. Additional updates on utilities and area sources were conducted. However, this database has become available only recently and may still be subject to change, particularly for emissions from the southeastern United States (EPRI, 1985).

After a review of the available databases and discussions with EPA (Clark, 1984), the NAPAP database (Version 2.0) was selected for use in the LRT modeling effort for the following reasons:

1. The NAPAP emission inventory, although based on NEDS data, had undergone extensive QA procedures to update and complete the inventory to 1980.
2. Discussions with state agencies [Georgia Environmental Protection Division (EPD), 1984; Alabama Department of Environmental Management (DEM), 1984; North Carolina DEM, 1984; Mississippi Department of Natural Resources (DNR), 1984] indicated in general that NAPAP data were consistent with state inventories.
3. The NAPAP inventory was readily available.

Although not complete, the EPRI database was compared to the NAPAP database. The results of this comparison found that emissions in both databases were comparable even though they were for different years.

#### 3.2.2.2 Processing and Quality Review of Data

Based on the information provided by DER, EPA, and FCG for Florida sources, the emission data were summarized into total emissions for the state. The data supplied by FCG for the utilities were reviewed to verify that the data were accurate based on full usage and reasonable based on emissions from previous years. Any significant change in emissions (i.e., more than 20 percent) from the study period to other years was identified, and the affected utility was notified and asked to confirm the emissions and provide reasons for the significant change. For major sources, fuel usage and emissions were checked using AP-42 procedures.

The emission data for the nonutilities with actual emissions greater than 1,000 tons/yr were identified and verified with the actual APIS data for each point source within each plant. The APIS summary data were initially evaluated for obvious errors, such as very large emissions (>10,000 tons/yr) compared to the type of source (e.g., gas turbine generator). Errors which could not be resolved from the APIS data alone were clarified by contacting DER. Engineering calculations were also performed for each to provide additional verification.

The Florida area source data were verified by requesting from EPA an updated NEDS inventory through 1982 and 1983. The area and source emissions from NEDS were further validated by checking NEDS emission data with that calculated from major source categories (i.e., fuel consumption and transportation) from supplemental information. Supplemental information was available for fuel consumption and transportation from the Florida Department of Transportation (DOT).

For non-Florida sources, the NAPAP database was reviewed to a much lesser extent than Florida data but compared favorably to the EPRI data. However, the NAPAP data had undergone extensive quality review (Endlich et al., 1983) and will continue to be upgraded and maintained as modifications and corrections are needed.

### 3.2.2.3 Limitations

The major limitation of the emission inventory developed for the LRT modeling effort centers around potential differences between the time frames of the four databases (i.e., Florida utility, Florida nonutility, Florida area source, and non-Florida emissions). However, comparisons of the data were performed to assess differences between different years (e.g., 1980 and 1982) as well as differences between inventories for the same year (e.g., Florida DER annual operating reports and utility inventory for 1983). Intercomparisons of these data for the different annual periods suggest that differences are probably no greater than 5 to 15 percent. The uncertainty in the monthly emissions is probably much larger but cannot be determined accurately since monthly data are not available for most of the four databases.

There are, nonetheless, several reasons why the developed inventory is reasonable on a monthly basis. Since the main objective of the Source Attribution Program focused on determing source contributions to acid precursor deposition from Flordia utilities, great emphasis was placed on obtaining accurate estimates of Florida utilities' emissions. This coupled with the fact that the utilities in Florida contribute a majority of $SO_2$ emissions suggests that monthly emissions will be reasonably accurate. In addition, it is more likely that utility emissions in Florida fluctuate more on a monthly basis than do area or nonutility emissions. Therefore, for estimating source contributions from Florida utilities to Florida, the monthly emissions appear reasonable.

Estimates of monthly source contributions outside of Florida, however, will be less certain. Differences in individual state emissions varied by as great as 30 percent from the 1980 NAPAP estimate to the 1982 EPRI estimate. To account for such variability, sources have been grouped in an attempt to average out individual state differences. These combined source regions, on the average, were found to be within 10 to 15 percent for the 1980 and 1982 periods. Also, estimates of source contributions will be based on combining the results of several months of analysis.

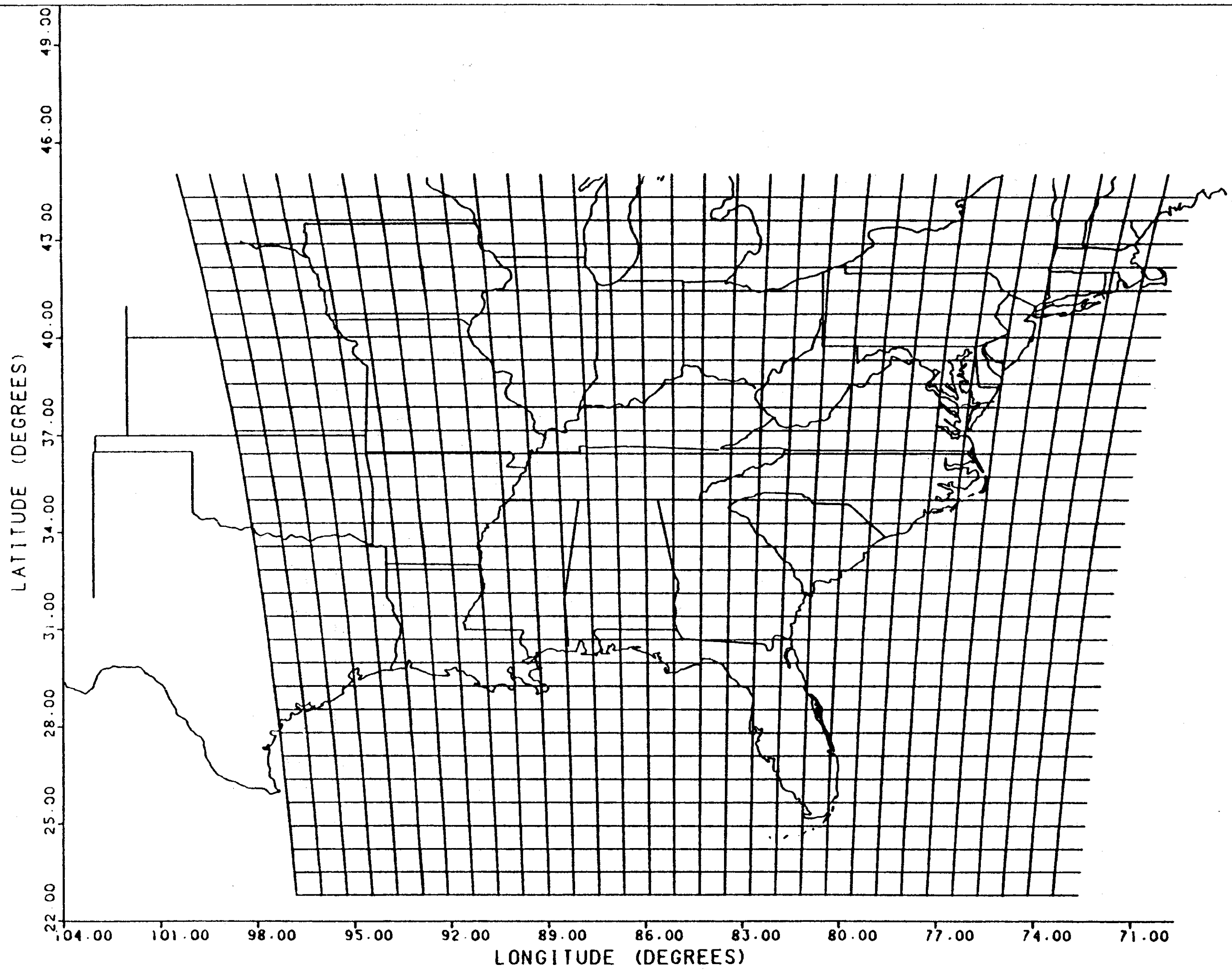

Figure 3.2-1
MODEL DOMAIN

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Table 3.2-2. Features of Model Domain

| Parameter | Value |
|---|---|
| Model Domain Size | |
| East-west direction | 2,480 km |
| North-south direction | 2,480 km |
| Total area | 6,150,400 km$^2$ |
| Number of Cells | |
| East-west direction (columns) | 31 |
| North-south direction (rows) | 31 |
| Total number of cells | 961 |
| Grid Cell Size | |
| East-west direction | 80 km |
| North-south direction | 80 km |
| Total area | 6,400 km$^2$ |
| Model Domain Origin* | 30°N, 85°W (0.0, 0.0) |
| Model Domain Corners* | |
| Southwest | 22.81°N, 96.80°W<br>(-1210.0, -800.0) |
| Northwest | 45.11°N, 100.42°W<br>(-1210.0, 1680.0) |
| Northeast | 45.11°N, 68.82°W<br>(1270.0, 1680.0) |
| Southeast | 22.81°N, 72.61°W<br>(1270.0, -800.0) |

*Latitude, longitude (x,y grid coordinates, km).
km$^2$ = square kilometers.

Source: ESE, 1986.

As each puff moves along a trajectory path, the rate of loss of $SO_2$ pollutant mass resulting from transformation and wet- and dry-deposition processes is assumed to be proportional to the total $SO_2$ mass within the puff. Similarly, the rate of loss of $SO_4^{-2}$ pollutant mass resulting from wet and dry deposition processes is assumed to be proportional to $SO_4^{-2}$ mass within the puff.

The amount of pollutant mass that is removed from a puff during each 3-hour time interval is dependent on the specified dry and wet deposition rates. This amount is then deposited within the appropriate cell(s) of the receptor grid.

Outputs from ENAMAP include tables of $SO_2$ and $SO_4^{-2}$ concentrations, wet and dry deposition throughout the study area as well as monthly, seasonal, and annual source-receptor relationships between cells (i.e., transfer matrices).

More advanced versions of ENAMAP are being tested and documented by EPA, Stanford Research Institute (SRI) International, and EPRI (Clark, 1983; Endlich et al., 1983; EPRI, 1984). Anticipated modifications to the model will include the capability for simulating episodic concentration/deposition and nitrogen chemistry. The nitrogen chemistry module initially will operate independently of the present sulfur chemistry module and will calculate the interconversion and deposition of $NO_x$, $HNO_3$, PAN, and particulate $NO_3^-$. However, for this study, nitrogen chemistry was not evaluated.

### 3.2.3.3 ESE Program Development/Modifications for Florida Application

Because LRT modeling to date has not concentrated on the southeastern United States, and, in particular, Florida, and most of the data or models were not available prior to this project, a significant number of databases and computer programs to be used in the LRT modeling analyses had to be identified, acquired, and/or developed. This effort, which relates to processing raw data (i.e., data recorded in observational format) to produce other parameters (i.e., concentrations), providing QA checks, or reformatting data, dealt with providing preprocessing and postprocessing programs for the following main programs:

1. ENAMAP,
2. WNDFLD,
3. Atmospheric stability,
4. Precipitation,
5. Dry deposition, and
6. Emissions.

As discussed previously (ESE, 1985), the ENAMAP and WNDFLD programs, which were obtained from SRI International, required modifications to execute properly on an IBM-compatible computer. Errors were found in the code and were changed based on discussions with SRI personnel. Based on the development and application of the programs by SRI International, both programs are research-oriented and have undergone significant changes since their original development. With the continued research and field work being conducted in acidic deposition modeling and similar applications as in this project, these models will continue to evolve as new information and techniques become available. To support these programs, additional preprocessor programs, such as for atmospheric stability and precipitation, must be developed to process data into gridded format. Unlike the User's Network of Applied Models of Air Pollution (UNAMAP) (EPA, 1983), the LRT models and associated programs are not standardized with respect to model input requirements, computation of model components, output of results, or documentation. As such, more than 30 programs were developed in this project to handle data processing and computations.

A summary of major program developments or modifications is as follows:

ENAMAP Model

1. Change in model domain and grid-cell sizes to cover the entire southeastern United States. The model domain and grid cells are

shown in Figure 3.2-1. A detailed description of the model domain features is presented in Table 3.2-2.

2. Account for deposition and transformation for each cell within a puff based on that cell's attributes (e.g., precipitation, land use).
3. For dry-deposition computations, define length of seasons within model domain to account for seasonal variation as a function of latitude (as described by Sheih et al., 1979 and Sheih, 1984).
4. User-specified values to change constants for wet deposition.
5. Correct coding error for calculating upper-level wind component.

WNDFLD Model

1. Model domain same as in ENAMAP.
2. Change in temporal interpolation scheme to check upper-air station data to ensure that stations have data for two consecutive observations (i.e., 00 and 12Z) before interpolation is performed.
3. Change in spatial interpolation scheme from station to grid data by computing weighted average wind data using the inverse of the distance squared.
4. Develop more efficient and better understood computer code logic by reading and processing NAMER-WINDTEMP data in one step, eliminating subroutines and variables never used, initializing variables in new subroutines, and inserting comments to describe variable, routine, or calculation.

Atmospheric Stability

1. ESE preprocessor program to WNDFLD to develop atmospheric stability using the Turner (1970) scheme based on surface observations of wind speed, cloud cover, and height from NWS stations within the model domain.
2. Spatial interpolation scheme based on method used in WNDFLD. No temporal interpolation needed because data were available every third hour which is the temporal scale for calculations in ENAMAP.

Precipitation

1. Precipitation data obtained from University of Michigan (UM) in gridded format suitable for input to ENAMAP.
2. ESE program developed to compare gridded to station amounts.

Dry Deposition

1. ESE program developed to compute $SO_2$ and $SO_4^{-2}$ dry-deposition velocities for model domain based on published deposition velocities (Sheih et al., 1979, Sheih, 1980) calculated as a function of land-use type, stability, and season.
2. At night time, dry-deposition velocities over land were set to 0.05 cm/sec.

Emissions

1. ESE programs developed to process FCG, APIS, NAPAP, and NEDS data into suitable format for model domain.
2. Extensive review and QA checks were performed to ensure reasonableness of data (e.g., estimated emissions, plant location).

For input to these programs, national databases were used and were identified through contact with the following agencies or firms:

1. Florida Utilities;
2. DER, including branch offices;
3. EPA, including regional offices;
4. NOAA Air Resources Laboratory (ARL);
5. NCC;
6. UM;
7. Argonne National Laboratory;
8. Brookhaven National Laboratory;
9. NCAR;
10. EPRI;
11. State air quality control agencies; and
12. County air quality control agencies.

These contacts resulted in the development of comprehensive databases that are summarized in Table 3.2-3.

Because of the magnitude of these databases, there is a high probability that data for individual points, i.e., emission or meteorological points, may be sometimes incomplete or incorrect. For example, the NAPAP database for the entire United States contains point-source information for 50,224 plants and 201,131 emission points within those plants, and a total of 3,069 area-source records which correspond to each of the counties within the United States. The meteorological data supplied by NOAA (i.e., NAMER-WINDTEMP) contains upper-air wind and temperature data for two observations per day at over 150 stations in North America. Individual errors, however, could be averaged out in performing large model runs and should not influence the results beyond that originally anticipated in modeling of this type.

Table 3.2-3. Summary of Databases Used in LRT Modeling

| Data | Source | Description/Use | Processing Requirements |
|---|---|---|---|
| Emissions | | | |
| Florida APIS | Florida DER | Florida nonutility point-source emissions | Error checks; emission changes and updates; reformat and grid for model input |
| NEDS | EPA | Florida area-source emissions | Error checks; emission changes and updates; reformat and grid for model input |
| FCG Utility-ESE Format | FCG | Florida utility point-source emissions | Error checks; emission changes and updates; reformat and grid for model input |
| NAPAP | EPA | Non-Florida point- and area-source data | Error checks; emission changes and updates; reformat and grid for model input |
| Meteorological Data | | | |
| NAMER-WINDTEMP (upper-air data) | NOAA-ARL | Computation of transport winds, mixing heights | Develop wind components and mixing heights; error checks; reformat and grid for model input |
| Precipitation | UM | Hourly precipitation for wet-deposition calculations | UM prepared data in proper grid format |
| Surface Observations | NCC | Computation of atmospheric stability for deposition calculations | Develop stability; reformat and grid for model input |

Table 3.2-3. Summary of Databases Used in LRT Modeling (Continued, Page 2 of 2)

| Data | Source | Description/Use | Processing Requirements |
|---|---|---|---|
| WNDFLD Data | NAMER-WINDTEMP | Gridded meteorological data for ENAMAP | Develop/use 6 meterological parameters: wind direction and speed, stability, mixing height, horizontal and vertical diffusion coefficients |
| <u>Dry Deposition</u> | | | |
| Land use | Argonne National Laboratory | 12 land-use types for eastern United States every 0.5-degree increment; deposition rates as function of stability, land-use type, season | Reformat and grid for model input as function of stability and season |
| <u>Terrain</u> | | | |
| Terrain heights | Brookhaven National Laboratory | Terrain heights for model grid at 0.25-degree increments | Reformat and grid for model input |
| <u>Monitoring Data</u> | | | |
| $SO_4^{-2}$ wet deposition, $SO_2$ and particulate $SO_4^{-2}$ concentrations | FOG | Monthly deposition and concentration fields for Florida; compare with model results | Categorize data into appropriate grid cells; calculate monthly values |
| $SO_4^{-2}$ wet deposition | UAPSP | Monthly deposition fields for eastern U.S.; compare with model results | Categorize data into appropriate grid cells; calculate monthly values |

Source: ESE, 1986.

### 3.2.3.4 Model Application and Evaluation

The application and evaluation of the ENAMAP model to Florida involved two primary tasks: (1) model application and adjustment, and (2) model performance evaluation.

Prior to applying an LRT model to Florida, it was recognized that the model must first be specifically applicable to the conditions in the modeling domain. As discussed previously (Subsection 3.2.3.3), extensive modifications were made to ENAMAP that focused on the Florida-specific conditions and required: (1) establishing a new study area for Florida, and (2) reviewing all model assumptions and algorithms that may be influenced by Florida's meteorology (i.e., deposition rates). Although the early version of ENAMAP used in the United States-Canada Work Group investigation included Florida in its study area, Florida defined the extreme southeastern model boundary. However, boundary conditions, such as loss of mass flux by transport out of the model domain, can distort the results. In order to ensure minimum boundary effects, therefore, the ENAMAP domain used in this study was oriented over the southeastern United States to allow a more realistic simulation of winds and precipitation in and around Florida. In addition, certain parameterizations, i.e., $SO_2/SO_4^{-2}$ transformation rates, were also modified to better account for possible Florida-specific effects.

In the first task, the application and adjustment of ENAMAP was made by first comparing the model estimates to observed concentration and deposition fields for a selected period (i.e., 3 months). Then, based on these initial model comparisons, selected algorithms of the model were adjusted to produce estimates of concentration/deposition fields that compare better with the observed monitoring data. After these adjustments were finalized, the model was rerun for the entire set of data (i.e., 6 months), and a final set of statistics was produced to evaluate overall model performance.

The selection of the monitoring data for these tasks was similar to that followed by the United States-Canada Work Group 2 (1982). For the MOI study, model estimates were made and compared with concentration/deposition fields for 2 months, January and July. The monitoring data used in the MOI study were considered to cover a range of concentration/deposition fields likely to occur in the model domain, be spatially representative of the model domain, and be of known and consistent quality. As a consequence, the selection of the monitoring data for applying and evaluating ENAMAP for Florida was based on being:

1. Representative of a range of $H^+$ and excess $SO_4^{-2}$ depositions and representative of the range in concentrations of particulate $SO_4^{-2}$ and $SO_2$,
2. Regionally representative of Florida, and
3. Of documented quality.

To meet these selection requirements, the data collected from the monitoring network was reviewed for the period September 1982 through September 1983. During this period, a nine-station network was operated at spatially representative sites in Florida (see Figure 2.3-1). These nine monitoring sites were located at intervals of approximately 160 km and were generally more than 50 km from major sources of emissions. Two sites, however, were located within 50 km of major point sources. Statistical analyses of precipitation chemistry data from the network found $H^+$ and excess $SO_4^{-2}$ at these sites to be generally higher than other sites; consequently the final evaluation of modeling results will consider the effect of these sites. Thus, the data collected at these sites are representative of Florida (i.e., grid scale greater than 80 km) and generally did not include the influences of nearby emission sources.

In addition, as presented in Subsection 2.4, the data quality was consistent throughout the network with precision and accuracy within identified ranges. The monthly periods to be modeled were selected by the following four steps:

1. Determining concentration ($SO_2$ and particulate $SO_4^{-2}$) and wet-deposition ($H^+$ and $SO_4^{-2}$) averages on individual station and statewide bases for monthly time periods.
2. Identifying the monthly average concentration and deposition and determining the locations and time periods during which the lowest to highest values were observed at each monitoring site. This procedure would allow a relative comparison of the spatial and temporal differences of the measurements to be identified among all stations.
3. Analyzing the monthly average concentration and deposition for each site to identify those periods during which the range of monthly averages was obtained for individual stations and all stations.
4. Selecting monthly periods which would produce a representative range of concentrations and depositions. Note: These periods did not have to include the highest or lowest concentration or deposition measured at each site; rather the concentrations and depositions measured during these monthly periods provide a representative data set of highest to lowest values measured over the entire monitoring network.

The results of this evaluation indicated that 6 months could accomplish the objective of the modeling effort. The 6 months selected, which include both frontal and convective precipitation across the state, were: February, March, April, June, July, and August 1983. During these months, a wide range of $SO_2/SO_4^{-2}$ concentrations and $H^+/SO_4^{-2}$ depositions was observed on a statewide basis and at individual sites. This is illustrated by Table 3.2-4 which presents the monthly $H^+$ deposition, excess $SO_4^{-2}$ deposition, rainfall amount, particulate $SO_4^{-2}$, and $SO_2$ concentrations as ratios of the average observations over the period September 1982 through September 1983. For the 6 months selected, $H^+$ and excess $SO_4^{-2}$ deposition differed by factors of 2.3 and 1.4, respectively. During this same period, particulate $SO_4^{-2}$ and $SO_2$ differed by factors of

Table 3.2-4. Monthly $H^+$ Deposition, Excess $SO_4^{-2}$ Deposition, Rainfall Amount, Particulate $SO_4^{-2}$ Concentrations, and $SO_2$ Concentrations as Ratios of Monthly Averages Over the Period September 1, 1982, Through September 30, 1983

| | 1982 | | | | 1983 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sept. | Oct. | Nov. | Dec. | Jan. | Feb. | Mar. | Apr. | May | June | July | Aug. | Sept. |
| $H^+$ Deposition (Ratio of Monthly to 13-Month Average) | 1.66 | 0.46 | 0.20 | 0.29 | 0.65 | 0.90 | 1.09 | 0.85 | 0.52 | 1.55 | 1.86 | 1.92 | 0.99 |
| Excess $SO_4^{-2}$ Deposition (Ratio of Monthly to 13-Month Average) | 1.48 | 0.56 | 0.26 | 0.38 | 0.85 | 1.08 | 1.44 | 1.30 | 0.66 | 1.18 | 1.55 | 1.42 | 0.87 |
| Rainfall Amount (Ratio of Monthly to 13-Month Average) | 1.25 | 0.72 | 0.33 | 0.57 | 1.13 | 1.39 | 1.40 | 1.09 | 0.49 | 1.66 | 0.90 | 1.13 | 0.94 |
| Particulate $SO_4^{-2}$ (Ratio of Monthly to 11-Month Average) | * | * | 0.60 | 0.68 | 0.91 | 0.89 | 1.38 | 1.13 | 1.26 | 0.84 | 1.50 | 1.03 | 0.82 |
| $SO_2$ (Ratio of Monthly to 11-Month Average) | * | * | 0.56 | 1.16 | 1.65 | 1.33 | 1.20 | 1.16 | 0.93 | 0.65 | 0.83 | 0.78 | 0.81 |

*Ambient air monitoring equipment not in operation.

Source: ESE, 1986.

1.7 and 2.0, respectively. The months of February, March, and April 1983 experienced 22 percent of the 13-month $H^+$ deposition, whereas June, July, and August 1983 experienced 41 percent; the 6-month total was 63 percent. Similarly, the excess $SO_4^{-2}$ deposition was 29 percent and 32 percent for the periods February-March-April and June-July-August, respectively.

Although the focus of the modeling effort was on Florida wet deposition, monitoring data for the eastern United States was used in both the model application and adjustment, and performance evaluation tasks. The data used for this purpose consisted of 14 sites operated by the UAPSP network. Data from this network was selected because it was spatially representative over the adjusted ENAMAP grid and the sampling and analytical procedures were similar to the Florida network.

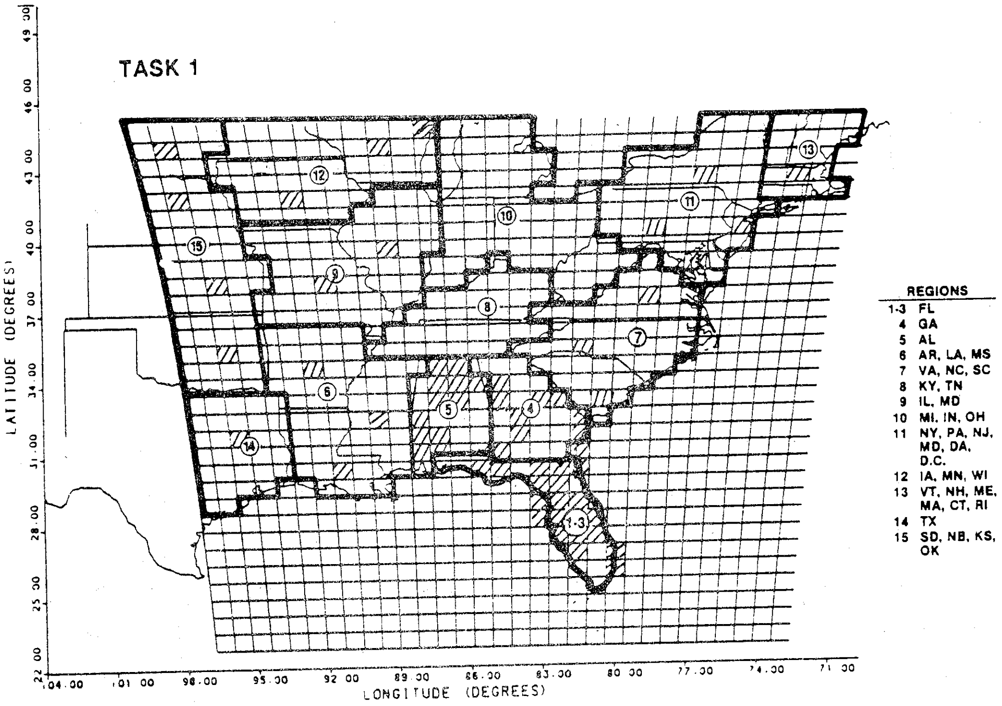
A detailed description of Tasks 1 and 2 follows.

Task 1--Model Application and Adjustment

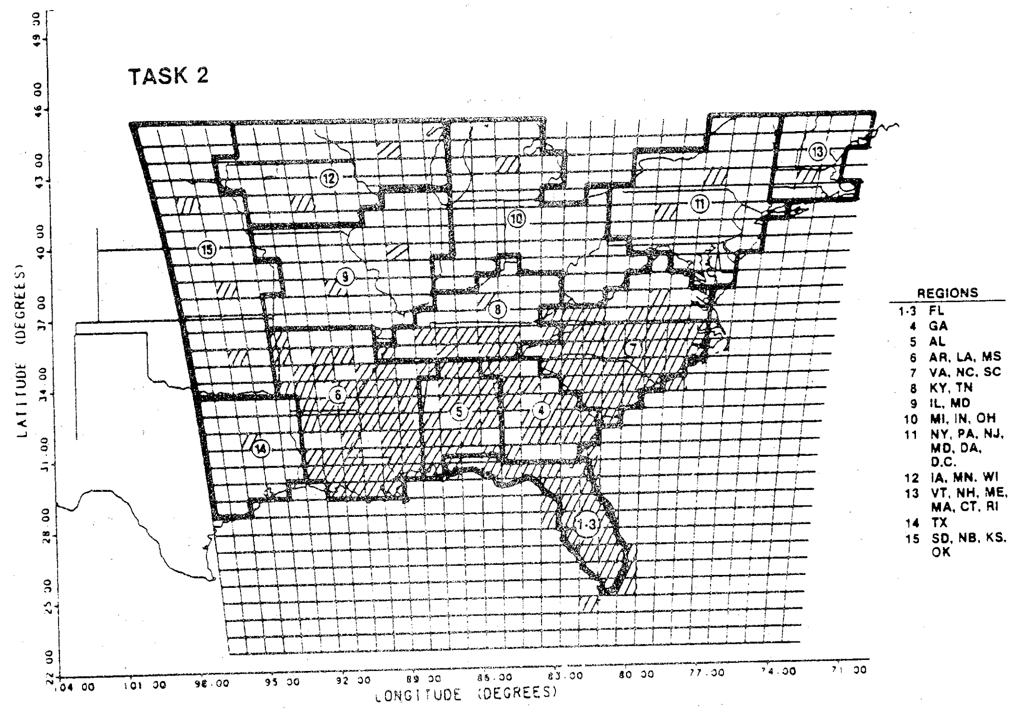
Objective: Compare model simulations to monitored data and adjust model methods and assumptions to produce better comparison.

1. For the purpose of computation and economy, treatment of $SO_2$ emissions differed in several respects from model application and adjustment (Task 1) to model performance evaluation (Task 2). These differences are illustrated in Figure 3.2-2. During initial model applications and adjustments, consolidated emission cells were used to represent Florida, Georgia, and Alabama sources. This was performed by eliminating cells with total (i.e., point plus area) emissions of less than 1,000 kg of $SO_2$ per hour, and assigning those emissions to a nearby cell with emissions greater than 1,000 kg of $SO_2$ per hour. Total emissions within each state were thus preserved; however, the spatial resolution of emissions was reduced. For all other states in the model domain, except Delaware and the New England states, emissions were located in a single cell (centroid)

TASK 1



TASK 2



▨ EMISSION GRIDS

Figure 3.2-2
EMISSION CONFIGURATION USED IN
ENAMAP SIMULATIONS

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within each state. Delaware emissions were consolidated with those from Maryland. New England state emissions were assigned to a single cell located in central Massachusetts (i.e., the New England state with the highest emissions). These modifications of the emission field were considered necessary to maintain computational economy during successive iterations and adjustments of ENAMAP.

2. Run the model for 3 of the 6 months selected (i.e., February, July, and August). The 3 months chosen for developing and testing the model had monthly average concentrations and depositions that represent the range of values measured over the entire network. For those 3 months, model simulations produced monthly concentrations and depositions for all grid cells in Florida.
3. Based on comparison of the model simulations to the observed data, the model was adjusted to improve agreement between predictions and observations. Model adjustments made included, but were not limited to, the following:
    a. Transformation rates (currently, an arbitrary factor of 1.5 has been recommended and used by SRI for the heterogeneous portion).
    b. Wet-deposition rates and the area over which they apply (currently, the rates have been divided by a factor of 10, apparently to adjust rainfall data measured at a point to an area defined by a grid).
4. Based on the combination of adjustments made to the simulations, the resulting model predictions were compared with observations. The combination of model assumptions that produced the closest comparison between observed and predicted results was used in subsequent modeling analyses.

Task 2--Model Performance Evaluation

Objective: Perform model simulations for the 6-month database and make final model evaluation.

1. For this task, the spatial resolution of emissions was considered to be much more important. Therefore, gridded emissions were used for the nine southeastern states (Florida, Georgia, Alabama, Louisiana, Arkansas, Mississippi, North Carolina, South Carolina, and Tennessee) and centroids were used for all other states. Emissions from certain cells also were consolidated in the southeastern states, but, in this case, only for cells amounting to less than 200 kg of $SO_2$ per hour.
2. Executed the model for the remaining 3 months identified (i.e., February, April, and May) in Task 1 that were not modeled in Task 2. The model assumptions used were those selected in Task 1 that produced the best comparison of simulated to observed results. This procedure allowed a preliminary analysis using an independent data set that was different from that for which the model's assumptions were implemented.
3. Compared the simulated to observed concentration/deposition for the 3 months considered in the modeling to establish a preliminary quantification of model uncertainty and bias.

The difference, d(i), between the observed concentration (deposition) for a time period, Co(i), and simulated concentration (deposition) for the same time period, Cs(i), was the quantity used to generate statistics in assessing the performance of models. For a perfect model, all d(i)s would be zero, which is not realistic due to the practical limitation or model prediction. Thus, the model results showed d(i)s with non-zero values but had a mean value (bias) of zero and corresponded to a "noise" measure which can be defined as the estimated standard deviation of the differences. Based on the work of the United States-Canada Work Group 2 (1982), a model should meet the following criteria for each averaging period of interest:

a. The average of the difference, $\bar{d}$, between the observed concentration, Co, and simulated concentration, Cs, is equal to zero; $\bar{d}$ is the bias;

b. The standard deviation of d is small compared to the standard deviation of Cs, $\sigma$Cs [If $\sigma$d is not small in comparison to $\sigma$Cs, then either: (1) the spread in the residuals is large, or (2) the simulated values do not have a large spread ($\sigma$Cs is small), indicating that the simulations poorly reflect the observed values]; and

c. The average product of d(i) and Cs(i) is zero.

Therefore, the statistics and other techniques used in the modeling evaluation included:

a. Calculations of $\bar{d}$, $\sigma$d, and $\sigma$Cs; and

b. Comparison of Co versus Cs.

4. Final model results were presented for the entire model domain to produce a matrix of source and receptor region relationships for the 6 months of data evaluated. Figures also were produced to show the contour lines of simulated total concentration and deposition over the model domain. The source and receptor regions were identified for large areas (e.g., states or groups of states) for which the relative contribution of Florida and non-Florida sources to concentration and deposition in and out of Florida could be evaluated for the chosen time period. Large areas (i.e., source and receptor regions) were specified due to the uncertainty in modeling the impact of emissions from one location to another and/or attributing the total impact at one receptor from various source regions. However, based on this preliminary modeling exercise, the relative contribution of source emissions regions to receptor areas provided the first step in a qualitative assessment of acidic deposition in and out of Florida for the chosen time period.

As demonstrated by the methodology, an attempt was made to produce some representative source-receptor relationships through adjustments to the model. The model results and comparisons developed from this methodology are, however, preliminary. The results of these model simulations and methodologies are documented solely to gain additional information and experience in acid deposition modeling to Florida. Further model input/output and parameterization uncertainty analyses and a rigorous verification and validation study must be accomplished to establish the credibility of the model. Major efforts are currently being implemented and planned by national research groups (e.g., EPRI, EPA) to accomplish these tasks. The development, diagnostic applications, and evaluations of LRT models will continue to be reviewed to determine the applicability to Florida of the various modeling techniques and assumptions that are generally developed for the continental United States.

As a result of model limitations, the primary purpose of applying, adjusting, and evaluating an LRT model for this study was to:

1. Identify the modeling uncertainties involved in modifying the existing techniques and databases for a Florida-specific application;
2. Identify additional studies that should be performed or data that should be collected to improve the model parameterizations and overall model performance for Florida application;
3. Test and modify the current model assumptions and methods used in defining the chemical and physical processes involved in relating emissions to simulated concentration and deposition fields;
4. Produce simulations that compare better with monitored concentrations and depositions; and
5. Prepare a qualitative assessment of the relative contribution of Florida and non-Florida sources to atmospheric deposition in and out of Florida.

### 3.2.4 AIR MASS TRAJECTORY ANALYSIS

#### 3.2.4.1 NOAA-ATAD Model Description

The NOAA-ATAD trajectory model (Heffter, 1980) was used to compute 3-day backward trajectories for numerous locations (receptors) in Florida. The NOAA-ATAD model has been described previously (ESE, 1985). Briefly, the model estimates atmospheric transport:

1. From any origin in the northern hemisphere;
2. For four trajectories per day for a month or season;
3. Forward or backward in time;
4. For a duration of 1 to 5 days for each trajectory;
5. From observed and/or derived winds averaged in a layer above the terrain;
6. From at least two upper-air stations within 560 km, or one station within 280 km, of the last trajectory segment computation; and
7. Through a mixing layer calculated using atmospheric temperature profiles.

The meteorological data used in the model are upper-air observations collected by the United States Air Force (USAF), sorted by synoptic time, and stored on magnetic tape. ARL extracts data from these tapes and creates a database containing upper air winds, temperatures, and heights for North America from the surface to 500 mb (approximately 18,000 ft). Data have been archived beginning in 1975 and are available through December 1983. The data are collected primarily at the meteorological observing times of 00Z and 12Z corresponding to 1900 and 0700 hours Eastern Standard Time (EST), respectively. Limited data from USAF meteorological stations are also available for observation times of 06Z and 18Z, or 0100 and 1300 EST.

Output from the model consists of a series of trajectories that illustrate the estimated path of transport either away from a point (forward trajectory) or toward a point (backward trajectory). Also produced by NOAA-ATAD are mixing depths which are essential for calculating import to and export from Florida.

A backward trajectory ends at a specified location (or receptor) and time; it is based on data from the previous 1 to 5 days. A forward trajectory begins at a specified location (or source) and time; it is based on data from the following 1 to 5 days. The trajectories are composed of 3-hour segments, with each segment computed assuming persistence of the winds reported closest to the segment time. For example, the segments from 15 to 18Z and 18 to 21Z are computed from the 18Z observations.

The model domain used in this study was bounded by latitude 20 to 50°N and longitude 65 to 105°W. This region covers the entire eastern United States, portions of the Atlantic Ocean and Gulf of Mexico, and a small portion of Canada. Four monitoring stations were chosen during Phase IV as receptors in the model to represent the spatial variations of atmospheric transport across the state. The monitoring stations selected were:

- Caryville, located in the Florida panhandle at latitude 30.79°N and longitude 85.81°W;
- Gainesville, located in the northern Florida peninsula at latitude 29.63°N and longitude 82.49°W;
- Archbold, located in the central Florida peninsula at latitude 27.18°N and longitude 81.35°W; and
- The Everglades, located in the southern Florida peninsula at latitude 25.75°N and longitude 80.96°W.

### 3.2.4.2 Five-Year Climatology of Trajectories

The purpose of the climatological analysis is to develop information on the principal modes of atmospheric transport into Florida and potential year-to-year differences in atmospheric transport. For this analysis, air mass trajectories were calculated over the 5-year period January 1, 1979, through December 31, 1983, for Gainesville, Caryville, Archbold, and the Everglades.

Directional frequency distributions of 24-hour, 48-hour, and 72-hour backward trajectories were developed by classifying trajectories into eight 45° sectors around each of the monitoring stations:

1. North, >337.5° to 22.5°;
2. Northeast, >22.5° to 67.5°;
3. East, >67.5° to 112.5°;
4. Southeast, >112.5° to 157.5°;
5. South, >157.5° to 202.5°;
6. Southwest, >202.5° to 247.5°;
7. West, 247.5° to 292.5°; and
8. Northwest, >292.5° to 337.5°.

Figure 3.2-3 illustrates the eight sectors that were used in classification, centered on the Gainesville receptor. Trajectories were classified by determining the direction of a trajectory endpoint with respect to its origin (i.e., receptor).

The eight 45° sectors selected as trajectory directions provide a sector large enough to reduce errors in estimating the trajectory direction, yet small enough to discriminate between major source regions in the eastern United States. Pack _et al_. (1978) and Mueller (1983) have reported mean directional errors in trajectory calculations on the order of ±15° to ±20°. Although these findings pertain to different geographic areas and time periods than those presented here, they imply that trajectories can be classified reliably by direction only if sector width exceeds 30° to 40°, or 2 times the mean directional error.

Frequency distributions of 6-hour through 72-hour backward trajectories were also developed by location for well-defined regions within the model

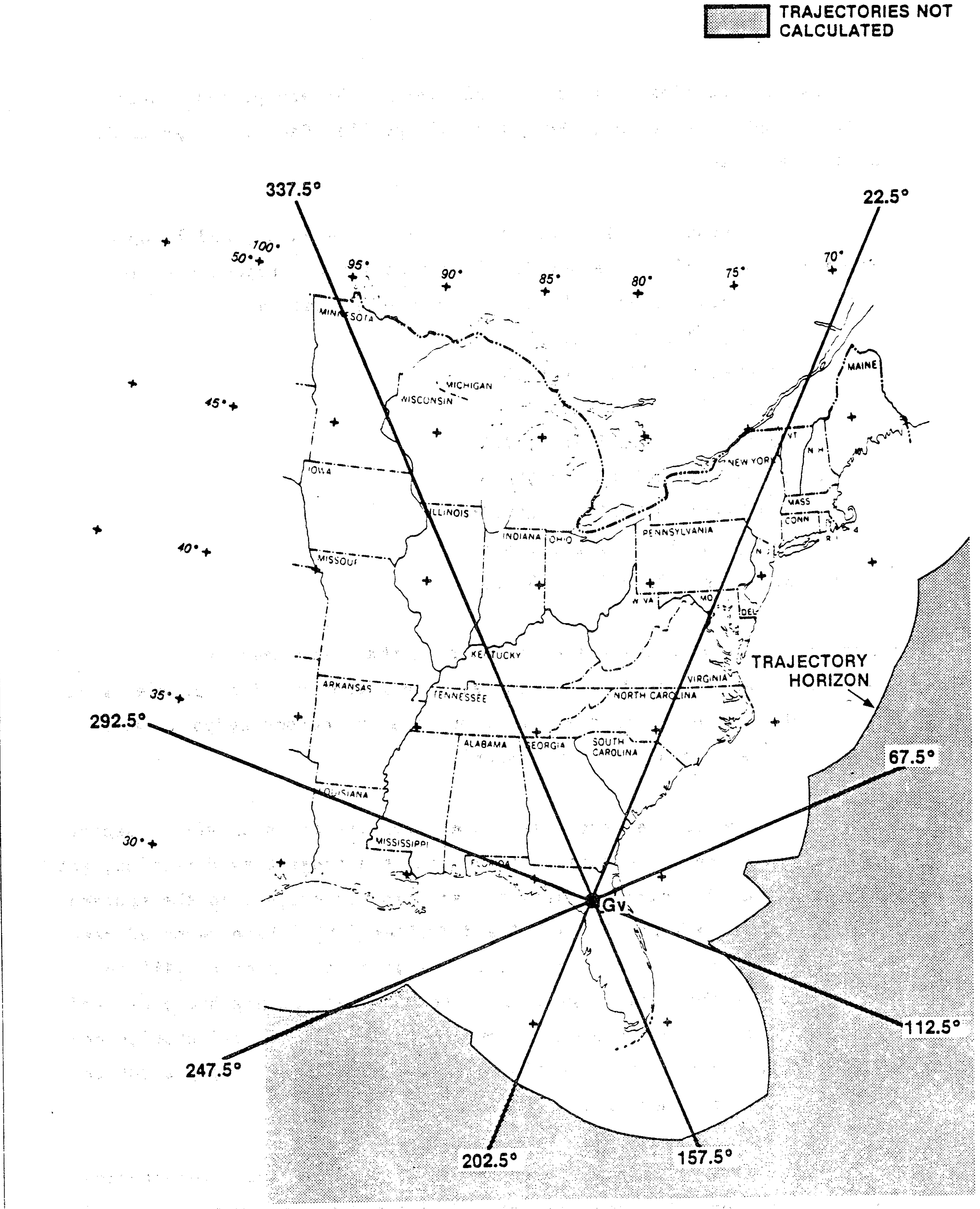

Figure 3.2-3
DIRECTIONS USED TO CLASSIFY TRAJECTORIES FOR GAINESVILLE, FLORIDA

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domain. These regions are defined by individual states or groups of states (see Table 3.2-5). To better define transport within Florida, the state was divided into three regions: panhandle, northern peninsula, and southern peninsula. In general, states were grouped together in order to: (1) produce regions of increasing area with increasing distance to Florida, and (2) consolidate states with similar emission densities for $SO_2$.

This method of trajectory evaluation has two advantages over the sectoral analysis previously described. First, whereas sectoral analysis relies on a coordinate system unique to each receptor, allocation of trajectory endpoints to states (regions) does not depend on receptor location. Trajectory distributions, therefore, may be easily compared across receptors. Second, summation of trajectory segment allocations can be used to estimate air mass residence time within each region (i.e., 6 hours per segment). This, in turn, can be used to elucidate the major corridors of air mass transport to Florida.

The principal disadvantage of state-by-state (or regional) trajectory allocation is that errors in trajectory calculation (i.e. length and direction) increase with distance from the receptor. However, for the sectoral analysis, the dimensions of each sector expand with distance from the receptor in a manner roughly consistent with estimates of trajectory uncertainty (Pack et al., 1978).

### 3.2.4.3 NAMER-ATOLL Trajectories

Results of trajectory calculations performed earlier indicated that a significant fraction of trajectories could not be calculated due to the lack of NAMER-WINDTEMP data over the Atlantic Ocean and Gulf of Mexico. The frequency and duration with which trajectories were calculated decreased significantly from panhandle Florida (i.e., Caryville) to southern Florida (i.e., Archbold). For example, 3-day backward trajectories for Archbold could be calculated only approximately 28 percent of the time (ESE, 1984).

Table 3.2-5. Regions Used in Residence Time Analysis of Air Mass Trajectories

| Region Number | Region | Area ($10^5$ km$^2$) | $SO_2$ Emission Density* |
|---|---|---|---|
| 1 | Florida-Panhandle | 0.35 | 4.9 |
| 2 | Florida-Northern Peninsula | 0.62 | 7.3 |
| 3 | Florida-Southern Peninsula | 0.55 | 6.9 |
| 4 | Georgia | 1.52 | 5.2 |
| 5 | Alabama | 1.34 | 5.8 |
| 6 | Arkansas, Louisiana, Mississippi | 3.88 | 2.1 |
| 7 | Virginia-North Carolina-South Carolina | 3.22 | 3.9 |
| 8 | Kentucky-Tennessee | 2.09 | 10.0 |
| 9 | Illinois-Missouri | 3.26 | 7.7 |
| 10 | Michigan-Indiana-Ohio-West Virginia | 4.15 | 14.4 |
| 11 | New York-Pennsylvania-New Jersey-Maryland-Deleware | 2.98 | 10.4 |
| 12 | Iowa-Minnesota-Wisconsin | 5.09 | 2.4 |
| 13. | Vermont-New Hampshire-Maine-Massachusetts-Connecticut-Rhode Island | 1.73 | 3.7 |
| 14 | Texas | 6.92† | 1.8 |
| 15 | South Dakota-North Dakota-Kansas-Oklahoma | 12.5† | 0.5 |
| 16 | Canada | 3.07† | 1.8 |
| 17 | Mexico | 4.61† | <0.5** |
| 18 | Gulf of Mexico | ND | <0.5** |
| 19 | North Atlantic | ND | <0.5** |
| 20 | South Atlantic | ND | <0.5** |

NOTE: ND = Not determined.
*Units are metric tons per square kilometer (MT/km$^2$); emission data taken from NAPAP 1980 inventory for non-Florida regions
†Area within a model domain.
**Estimate

Source: ESE, 1986.

Based on these results, a review of supplemental meteorological databases for the NOAA-ATAD model was conducted such that these data could reliably calculate trajectories over large water bodies. The two databases reviewed and evaluated were the Limited Fine Mesh (LFM) analysis produced by the National Meteorological Center (NMC) and the Atlantic Tropical Oceanic Lower Layer (ATOLL) analysis produced by the National Hurricane Center (NHC). The LFM wind field is computed by a general circulation model of atmospheric dynamics, whereas the ATOLL database relies on satellite imagery of cloud movements, as well as ships' observations.

Based on an evaluation of these two data sets, the ATOLL data were selected for use in the ATAD model for two reasons. First, since the NAMER-WINDTEMP data are based on direct measurements of upper-air parameters, use of ATOLL winds as a supplemental database may provide more consistent model input because it is derived, in part, from observational data. Second, the spatial resolution of ATOLL data is somewhat better than the spatial resolution of LFM and should be a distinct advantage for trajectory calculations. It should be noted that LFM is a more highly computerized simulation and as such has twice the temporal resolution compared to the ATOLL (i.e., four versus two analyses per day). However, since the NAMER-WINDTEMP data are produced only twice per day at most upper-wind stations, full advantage of the temporal resolution of LFM could be made only if it were adopted as the primary database for the NOAA-ATAD model. This option was considered but ultimately rejected, since the NAMER-WINDTEMP data contain temperature information essential for calculation of mixing depths by the NOAA-ATAD model.

The NOAA-ATAD model was modified to accept wind data from the ATOLL dataset. In order for the NAMER-WINDTEMP and ATOLL datasets to be consistent, the model was modified to compute the U and V wind components within the transport layer using the NAMER-WINDTEMP data. Trajectories were calculated for both data sets for the four monitoring stations.

Also, trajectories were calculated for the period September 13, 1982, through September 11, 1983. Preliminary analyses were performed to assess trajectory calculations for the following data input to the model:

- NAMER-WINDTEMP data only,
- ATOLL data only, and
- NAMER-WINDTEMP and ATOLL data.

In general, whenever ATOLL data were used, the following model assumptions were made:

1. When only ATOLL data were used, the trajectories were computed from at least one ATOLL grid point within 83 km (i.e., 45 nautical miles) of the last trajectory segment calculation (no adjustment in search distance was made for the NAMER-WINDTEMP data).
2. When both ATOLL and NAMER-WINDTEMP data were used, the trajectories were calculated primarily on NAMER-WINDTEMP data unless these data were missing (i.e., beyond the trajectory horizon). The ATOLL data were used to continue the trajectory calculation beyond the trajectory horizon from the last trajectory segment determined from the NAMER-WINDTEMP data.

The first assumption was made to reduce the bias that would be introduced in the trajectory calculations due to the large number of available ATOLL grid point values (i.e., every 1.5°, or approximately 140 km) compared to the available NAMER-WINDTEMP data (i.e., upper-air stations located 300 to 500 km apart). Since trajectories using the NAMER-WINDTEMP data were generally based on observations from one or two upper-air stations, this number of observations was also applied to the ATOLL data. From preliminary evaluations using the ATOLL data, one or two grid point values were used in trajectory computations if the separation distance between the grid point and trajectory segment was approximately 83 km.

The second assumption was made to place greater emphasis on a transport wind that is based on observational data obtained within a defined transport layer. The transport wind derived from NAMER-WINDTEMP data was developed using wind observations up to the mixing height. The wind data available from the ATOLL data set were assumed to represent a transport wind but were actually based on observations for one height. Therefore, errors in trajectory computations were introduced if winds measured at that height were not representative of the transport layer. However, the wind speed and direction of transport winds derived from comparing NAMER-WINDTEMP data and ATOLL data were within (95-percent confidence interval) ±1 meter per second (m/sec) and ±15°, respectively.

### 3.2.4.4 Analysis of Trajectory and Monitoring Data

The purpose of this analysis was to develop relationships between several broadly defined categories of trajectory origin, precipitation chemistry (e.g., $H^+$, $SO_4^{-2}$, $NO_3^-$), air chemistry (i.e., particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$), and emission (i.e., $SO_2$ and $NO_x$) data. For this analysis, air mass trajectories calculated over the period September 11, 1982, through September 13, 1983, were analyzed with the monitoring data collected at the Caryville, Gainesville, Archbold, and the Everglades sites. This year was selected since it represents the same year that LRT modeling was performed and daily precipitation chemistry data as well as ambient air monitoring data were available for these four sites. Analysis of trajectory climatologies indicated that year-to-year variability was low and that the study year would produce representative results. In addition, difficiencies in precipitation chemistry and ambient air concentrations were found for different meteorological conditions at different sites, suggesting that trajectory analysis was require for these four sites in Florida. Three basic procedures were performed:

1. Selection of trajectory endpoints and classification by sector;
2. Sorting precipitation and air samples by trajectory sector; and
3. Analysis of trends in precipitation and air chemistry and emissions data as a function of trajectory sector.

Trajectory Data--Backward trajectories from the Phase III period were selected for periods of precipitation which occurred at monitoring sites located in Caryville (Site 2), Gainesville (Site 5), Archbold (Site 9), and the Everglades (Site 13). Trajectory endpoints 12, 24, 48, and 72 hours prior to the end of representative precipitation events were then selected and classified by sector, as described previously. The time of precipitation was determined from rain gage charts for each site. The most representative trajectory (i.e., 00Z, 06Z, 12Z, or 18Z) was then used in the analysis. For the analysis, trajectories 6 hours before and after the precipitation event were used. If two precipitation events were noted during a 24-hour sample collection interval, individual trajectories were selected only if the events were separated by 6 hours or more. In this case, each trajectory was assigned a portion of the 24-hour total rainfall based upon the amount of rainfall occurring within each event.

Precipitation and Air Chemistry Data--Precipitation and air chemistry data for each site were sorted into groups as a function of trajectory sector at the cessation of rainfall. To ensure that all samples used in this analysis meet all QA criteria, only samples with sufficient volume for complete chemical analysis were used. In practice, this excludes only those events with less than approximately 0.05 inch of precipitation and, on average, less than 1 percent of annual precipitation at the monitoring sites. Precipitation and air chemistry data for each site and each group were treated as individual data points for the statistical analysis.

Analysis--VWM precipitation chemistry for each sector (or sector group) and for each site was computed for the following ions: laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$-N; mean air chemistry data for each sector (or sector group) and for each site were computed for particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$. Rainfall amount was also determined for the precipitation chemistry classification. For the case study periods, total emissions by sector were computed for $SO_2$ and $NO_x$.

### 3.2.4.5 Atmospheric Transport Across Florida Boundaries

Atmospheric transport of $SO_x$ and $NO_x$ into Florida was estimated by using air mass trajectory data and air monitoring data for the period September 1982 through September 1983. In the context of this study, $SO_x$ and $NO_x$ are defined as particulate $SO_4^{-2}$ plus $SO_2$ and $HNO_3$ plus $NO_2$, respectively. Imports of $SO_x$ and $NO_x$ to the state were evaluated for the following boundaries: northern, eastern, western, and southern (see Figure 3.2-4). The northern boundary is 600 km in length and is situated along latitude 31°N between longitude 85.1°W and 87.5°W. The eastern boundary (670 km in length) is situated at longitude 80°W between latitude 25°N and 31°N. The western boundary (450 km in length) is situated at longitude 83°W between latitude 25°N and 29°N. The southern boundary consists of a western section and an eastern section. The western section corresponds to the southern boundary for the Florida panhandle, and the eastern section corresponds to the southern boundary for the Florida peninsula. The western section of the southern boundary is 440 km in length and is situated along latitude 29°N between longitude 83°W and 87.5°W. The eastern section of the southern boundary (300 km in length) is situated along latitude 25°N between longitude 80°W and 83°W.

Import estimates for the state were performed by summing the transport of $SO_x$ and $NO_x$ across each of the defined boundaries, as shown in the following expression:

$$F = \sum_{i=1}^{5} B_i \times \bar{L}_i \times \bar{H}_i \times \bar{C}_i \qquad (3.2\text{-}1)$$

where:

$F$ = 24-hour average flux of $SO_x$ and $NO_x$,

$B_i$ = length of $i^{th}$ boundary,

$\bar{L}_i$ = mean 24-hour average length of backward trajectories crossing $i^{th}$ boundary,

$\bar{H}_i$ = mean 24-hour average mixing depth for backward trajectories crossing $i^{th}$ boundary,

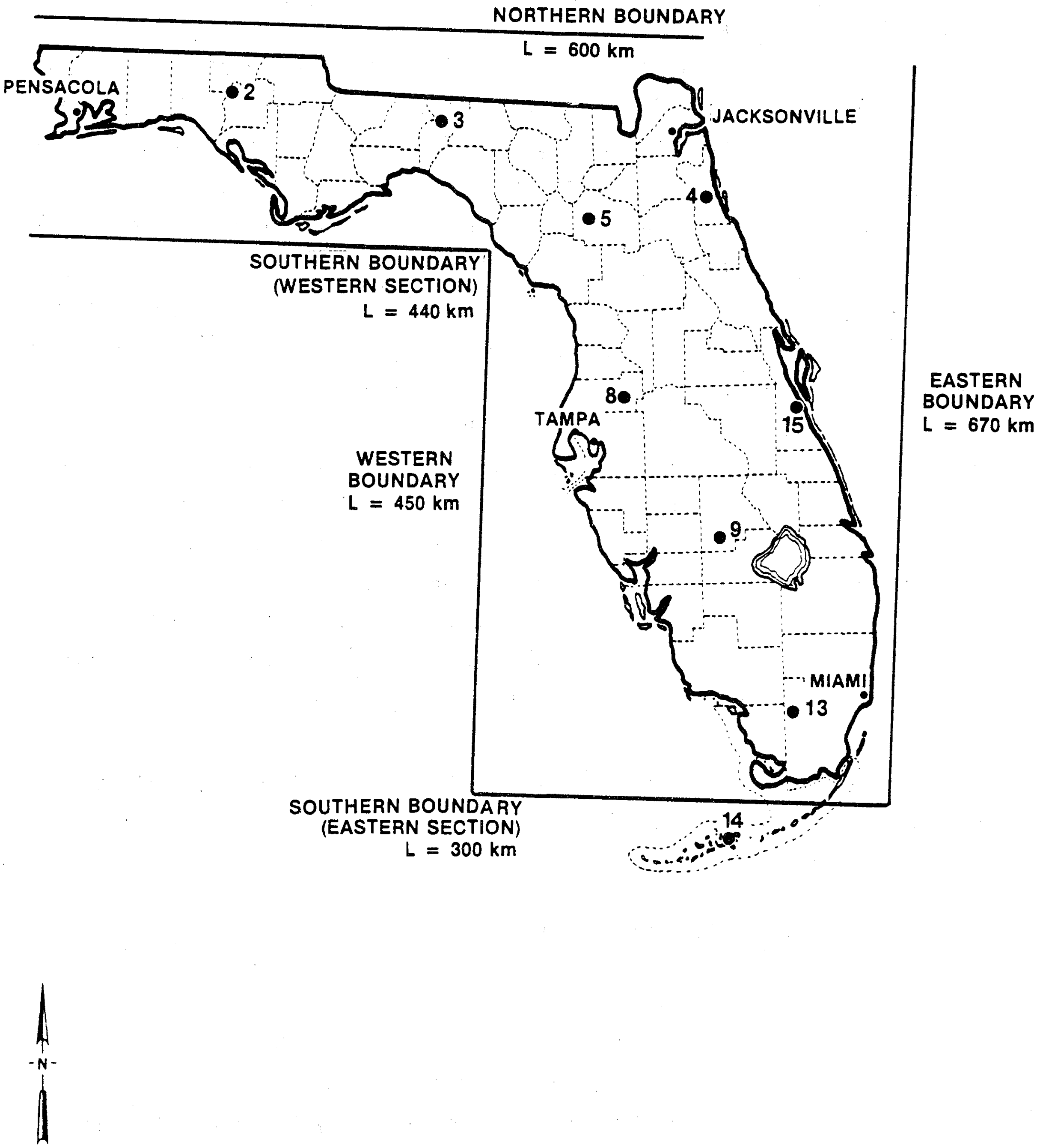


Figure 3.2-4
BOUNDARIES AND AIR MONITORING SITES USED TO ESTIMATE IMPORT OF $SO_X$ AND $NO_X$ TO FLORIDA

ENVIRONMENTAL SCIENCE
AND ENGINEERING, INC.

$\bar{C}_i$ = mean 24-hour average concentration of $SO_x$ and $NO_x$ crossing $i^{th}$ boundary,

$SO_x$ = particulate sulfate anion as sulfur ($SO_4^{-2}$-S) plus sulfur dioxide as sulfur ($SO_2$-S), and

$NO_x$ = nitric acid as nitrogen ($HNO_3$-N) plus nitrogen dioxide as nitrogen ($NO_2$-N).

This flux equation assumes that atmospheric concentrations taken from 10-m air sampling towers are representative of average concentrations through the mixing depth. Sufficient data are not currently available to test this assumption. However, the air sampling locations that were used in the computation of flux estimates were usually over 50 km from major point sources of $SO_x$ or $NO_x$. At such distances (i.e., >50 km), uniform concentrations from such sources will likely occur through the mixing depth especially over the sampling interval of 24 hours. As a consequence, the assumption appears reasonable as an initial estimate of $SO_x$ and $NO_x$ fluxes into Florida.

Trajectory lengths ($L_i$) were determined by calculating 24-hour backward trajectories for receptors close to each boundary. Site 2 was used as the receptor for air masses crossing the northern boundary and the western section of the southern boundary. Sites 5 and 9 were used as receptors for the eastern and western boundaries. Site 14 was used as the receptor for the eastern section of the southern boundary. Backward trajectories were calculated for Daytona Beach (see Figure 3.2-3) in order to test data from Sites 5 and 9 for evaluating transport across the eastern boundary. Trajectories for each receptor were then sorted by sector (i.e., direction) to determine the frequency of import across each border. As an example, Site 2 trajectories were sorted into a northern sector (i.e., 337.5° to 22.5°) used to calculate transport across the northern boundary. Trajectories which were sorted into the southern sector (i.e., 157.5° to 202.5°) were used for transport across the western section of the southern boundary.

Mixing depths, also taken from ATAD, were averaged over the 24-hour duration of each trajectory to produce typical values for each of the state boundaries. The product of boundary length times mean 24-hour average mixing depth times trajectory length yielded air mass transport across each of the state boundaries.

Atmospheric $SO_x$ (i.e., particulate $SO_4^{-2}$-S + $SO_x$-S) and $NO_x$ (i.e., $HNO_3$-N + $NO_2$-N) crossing each boundary were determined using air monitoring data from selected stations. To minimize the influence of local emissions, only the station(s) nearest each boundary were used in the import calculation. Thus, data from Sites 2 and 3 were averaged to produce influx concentrations for the northern boundary; and data from Sites 5, 9, and 13 were averaged to produce concentrations for the western boundary. Sites 4 and 15 were averaged to produce concentrations for the eastern boundary, whereas Sites 2 and 14 were used for the western section and the eastern section of the southern boundary, respectively. Trajectories for each air sampling date were sorted by sector, and average ambient concentrations by sector were then computed. These average concentrations were then used in Equation 3.2-1 to compute annual $SO_x$ and $NO_x$ import across each boundary. Total import of $SO_x$ and $NO_x$ was determined by summing across all boundaries.

### 3.2.4.6 Mass-Balance Model

The mass-balance model consisted of combining the results of:

1. The anthropogenic emission inventory for Florida (Subsection 3.3.1),
2. The estimates of total deposition (Subsection 2.3.1.5),
3. The estimates of mass flux across Florida's boundaries (Subsection 3.3.3.4), and
4. Estimates of biogenic emissions. The mass-balance model developed for Florida can be represented as follows:

$$\sum \text{Sources} - \sum \text{sinks} = \text{Export}$$

where: sources = 1) anthropogenic,
2) biogenic, and
3) import; and
sinks = 1) wet deposition, and
2) dry deposition.

For this analysis, import was considered a source term and export was determined as the difference between sources and sinks. Mass-balance models were developed for both $SO_x$ (as sulfur) and $NO_x$ (as nitrogen) and provide a semiquantitative estimate of in-state and out-of-state source contributions to total deposition.

Biogenic sulfur emissions were estimated using preliminary results from the Florida International University (FIU)-University of Miami biogenic emission study sponsored by FCG (Cooper, 1986). In general, data from the FIU-University of Miami survey suggest that statewide biogenic sulfur emissions are toward the lower end of the range previously estimated (ESE, 1984).

## 3.3 RESULTS

### 3.3.1 EMISSIONS

A summary of the estimated actual emissions of $SO_2$ and $NO_x$ for the State of Florida from September 15, 1982, to September 15, 1983, is presented in Table 3.3-1. The total statewide $SO_2$ and $NO_x$ emissions, including point and area sources, are approximately 937,000 and 810,000 tons/yr respectively. For $SO_2$ emissions, the emissions from point sources contributed 91.2 percent to the total, with the contribution from utilities accounting for 68.3 percent of the total emissions. For $NO_x$, emissions from point sources were similar to those from area sources, with contributions of 52.4 and 47.6 percent to the total emissions, respectively. Utility sources accounted for 31.6 percent of total annual $NO_x$ emissions. It should be noted that the nonutility point-source and the entire area-source emissions have been estimated for this period based on updates through 1982 and 1983. Because the databases did not allow for detailed temporal (e.g., monthly) distribution, the emissions should be considered only approximate and within 10 to 15 percent based on intercomparisons of databases and findings from other emission estimates calculated for other databases using similar procedures (EPRI, 1985).

Summaries of the Florida utility monthly $SO_2$ and $NO_x$ emissions during this period are presented in Tables 3.3-2 and 3.3-3, respectively. The $SO_2$ and $NO_x$ emissions from all utilities are highest in July with lowest emissions occurring in November for $SO_2$ and in February for $NO_x$. In general, the $SO_2$ and $NO_x$ emissions are highest during the summer months and lowest in the late fall and winter.

A summary of estimated seasonal $SO_2$ and $NO_x$ emissions for Florida area sources and nonutility point sources is presented in Table 3.3-4. The $SO_2$ emissions for area sources and nonutility point sources show little variation among the seasons with highest emissions occurring in the winter. The $NO_x$ emissions for the same categories are more variable with

Table 3.3-1. Summary of Estimated Anthropogenic $SO_2$ and $NO_x$ Emissions for Florida for 09/15/82 Through 09/15/83.

| Source Category | $SO_2$ Emissions (tons/yr) | $SO_2$ Percent of Total | $NO_x$ Emissions (tons/yr) | $NO_x$ Percent of Total |
|---|---|---|---|---|
| Point Sources | | | | |
| Utility | 639,623 | 68.3 | 256,019 | 31.6 |
| Nonutility | 214,333 | 22.9 | 168,295 | 20.8 |
| Total for Point Sources | 853,956 | 91.2 | 424,314 | 52.4 |
| Area Sources | | | | |
| Fuel Consumption | 39,533 | 4.2 | 25,333 | 3.1 |
| Solid Waste | 260 | 0.03 | 1.618 | 0.2 |
| Transportation | 42,603 | 4.5 | 347,191 | 42.9 |
| Miscellaneous | 360 | 0.04 | 11,551 | 1.4 |
| Total for Area Sources | 82,756 | 8.8 | 385,693 | 47.6 |
| Total for Point and Area Sources | 936,712 | 100.0 | 810,007 | 100.0 |

Sources: FCG, 1985.
DER, 1983.
Endlich *et al.*, 1983.

Table 3.3-2. Summary of Florida Utility Monthly $SO_2$ Emissions* from 09/15/82 Through 09/15/83

| Utility Company† | 1982 | | | | 1983 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SEP | OCT | NOV | DEC | JAN | FEB | MAR | APR | MAY | JUN | JULY | AUG | SEP | TOTAL |
| Florida Power Corporation | 7.5 | 13.0 | 10.2 | 13.2 | 11.6 | 8.8 | 11.2 | 12.5 | 13.9 | 15.7 | 17.6 | 15.2 | 6.8 | 157.1 |
| Florida Power and Light Company | 6.6 | 12.8 | 9.6 | 10.7 | 14.5 | 11.4 | 14.6 | 12.9 | 13.8 | 15.7 | 15.8 | 14.3 | 7.3 | 159.9 |
| Ft. Pierce Utilities Authority | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Gainesville Regional Utilities | 0.4 | 0.7 | 0.7 | 0.7 | 0.8 | 0.7 | 0.4 | 0.7 | 0.7 | 0.7 | 0.8 | 0.8 | 0.4 | 8.8 |
| Gulf Power Company | 4.1 | 6.3 | 6.3 | 3.6 | 5.8 | 6.5 | 8.7 | 6.7 | 7.2 | 9.1 | 12.2 | 12.8 | 5.0 | 94.5 |
| Jacksonville Electric Authority | 0.8 | 0.9 | 0.5 | 0.6 | 0.9 | 0.7 | 0.5 | 0.4 | 0.7 | 1.4 | 2.0 | 2.1 | 0.8 | 12.2 |
| City of Lakeland | 0.2 | 0.7 | 0.5 | 0.4 | 0.2 | 0.3 | 0.1 | 0.3 | 0.6 | 0.5 | 0.6 | 0.8 | 0.5 | 5.6 |
| Lake Worth Utilities Board | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Orlando Utilities Commission | 0.1 | 0.3 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 0.1 | 0.1 | 0.3 | 0.5 | 0.3 | 0.2 | 2.7 |
| City of Tallahassee | 0.1 | 0.2 | ** | 0.2 | 0.3 | 0.3 | 0.1 | ** | 0.1 | 0.1 | 0.2 | 0.2 | ** | .8 |
| Tampa Electric Authority | 9.1 | 16.2 | 14.2 | 15.6 | 17.0 | 15.8 | 16.8 | 15.2 | 14.7 | 16.6 | 17.6 | 18.7 | 9.5 | 197.1 |
| City of Vero Beach | 0.0 | ** | ** | ** | ** | ** | ** | 0.0 | ** | ** | ** | ** | ** | 0.1 |
| TOTAL | 28.9†† | 51.1 | 42.1 | 45.1 | 51.4 | 44.6 | 52.5 | 48.8 | 51.8 | 60.1 | 67.3 | 65.2 | 30.5†† | 639.8 |

* All emissions are in 1,000 tons.
† Key West Utilities Board data unavailable.
** Less than 50 tons (i.e., <0.05 x $10^3$ tons).
†† Only one-half of monthly emissions.

Source: ESE, 1986.

Table 3.3-3. Summary of Florida Utility Monthly $NO_x$ Emissions* from 09/15/82 Through 09/15/83

| Utility Company† | 1982 | | | | 1983 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SEP | OCT | NOV | DEC | JAN | FEB | MAR | APR | MAY | JUN | JULY | AUG | SEP | TOTAL |
| Florida Power Corporation | 1.7 | 2.6 | 2.5 | 3.1 | 3.5 | 2.9 | 3.1 | 3.7 | 4.3 | 4.8 | 5.3 | 4.6 | 2.2 | 44.4 |
| Florida Power and Light Company | 3.4 | 6.5 | 5.7 | 5.6 | 6.4 | 5.0 | 7.5 | 6.9 | 8.1 | 9.4 | 10.7 | 9.7 | 5.2 | 90.1 |
| Ft. Pierce Utilities Authority | ** | ** | 0.1 | ** | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 |
| Gainesville Regional Utilities | 0.3 | 0.6 | 0.5 | 0.6 | 0.6 | 0.6 | 0.4 | 0.6 | 0.6 | 0.6 | 0.8 | 0.6 | 0.3 | 7.0 |
| Gulf Power Company | 0.9 | 1.4 | 1.5 | 0.9 | 1.4 | 1.6 | 2.0 | 1.6 | 1.7 | 2.2 | 2.9 | 3.0 | 1.1 | 22.3 |
| Jacksonville Electric Authority | 0.3 | 0.4 | 0.3 | 0.3 | 0.4 | 0.3 | 0.2 | 0.1 | 0.2 | 0.3 | 0.5 | 0.5 | 0.2 | 3.9 |
| City of Lakeland | 0.3 | 0.9 | 0.9 | 0.7 | 0.2 | 0.4 | 0.2 | 0.9 | 1.7 | 1.4 | 1.6 | 1.9 | 1.0 | 12.0 |
| Lake Worth Utilities Board | ** | ** | ** | ** | ** | ** | ** | ** | ** | ** | ** | 0.0 | 0.0 | 10.3 |
| Orlando Utilities Commission | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 1.5 |
| City of Tallahassee | 0.3 | 0.3 | 0.1 | 0.6 | 0.5 | 0.3 | 0.5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 3.6 |
| Tampa Electric Authority | 3.1 | 5.8 | 5.2 | 5.9 | 6.2 | 5.5 | 5.4 | 4.9 | 5.2 | 6.3 | 6.5 | 6.7 | 3.3 | 70.1 |
| City of Vero Beach | ** | 0.1 | 0.1 | 0.1 | 0.1 | ** | ** | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | ** | 0.9 |
| TOTAL | 10.4†† | 18.8 | 17.2 | 17.9 | 19.4 | 16.7 | 19.4 | 19.1 | 22.2 | 25.4 | 28.8 | 27.4 | 13.5 | 266.2 |

* All emissions are in 1,000 tons.

† Key West Utilities Board data unavailable.

** Less than 50 tons (i.e., <$0.05 \times 10^3$ tons).

†† Only one-half of monthly emissions.

Source: ESE, 1986.

Table 3.3-4. Summary of Seasonal $SO_2$ and $NO_x$ Emissions* for Florida Nonutility Point and Area Sources

| Source | Winter | | Spring | | Summer | | Fall | | Total | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ | $SO_2$ | $NO_x$ |
| Point Source | | | | | | | | | | |
| Nonutility | 55.8 | 47.0 | 53.4 | 37.5 | 52.3 | 46.1 | 52.8 | 37.7 | 214.3 | 168.3 |
| Area Sources | | | | | | | | | | |
| All | 21.5 | 95.1 | 20.9 | 97.5 | 19.7 | 102.4 | 20.5 | 90.8 | 82.8 | 385.7 |
| Total | 77.3 | 142.1 | 74.3 | 135.0 | 72.0 | 148.5 | 73.3 | 128.5 | 297.1 | 554.0 |

*All emissions are in 1,000 tons/yr.

Source: ESE, 1986.

the highest area source emissions occurring in summer and highest nonutility point source emissions in the winter. In general, the lowest $NO_x$ emissions occur in the spring and fall.

A summary of the $SO_2$ and $NO_x$ emissions by state from the 1980 NAPAP inventory is provided in Table 3.3-5. Area-source emissions represent a small percentage of total $SO_2$ emissions but nearly half of total $NO_x$ emissions. States with the highest $SO_2$ emissions include Ohio, Pennsylvania, Indiana, and Illinois. States with the highest $NO_x$ emissions are Texas, Ohio, Illinois, and Pennsylvania.

Summaries of $SO_2$ and $NO_x$ emissions for each state by season are presented in Tables 3.3-6 and 3.3-7, respectively. These were derived from the NAPAP inventory using the seasonal throughput percentages shown on each point-source record and area-source seasonal allocation factors for each county. Although some variations occur from state to state, the total emissions for $SO_2$ and $NO_x$ are highest in the winter and summer months. Emissions in the spring and fall are less and approximately the same.

As reported previously (ESE, 1984), biogenic sulfur emissions in Florida were estimated to range from 6,300 tons to 249,000 metric tons (MT), which would indicate that biogenic emissions ranged from 1 to 54 percent of anthropogenic emissions. Because of the potential range in biogenic emissions and its importance if emissions were in the higher range, a separate study was contracted with a team from FIU and the University of Miami. This study is currently nearing completion, but the complete results are not available to incorporate into this final report. Preliminary results suggest that biogenic sulfur emissions may range from 5,500 to 22,000 tons/yr as sulfur.

Table 3.3-5. Summary of 1980 $SO_2$ and $NO_x$ Emissions* for States within Model Domain†

| State | $SO_2$ Point | $SO_2$ Area | $SO_2$ Total | $NO_x$ Point | $NO_x$ Area | $NO_x$ Total |
|---|---|---|---|---|---|---|
| Alabama | 774 | 76 | 850 | 273 | 252 | 525 |
| Arkansas | 59 | 30 | 89 | 65 | 167 | 232 |
| Connecticut | 51 | 18 | 69 | 41 | 103 | 144 |
| Delaware | 105 | 22 | 127 | 36 | 33 | 69 |
| District of Columbia | 11 | 6 | 17 | 5 | 22 | 27 |
| Georgia | 847 | 30 | 877 | 279 | 308 | 587 |
| Illinois | 1,360 | 99 | 1,459 | 655 | 462 | 1,117 |
| Indiana | 1,746 | 134 | 1,880 | 536 | 324 | 860 |
| Iowa | 366 | 24 | 390 | 167 | 182 | 349 |
| Kansas | 198 | 33 | 231 | 302 | 290 | 592 |
| Kentucky | 1,113 | 45 | 1,158 | 373 | 231 | 604 |
| Louisiana | 343 | 158 | 501 | 568 | 253 | 821 |
| Maine | 122 | 12 | 134 | 21 | 43 | 64 |
| Maryland | 273 | 23 | 296 | 114 | 164 | 278 |
| Massachusetts | 317 | 45 | 362 | 88 | 184 | 272 |
| Michigan | 844 | 34 | 878 | 378 | 368 | 746 |
| Mississippi | 256 | 50 | 306 | 99 | 196 | 295 |
| Missouri | 1,236 | 61 | 1,297 | 349 | 258 | 607 |
| Nebraska | 65 | 12 | 77 | 92 | 118 | 210 |
| New Hampshire | 102 | 5 | 107 | 30 | 30 | 60 |
| New Jersey | 234 | 69 | 303 | 160 | 274 | 434 |
| New York | 787 | 77 | 864 | 321 | 427 | 748 |
| North Carolina | 621 | 32 | 653 | 302 | 268 | 570 |
| North Dakota | 95 | 19 | 114 | 103 | 65 | 168 |
| Ohio | 2,655 | 50 | 2,705 | 665 | 554 | 1,219 |
| Oklahoma | 86 | 16 | 102 | 177 | 285 | 462 |
| Pennsylvania | 1,770 | 82 | 1,852 | 595 | 487 | 1,082 |
| Rhode Island | 10 | 4 | 14 | 6 | 20 | 36 |
| South Carolina | 324 | 18 | 342 | 154 | 148 | 302 |
| Tennessee | 1,103 | 31 | 1,134 | 336 | 237 | 573 |
| Texas | 1,081 | 260 | 1,341 | 1,543 | 1,943 | 3,486 |
| Vermont | 3 | 7 | 10 | 1 | 43 | 44 |
| Virginia | 338 | 48 | 386 | 160 | 251 | 411 |
| West Virginia | 1,091 | 13 | 1,104 | 352 | 121 | 473 |
| Wisconsin | 668 | 20 | 688 | 205 | 221 | 426 |
| Total | 21,054 | 1,663 | 22,717 | 9,551 | 9,342 | 18,893 |

*All emissions are in 1,000 tons/yr.
†Exclusive of Florida sources.

Source: Endlich *et al.*, 1983.

Table 3.3-6. Summary of Seasonal 1980 $SO_2$ Emissions* for States within Model Domain†

| State | Winter | Spring | Summer | Fall | Total |
|---|---|---|---|---|---|
| Alabama | 225 | 179 | 225 | 221 | 850 |
| Arkansas | 22 | 20 | 26 | 21 | 89 |
| Connecticut | 22 | 16 | 14 | 17 | 69 |
| Delaware | 34 | 31 | 29 | 33 | 127 |
| District of Columbia | 8 | 3 | 3 | 3 | 17 |
| Georgia | 219 | 191 | 258 | 209 | 877 |
| Illinois | 405 | 340 | 372 | 342 | 1,459 |
| Indiana | 507 | 450 | 470 | 453 | 1,880 |
| Iowa | 103 | 90 | 110 | 87 | 390 |
| Kansas | 59 | 51 | 65 | 56 | 231 |
| Kentucky | 305 | 249 | 318 | 286 | 1,158 |
| Louisiana | 147 | 131 | 105 | 118 | 501 |
| Maine | 39 | 37 | 27 | 31 | 134 |
| Maryland | 90 | 73 | 71 | 62 | 296 |
| Massachusetts | 108 | 101 | 89 | 64 | 362 |
| Michigan | 239 | 214 | 219 | 206 | 878 |
| Mississippi | 79 | 70 | 78 | 79 | 306 |
| Missouri | 337 | 286 | 370 | 304 | 1,297 |
| Nebraska | 21 | 21 | 21 | 14 | 77 |
| New Hampshire | 31 | 26 | 23 | 27 | 107 |
| New Jersey | 90 | 67 | 68 | 78 | 303 |
| New York | 255 | 205 | 199 | 205 | 864 |
| North Carolina | 173 | 157 | 172 | 151 | 653 |
| North Dakota | 31 | 27 | 25 | 31 | 114 |
| Ohio | 750 | 629 | 672 | 654 | 2,705 |
| Oklahoma | 27 | 26 | 21 | 28 | 102 |
| Pennsylvania | 481 | 425 | 474 | 472 | 1,852 |
| Rhode Island | 4 | 3 | 4 | 3 | 14 |
| South Carolina | 88 | 79 | 95 | 80 | 342 |
| Tennessee | 310 | 257 | 309 | 258 | 1,134 |
| Texas | 343 | 318 | 344 | 336 | 1,341 |
| Vermont | 3 | 3 | 2 | 2 | 10 |
| Virginia | 110 | 86 | 95 | 95 | 386 |
| West Virginia | 293 | 273 | 271 | 267 | 1,104 |
| Wisconsin | 189 | 176 | 170 | 153 | 688 |
| Total | 6,147 | 5,310 | 5,814 | 5,446 | 22,717 |

*All emissions are in 1,000 tons/yr.
†Exclusive of Florida sources.

Note: Winter = December through February; Spring = March through May; Summer = June through August; Fall = September through November.

Source: Endlich *et al.*, 1983.

Table 3.3-7. Summary of Seasonal 1980 $NO_x$ Emissions* for States within Model Domain†

| State | Winter | Spring | Summer | Fall | Total |
|---|---|---|---|---|---|
| Alabama | 135 | 119 | 138 | 133 | 525 |
| Arkansas | 61 | 55 | 63 | 53 | 232 |
| Connecticut | 40 | 34 | 33 | 37 | 144 |
| Delaware | 18 | 16 | 17 | 18 | 69 |
| District of Columbia | 8 | 7 | 6 | 6 | 27 |
| Georgia | 146 | 141 | 156 | 144 | 587 |
| Illinois | 296 | 272 | 279 | 270 | 1,117 |
| Indiana | 237 | 211 | 210 | 202 | 860 |
| Iowa | 93 | 84 | 86 | 86 | 349 |
| Kansas | 152 | 138 | 155 | 147 | 592 |
| Kentucky | 153 | 139 | 161 | 151 | 604 |
| Louisiana | 203 | 198 | 214 | 206 | 821 |
| Maine | 17 | 16 | 15 | 16 | 64 |
| Maryland | 76 | 68 | 68 | 66 | 278 |
| Massachusetts | 75 | 68 | 65 | 64 | 272 |
| Michigan | 202 | 183 | 177 | 184 | 746 |
| Mississippi | 75 | 68 | 74 | 78 | 295 |
| Missouri | 152 | 143 | 162 | 150 | 607 |
| Nebraska | 53 | 55 | 55 | 47 | 210 |
| New Hampshire | 16 | 14 | 14 | 16 | 60 |
| New Jersey | 117 | 105 | 104 | 108 | 434 |
| New York | 208 | 178 | 180 | 182 | 748 |
| North Carolina | 147 | 140 | 147 | 136 | 570 |
| North Dakota | 43 | 37 | 40 | 48 | 168 |
| Ohio | 331 | 292 | 299 | 297 | 1,219 |
| Oklahoma | 118 | 112 | 117 | 115 | 462 |
| Pennsylvania | 280 | 256 | 272 | 274 | 1,082 |
| Rhode Island | 9 | 9 | 9 | 9 | 36 |
| South Carolina | 76 | 76 | 78 | 72 | 302 |
| Tennessee | 150 | 135 | 148 | 140 | 573 |
| Texas | 852 | 833 | 924 | 877 | 3,486 |
| Vermont | 10 | 11 | 12 | 11 | 44 |
| Virginia | 109 | 96 | 103 | 103 | 411 |
| West Virginia | 126 | 115 | 117 | 115 | 473 |
| Wisconsin | 113 | 105 | 106 | 102 | 426 |
| Total | 4,897 | 4,529 | 4,804 | 4,663 | 18,893 |

*All emissions are in 1,000 tons/yr.

†Exclusive of Florida sources.

Note: Winter = December through February; Spring = March through May; Summer = June through August; Fall = September through November.

Source: Endlich _et_ _al_., 1983.

### 3.3.2 LRT MODEL EVALUATION AND APPLICATION

Despite the numerous modifications to ENAMAP described in Subsection 3.1, the resulting model simulations of regional deposition can only approximately reflect reality. This is due, in part, to the inherent simplicity of parameterizations used to represent complex natural processes. For example, precipitation scavenging, dry deposition, and $SO_2$ transformation are treated as first-order processes which permit sources to interact in a purely linear fashion. At present, there is no consensus in the scientific community as to how far these processes deviate from linearity (on a regional scale). Another more powerful model will be required to address this question. Such a model is presently being developed at the NCAR (1985) under the auspices of NAPAP.

Another factor contributing to model uncertainty is the limited nature of observational data used as inputs to ENAMAP. Upper-air wind data used for vertical and horizontal transport are typically collected over spatial separations of hundreds of kilometers and at 12-hour intervals. These data must be interpolated to the 80-km by 80-km grid spacing and 3-hour timestep currently employed in ENAMAP. Precipitation amount data also are collected at widely scattered locations across the eastern United States, and these too must be spatially averaged and temporally aggregated for use in wet scavenging simulations.

The net effect of these uncertainties and deficiencies in LRT models is that the practitioner is left with considerable latitude in selection of acceptable and defensible values for model parameters (e.g., wet scavenging). In practice, parameter values are typically adjusted to improve comparisons with observational data, (i.e., concentration and deposition) rather than to better simulate the mechanisms of atmospheric transport and deposition. This is necessarily the result of inherent limitations in this generation of LRT models (i.e., early 1980s). The objective of this section is twofold: (1) to present results of ENAMAP trial runs undertaken to evaluate the reasonableness and comparability of model outputs with observational data and, (2) to assess the sensitivity of model outputs to a variety of changes in parameter values (i.e., sensitivity analysis). Taken together, results of the evaluation and sensitivity analysis will be used to finalize parameter values used in subsequent source attribution applications.

Results of trial runs are evaluated by: (1) constructing mass balances for the eastern United States and comparing them with previously reported mass balances, (2) comparing observed versus predicted wet deposition at selected monitoring sites across the eastern United States, and (3) comparing observed and predicted air concentrations of $SO_2$ and $SO_4^{-2}$ from the Florida network. Mass balances give an overview of model output and convey a sense of the relative importance of the atmospheric processes simulated by ENAMAP. For the purpose of this comparison, the 1980 mass balance for the eastern United States developed by Galloway and Whelpdale (1980) is used as a point of reference. The salient features of the Galloway and Whelpdale (1980) model are twofold: first, annual wet and dry deposition across the eastern United States are approximately equal (i.e., within a factor of 2); second, the flux of sulfur out of the model domain represents about 40 to 60 percent of emissions. Although these findings are unverifiable, they appear to be consistent with the current understanding of the atmospheric sulfur cycle (NAS, 1983). It is important to note that the present model and that of Galloway and Whelpdale (1980) refer to different time periods (1983 versus 1980) and different time scales (monthly versus seasonal). Therefore large variability in monthly model comparisons is to be expected; however, assuming relatively constant meteorology and spatial patterns of emission densities on an annual basis, overall model results should be reasonably consistent.

The comparison of observed versus predicted wet deposition employs a subset of data from UAPSP precipitation monitoring stations (n=14) and all data from Florida Acid Deposition Study monitoring stations (n=9) in operation during 1983 (see Figure 3.3-1). These comparisons are performed by matching observational data from monitoring sites with simulated data from corresponding cells in the ENAMAP domain. More involved schemes have been employed for evaluating model results [e.g., inverse-distance-squared weighting (Endlich et al., 1983)]; however, these only serve to obfuscate the underlying fact that ENAMAP was neither designed nor intended to simulate wet or dry deposition at points (i.e., wet/dry precipitation collectors). Appropriate comparisons might involve regional averages (e.g., state) of observed and predicted values.

### 3.3.2.1 Model Application and Adjustment

Model characteristics have been described previously (see Subsection 3.2.1. The parameter variations used in initial model applications are shown in Table 3.3-8.

Trial runs were performed for 3 months: February, July, and August 1983. With the exception of the emissions configuration (see Subsection 3.2.3.4) and the values of certain parameters, all trial runs were made under the same conditions as source attribution runs. For the purpose of computational economy, all sources were considered together in trial simulations and the number of source cells was reduced as follows. For Florida, Georgia, and Alabama, point and area sources were summed within each cell, and those cells with emissions less than 1,000 kilograms per hour (kg/hr) were consolidated with nearby cells of larger emissions. For all other states in the model domain, point and area sources were consolidated into a single cell at the centroid of the state. Emission height for all sources were 300 m. The resulting source configuration conserved the mass of emissions within each state, while reducing the total number of source cells by a factor of 3 and the computer time for each run by a factor of 5. This simplified representation of emissions was used only in the initial model applications and adjustment task. The representation of emissions in initial model applications and the model evaluation task are described in

The final three trial runs for July illustrate the effects of varying the height of the lowest transport layer and wet scavenging of $SO_2$ and $SO_4^{-2}$. Increasing the height of the lowest transport layer from 200 m to 350 m resulted in a major increase in dry deposition and a significant decrease in wet deposition, apparently due to competition between the two processes. The dry-deposition increase is related to the simplified treatment of emissions, which in prior runs was within the middle transport layer. Release of emissions into the lowest transport layer permits dry deposition to occur at night, when the atmosphere is stably stratified.

Results of Trial Runs 5 and 6 show that total wet deposition over land is fairly insensitive to scavenging coefficients. Succesive reductions in scavenging coefficients by factors of 2, 4 (not shown), and finally 8 were required to bring wet deposition into near balance with dry deposition. It is noteworthy that the reduction of wet deposition in Runs 5 and 6 was accompanied by trivial increases in dry deposition. This is most likely the result of species-dependent wet and dry removal rates which favor $SO_4^{-2}$ and $SO_2$ deposition, respectively. Wet deposition of $SO_4^{-2}$ has little or no effect (within ENAMAP) on dry deposition, whereas dry deposition of $SO_2$ presents subsequent transformation to, and wet deposition as, $SO_4^{-2}$. Due to the time requirement for $SO_2$ transformation to $SO_4^{-2}$, this finding implies wet deposition may be more of an LRT phenomenon than dry deposition; however, this result may be an artifact of the atmospheric structure within the model.

With one exception, similar results were obtained for February and August trial simulations. Wet deposition for February was significantly under predicted. Therefore, trial runs for February involved successive increases in wet-scavenging coefficients. Optimal results were obtained with an increase of wet-scaveging coefficients by a factor of 2.

Observed versus predicted wet-deposition precipitation amounts and $SO_2/SO_4^{-2}$ concentrations for base-case and final-case simulations are shown in Table 3.3-10. Results for precipitation amount show that mean monthly totals recorded at precipitation chemistry sites agree reasonably (±10 to 20 percent) with amounts used for simulation purposes; however, the standard deviation of this agreement is large (i.e., ±15 to 30 percent). Assuming all other factors are equal, this variability suggests a lower limit for agreement between observations and ENAMAP predictions.

Differences between observed and predicted wet deposition are much greater and much more variable than those for precipitation, suggesting that factors other than precipitation amount contribute significantly to overall model uncertainty.

### 3.3.2.3 ENAMAP Simulation Runs and Model Performance

This subsection discusses results of ENAMAP simulations for February-April and June-August 1983. Simulations for these months were performed using "final" ENAMAP conditions for each season from the initial model application (see Table 3.3-8). As described previously, the representation of emissions also differed for simulation runs. In this case, the threshold for consolidation of emission cells was reduced to 200 kg $SO_2$ per hour for the following states: Florida, North Carolina, South Carolina, Tennessee, Georgia, Alabama, Arkansas, Mississippi, and Louisiana. Emissions for all other states were treated as a single emission centroid. Partial transfer matrices of wet deposition, dry deposition, total deposition, and $SO_2/SO_4^{-2}$ concentrations from the 6-month period are introduced, followed by presentation of simulated mass-balances over the eastern United States. Finally, statistical comparison of predicted versus observed wet deposition and $SO_2/SO_4^{-2}$ concentrations are evaluated.

Calculated source-receptor relationships for wet deposition during the 6-month simulation period are shown in Table 3.3-11. This table shows percentages of wet deposition in receptor regions attributed by ENAMAP, to emissions from all source regions. Transfer matrices for wet deposition and other parameters were produced by summation of results from monthly simulation for individual source regions. Note that this approach is straightforward only for models which assume that transformation of deposition processes are perfectly linear.

Two characteristics of the wet-deposition transfer matrix are of direct interest to this study: the axis which intersects Florida as a source region and that which intersects Florida as a receptor region. Data from these axes are more conveniently displayed and interpreted in pictorial format (i.e., partial transfer matrices).

Table 3.3-11. Calculated Source-Receptor Relationships for Wet Sulfur Deposition* During 1983

| | Receptor Regions | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Source Regions | FL | GA | AL | AR MS LA | VA NC SC | KY TN | IL MO | MI,IN OH,WV | NY PA,NJ MD,DE | IA WN WI | VT,NH ME,MA CT,RI | TX | SD,NB KS,OK |
| FL-Utility | 30.8 | 3.2 | 6.0 | 6.5 | 0.8 | 0.7 | 0.8 | 0.2 | 0.4 | 0.3 | 0.2 | 4.4 | 1.1 |
| FL-APIS | 10.1 | 1.6 | 2.2 | 2.4 | 0.3 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 1.4 | 0.4 |
| FL-Area | 3.5 | 0.4 | 0.5 | 0.6 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 |
| GA | 6.9 | 28.0 | 13.6 | 4.5 | 5.8 | 5.2 | 2.2 | 1.9 | 0.8 | 1.3 | 0.2 | 1.4 | 3.2 |
| AL | 9.6 | 10.5 | 27.7 | 10.0 | 2.8 | 7.8 | 2.3 | 2.0 | 0.6 | 2.0 | 0.3 | 2.7 | 5.3 |
| AR, MS, LA | 5.7 | 2.7 | 9.0 | 29.7 | 1.2 | 4.1 | 3.2 | 1.2 | 0.5 | 2.3 | 0.2 | 13.3 | 5.6 |
| VA, NC, SC | 2.9 | 7.9 | 3.6 | 1.3 | 17.9 | 3.3 | 1.0 | 2.1 | 3.6 | 0.2 | 0.7 | 0.3 | 0.4 |
| KY, TN | 7.1 | 18.8 | 15.4 | 6.0 | 19.9 | 42.5 | 7.9 | 11.9 | 4.5 | 9.6 | 3.5 | 0.1 | 6.8 |
| IL, MO | 8.2 | 8.6 | 7.5 | 7.7 | 14.9 | 18.4 | 44.2 | 15.2 | 4.7 | 22.6 | 3.1 | 1.0 | 6.2 |
| MI, IN, OH, WV | 6.3 | 10.7 | 5.2 | 2.1 | 26.1 | 8.0 | 14.8 | 53.7 | 41.4 | 20.5 | 23.4 | 0.3 | 3.2 |
| NY, NJ, PA, MD, DE | 1.9 | 3.5 | 1.5 | 0.5 | 6.2 | 1.1 | 1.4 | 1.7 | 38.2 | 2.0 | 33.8 | 0.1 | 0.0 |
| IA, MN, WI | 2.7 | 2.1 | 2.2 | 1.0 | 2.1 | 2.5 | 6.7 | 4.5 | 2.0 | 25.4 | 2.6 | 0.1 | 2.4 |
| VT, NH, ME, MA, CT, RI | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 1.4 | 0.0 | 31.6 | 0.0 | 0.0 |
| TX | 3.9 | 1.3 | 4.4 | 25.2 | 1.4 | 4.8 | 11.4 | 4.3 | 1.2 | 8.5 | 0.1 | 73.5 | 36.3 |
| SD, NB, KS, OK | 0.5 | 0.6 | 1.0 | 2.3 | 0.7 | 1.2 | 3.9 | 1.1 | 0.5 | 5.0 | 0.2 | 0.9 | 29.2 |

*Values represent percent of total wet sulfur deposition

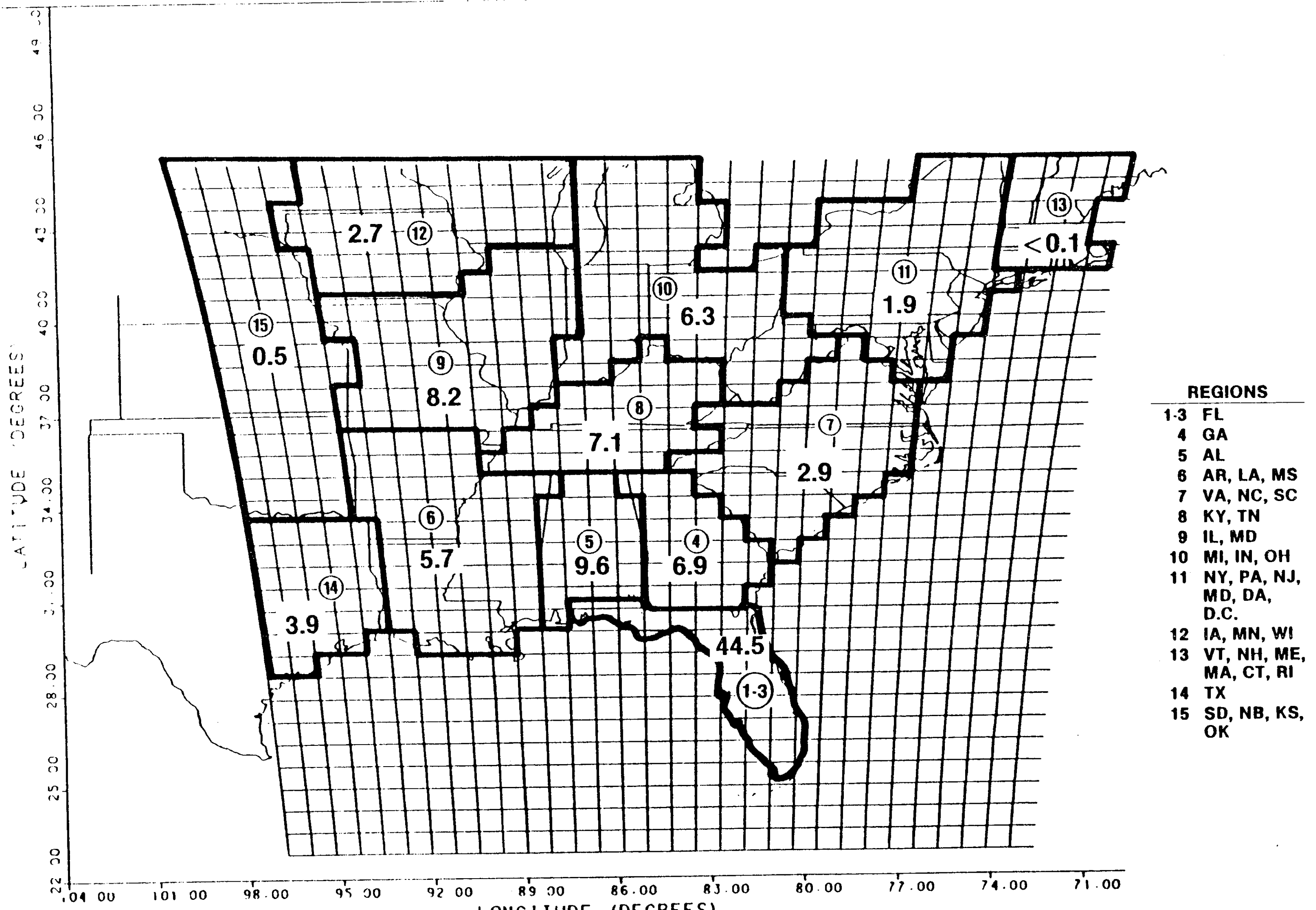
Source: ESE, 1986.

Percent contribution of individual source regions to wet deposition in Florida are displayed in Figure 3.3-2. Results indicate that all emission regions, except New England States (Vermont, New Hampshire, Maine, Massachusetts, Connecticut, and Rhode Island) and the Plains States (South Dakota, Nebraska, Kansas, and Oklahoma), contribute at least 1 percent of predicted values. In-state emissions for Florida represent the largest, although not the majority, source of wet deposition. Previous ENAMAP simulations (e.g., United States-Canada Work Group 2, 1982; Endlich et al., 1983) also suggest that receptor regions are typically influenced to a large degree by emissions within their own boundaries.

Anthropogenic sources of $SO_x$ in Florida are not major contributors to sulfur wet-deposition rates out of state, contributing less than 10 percent of sulfur wet deposition in all out-of-state locations (see Figure 3.3-3), and generally less than 2 percent of sulfur wet deposition in the Southern Appalachians and less than 1 percent in the Adirondacks.

Contributions of Florida utility emissions to wet deposition (Figure 3.3-4) are generally below 1 percent in all areas except Florida, the southeast, Texas, and the Plains States. Although all source-receptor relationships are subject to great uncertainty, those presented for Texas and the Plains States may be especially misleading because these regions form the western boundaries of the model domain (i.e., sources west of these states are not considered). The contribution of Florida utility emissions to wet deposition in Florida, Georgia, and Alabama ranks first, eighth, and sixth, respectively, among all sources contributing to wet deposition in those states.

Predicted contributions of source regions to dry deposition in Florida (Figure 3.3-5) suggest that local emissions are extremely important. In-state sources may account for approximately 90 percent of dry deposition of sulfur across Florida, with utility point-source, nonutility point-scurce, and area-source contributions of roughly



NOTE: VALUE FOR FLORIDA INCLUDES ALL IN-STATE SOURCES.

Figure 3.3-2
PERCENT CONTRIBUTION OF SOURCE REGIONS TO WET DEPOSITION IN FLORIDA FOR 6-MONTH SIMULATION PERIOD

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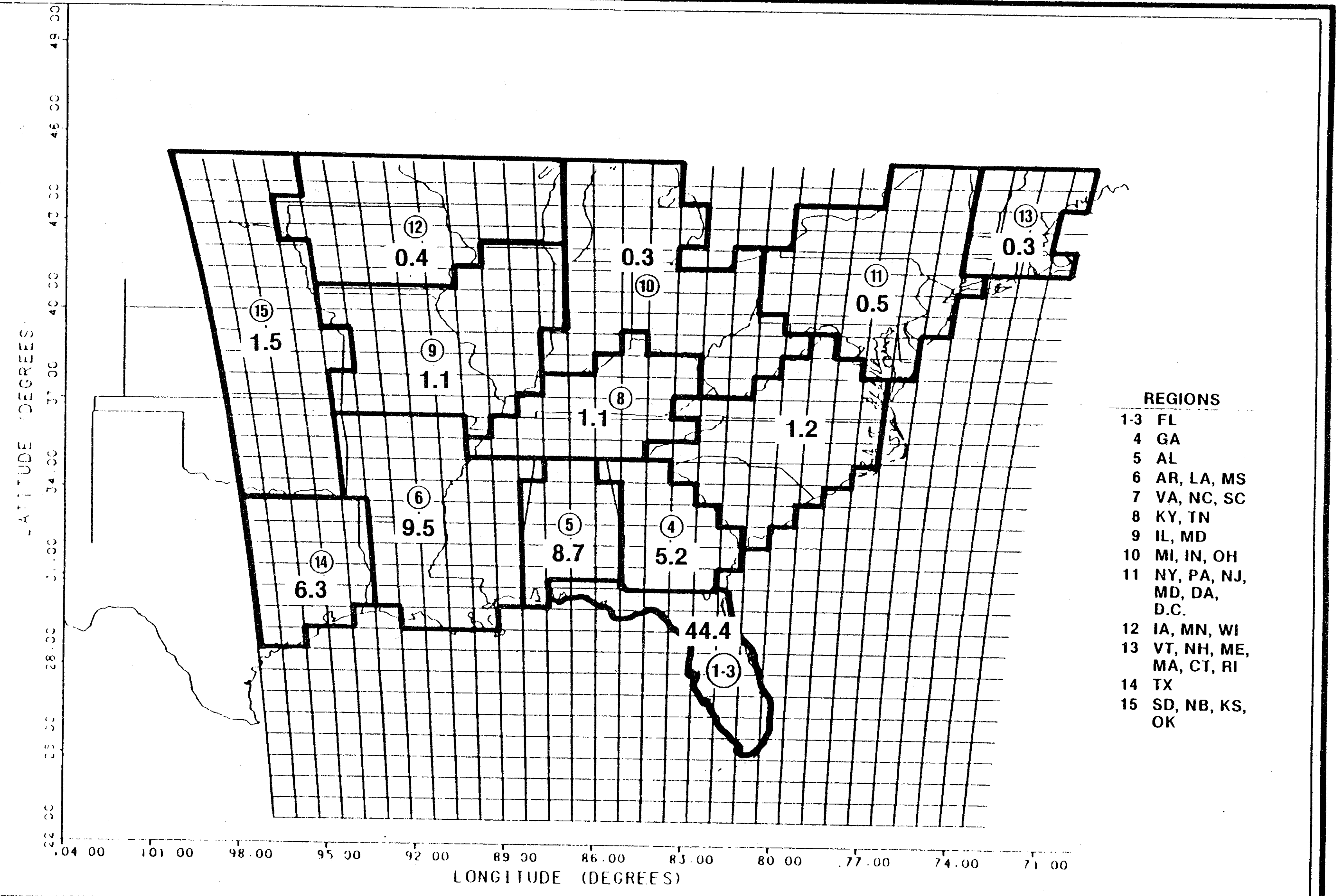

Figure 3.3-3
PERCENT CONTRIBUTION OF ALL FLORIDA SOURCES TO WET DEPOSITION IN RECEPTOR REGIONS FOR 6-MONTH SIMULATION PERIOD

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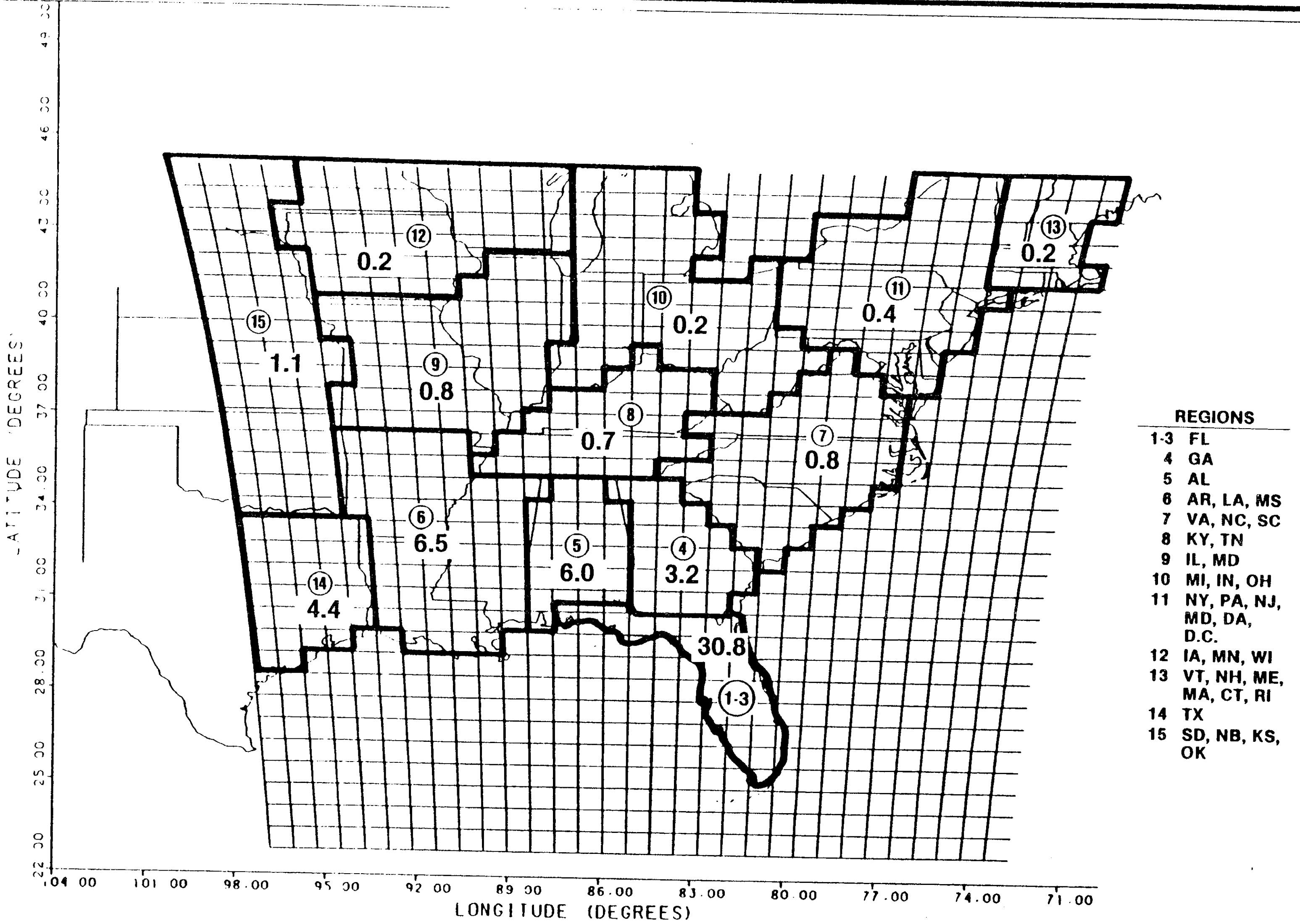

Figure 3.3-4
PERCENT CONTRIBUTION OF FLORIDA UTILITIES TO WET DEPOSITION IN RECEPTOR REGIONS OVER 6-MONTH SIMULATION PERIOD

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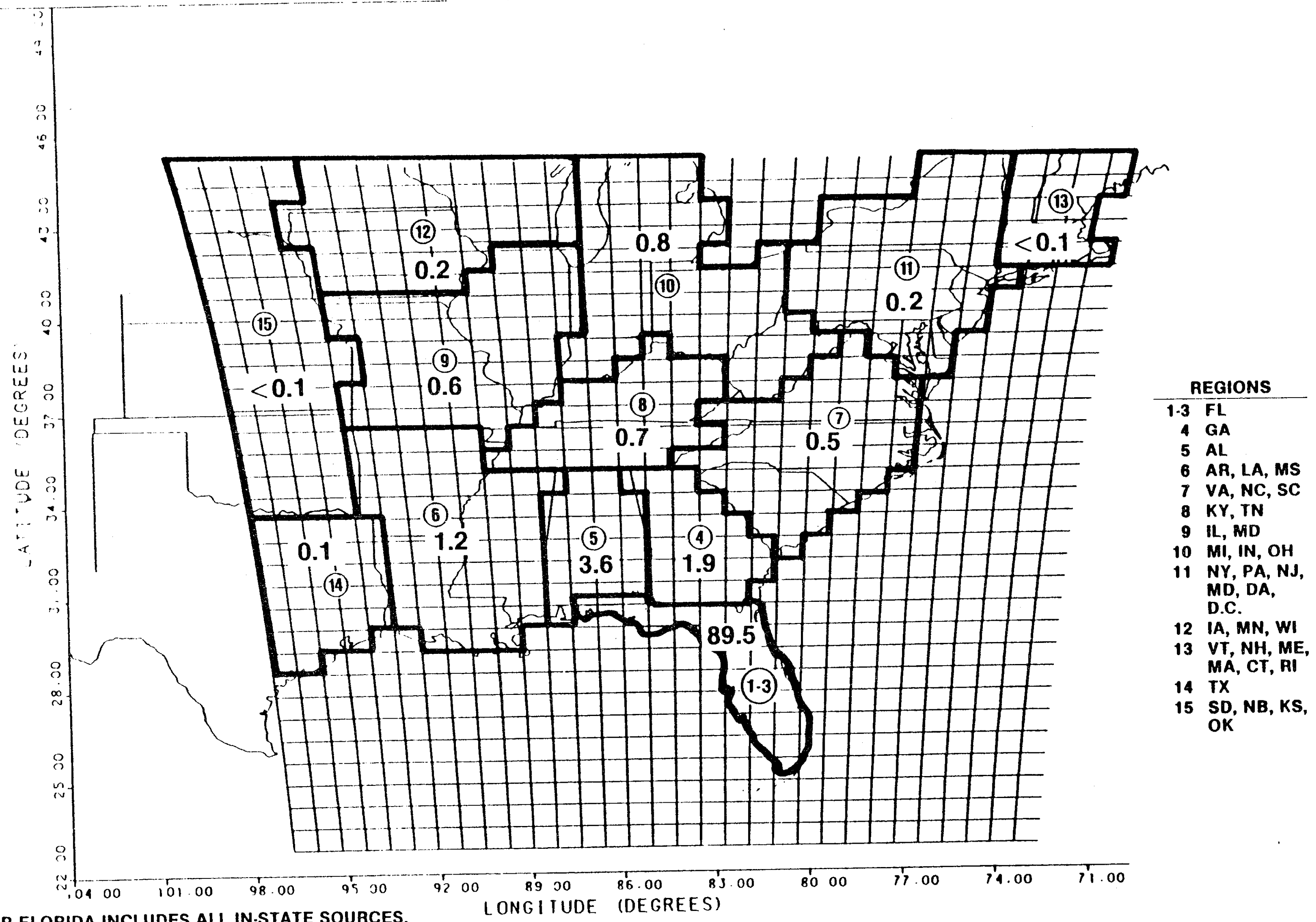

NOTE: VALUE FOR FLORIDA INCLUDES ALL IN-STATE SOURCES.

Figure 3.3-5
PERCENT CONTRIBUTION OF SOURCE REGIONS TO DRY DEPOSITION IN FLORIDA

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60 percent, 25 percent, and 8 percent, respectively. The relatively localized nature of dry deposition is illustrated in Figures 3.3-6 and 3.3-7. ENAMAP results indicate that Florida utility emissions account for less than 1 percent of dry deposition to all receptors except Florida and Alabama (3.3 percent). The relatively localized nature of dry deposition appears to be consistent with the expectation of relatively high and relatively low deposition velocities for $SO_2$ and $SO_4^{-2}$, respectively. However, ENAMAP may exaggerate this effect due to instantaneous dispersion of emissions within cells which permits widespread, rapid contact of $SO_2$ with depositional surfaces.

Utility sources as well as other Florida sources contribute significantly to in-state concentrations of $SO_2$ and $SO_4^{-2}$, but marginally to out-of-state concentrations (see Figures 3.3-8 through 3.3-13). As with wet and dry deposition, $SO_2$ and $SO_4^{-2}$ concentrations exhibit distinct spatial patterns. Out-of-state contributions of $SO_2$ to Florida are relatively minor (Figure 3.3-8) while those for $SO_4^{-2}$ are major (Figure 3.3-11).

Total deposition data from the 6-month simulation period are summarized in Figures 3.3-14 through 3.3-16. Florida sources were estimated to account for 66 percent of sulfur deposition in Florida, while Florida utilities are estimated to account for 44 percent of the sulfur deposition in Florida. Florida sources are not an important contributor to sulfur deposition in any out-of-state region, contributing at most 7 percent of all sulfur deposited in Alabama, and approximately 2 percent and 1 percent to potentially sensitive receptor regions in the Appalachians and Adirondacks, respectively.

Although specific source-receptor relationships are unverifiable and highly uncertain, overall model performance can be examined by calculation of mass balances and comparisons of observed versus predicted quantities.

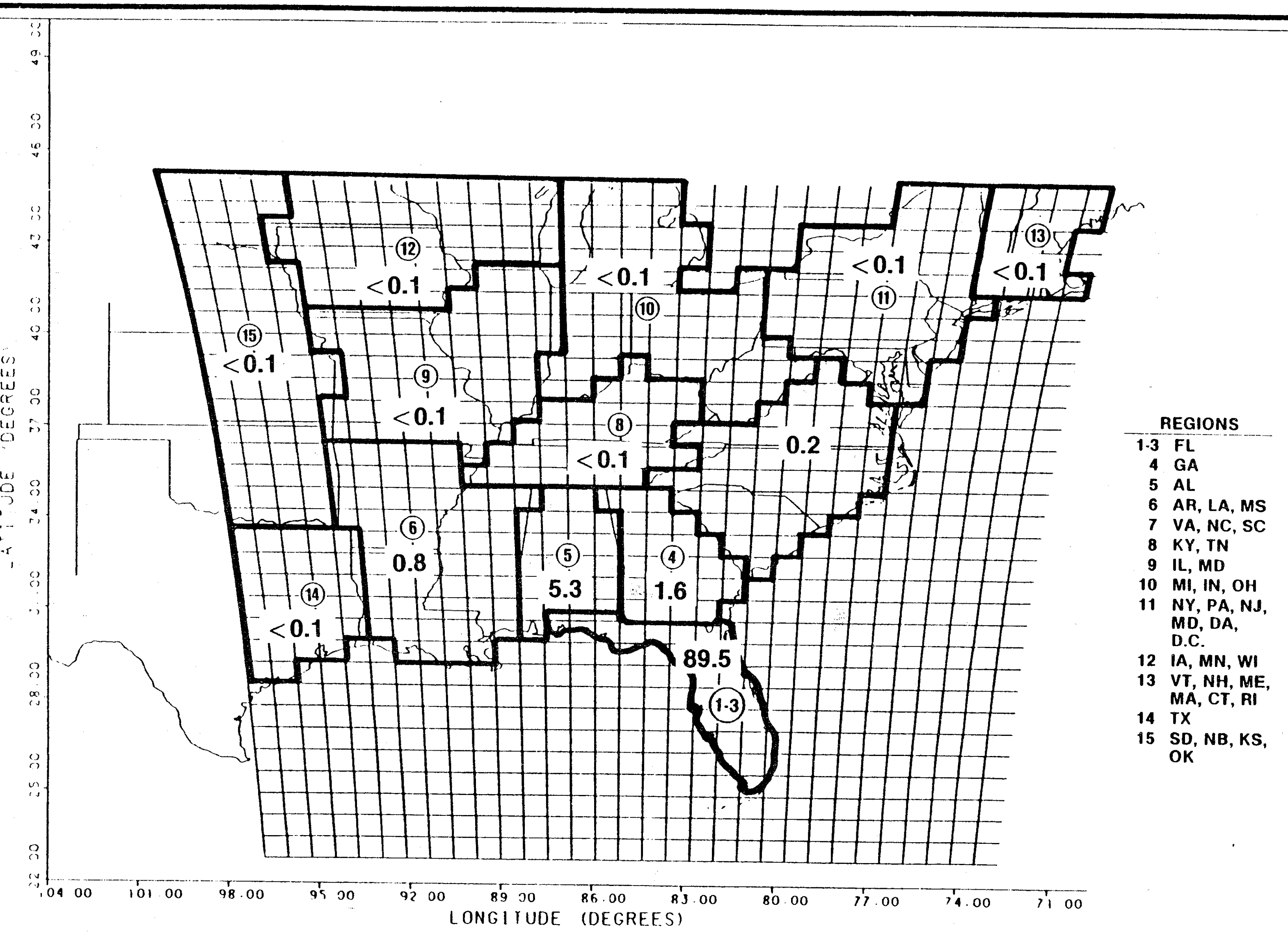

Figure 3.3-6
PERCENT CONTRIBUTION OF ALL FLORIDA SOURCES TO DRY DEPOSITION IN RECEPTOR AREAS FOR 6-MONTH SIMULATION PERIOD

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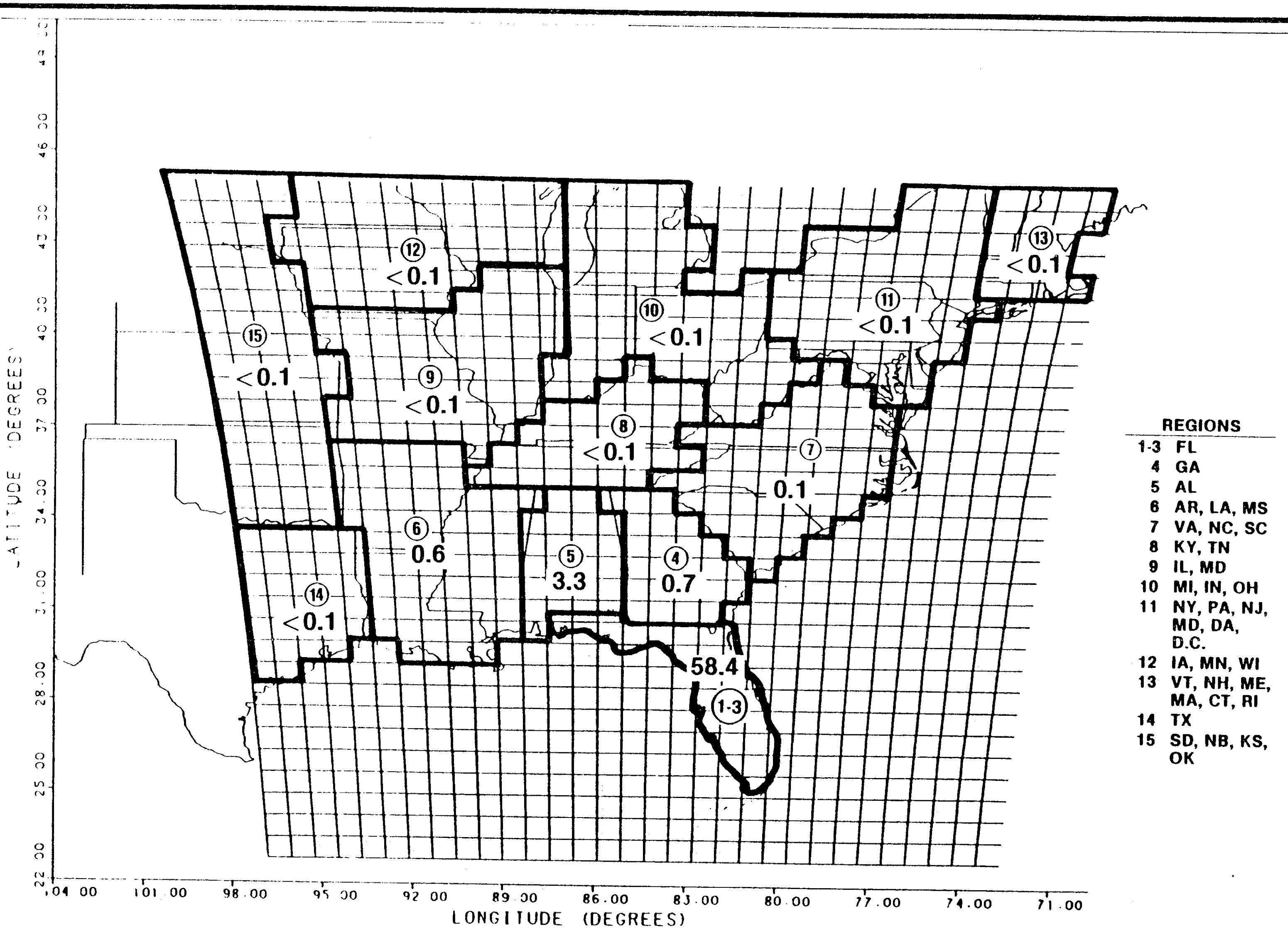

Figure 3.3-7
PERCENT CONTRIBUTION OF FLORIDA UTILITIES TO DRY DEPOSITION IN RECEPTOR REGIONS OVER 6-MONTH SIMULATION PERIOD

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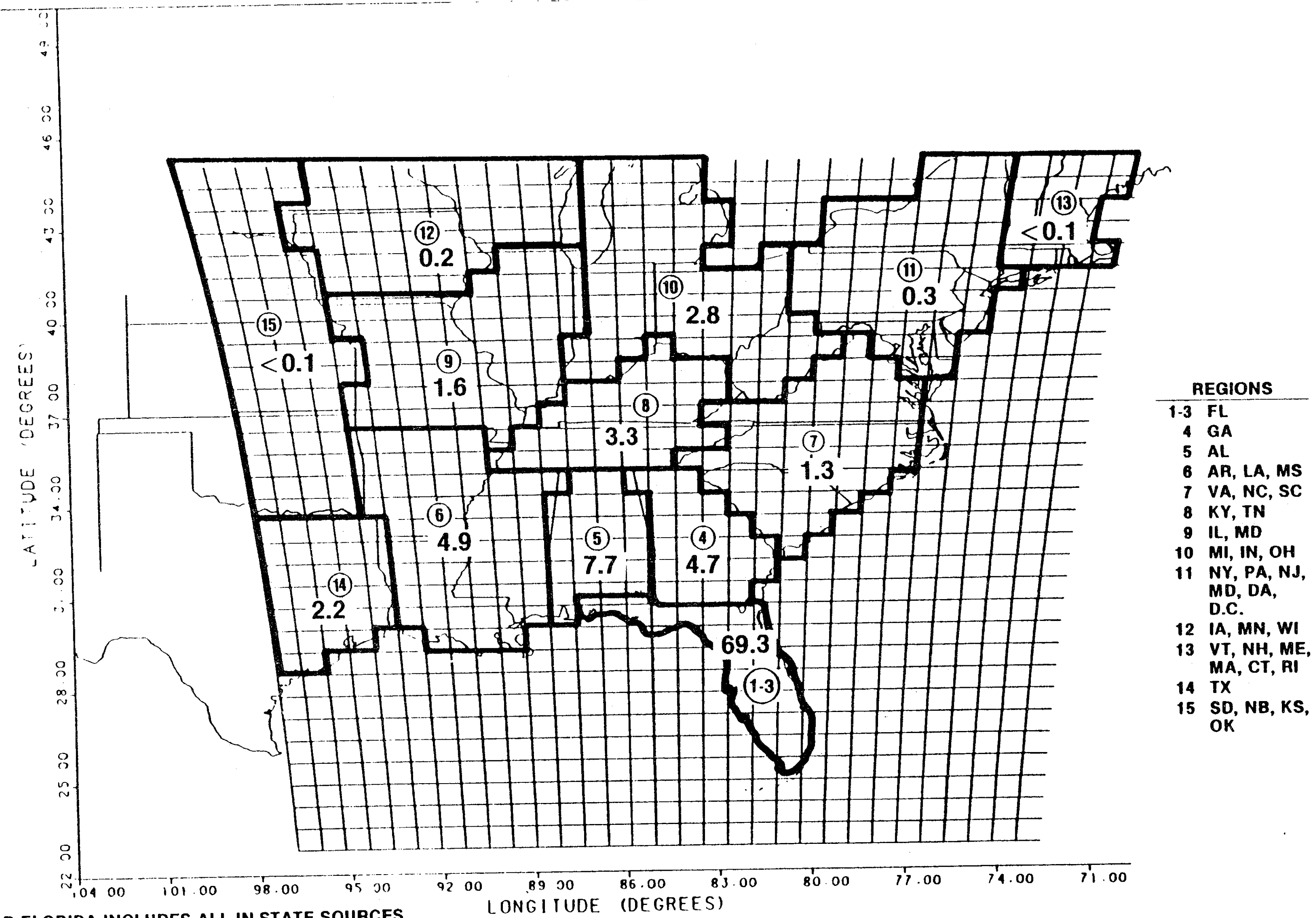

NOTE: VALUE FOR FLORIDA INCLUDES ALL IN-STATE SOURCES.

Figure 3.3-8
PERCENT CONTRIBUTION OF SOURCE REGIONS TO $SO_2$ CONCENTRATIONS IN FLORIDA

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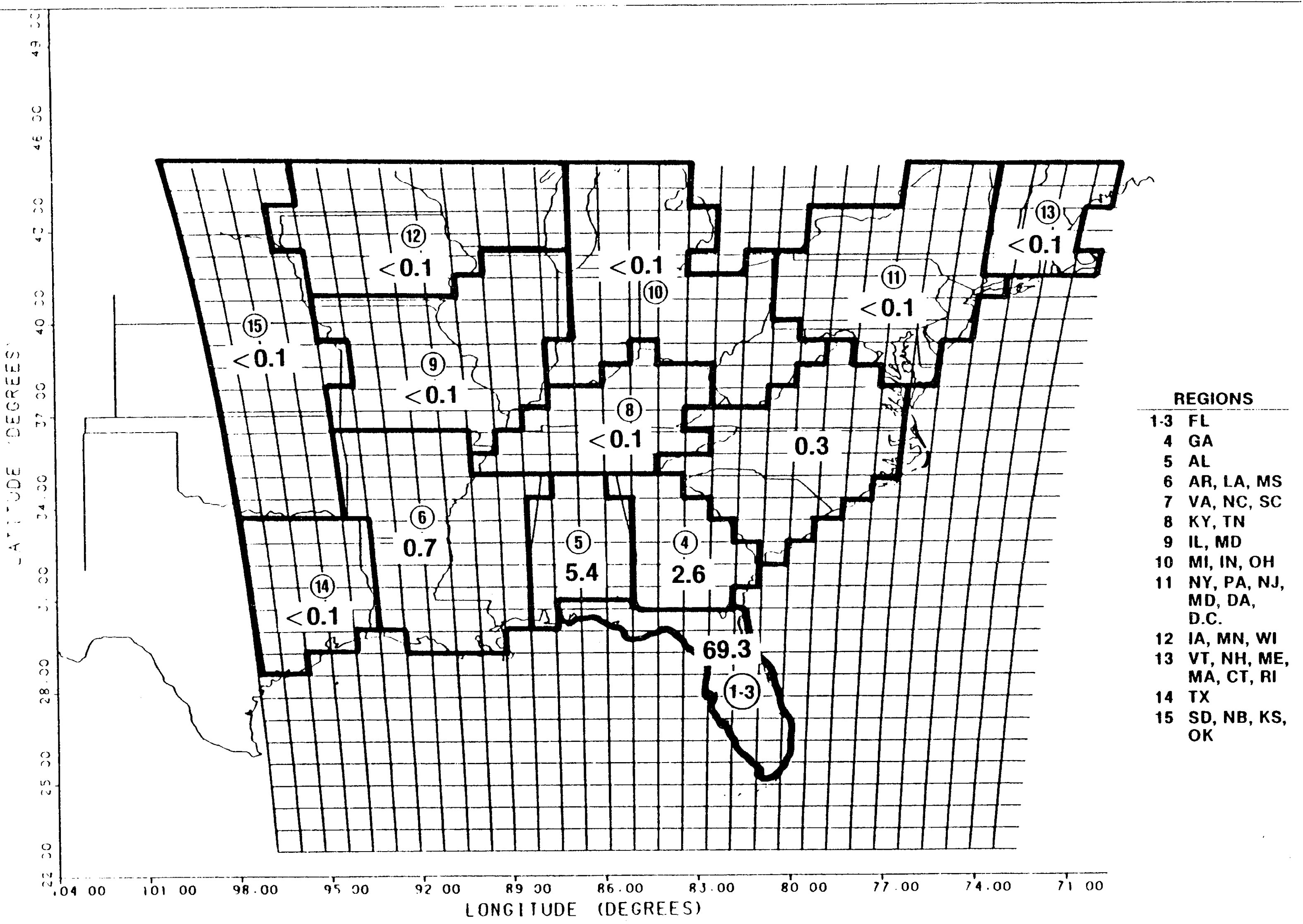

Figure 3.3-9
PERCENT CONTRIBUTION OF ALL FLORIDA SOURCES TO $SO_2$ CONCENTRATIONS IN RECEPTOR REGIONS

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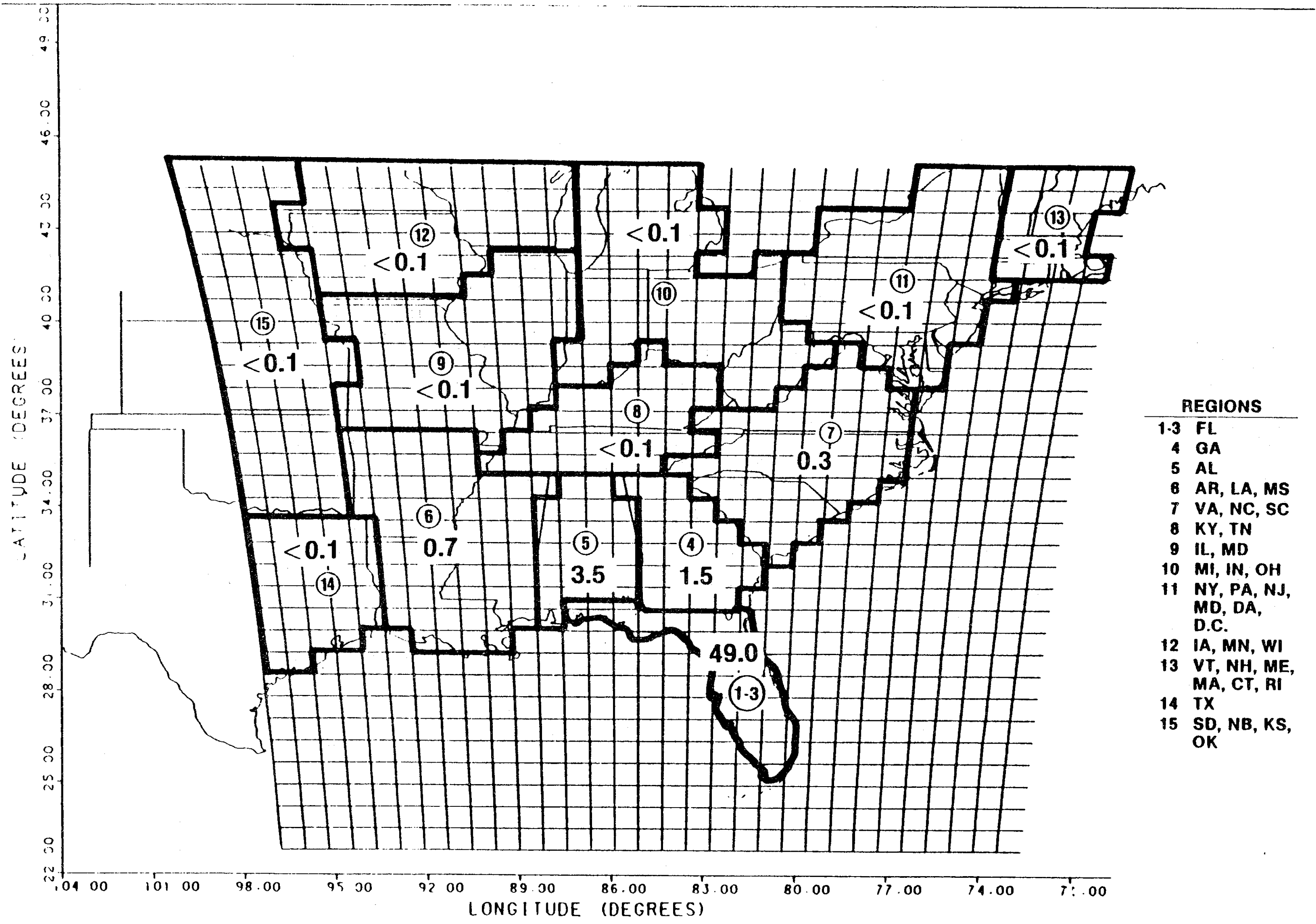

Figure 3.3-10
PERCENT CONTRIBUTION OF FLORIDA UTILITIES TO $SO_2$ CONCENTRATIONS IN RECEPTOR REGIONS FOR 6-MONTH SIMULATION PERIOD

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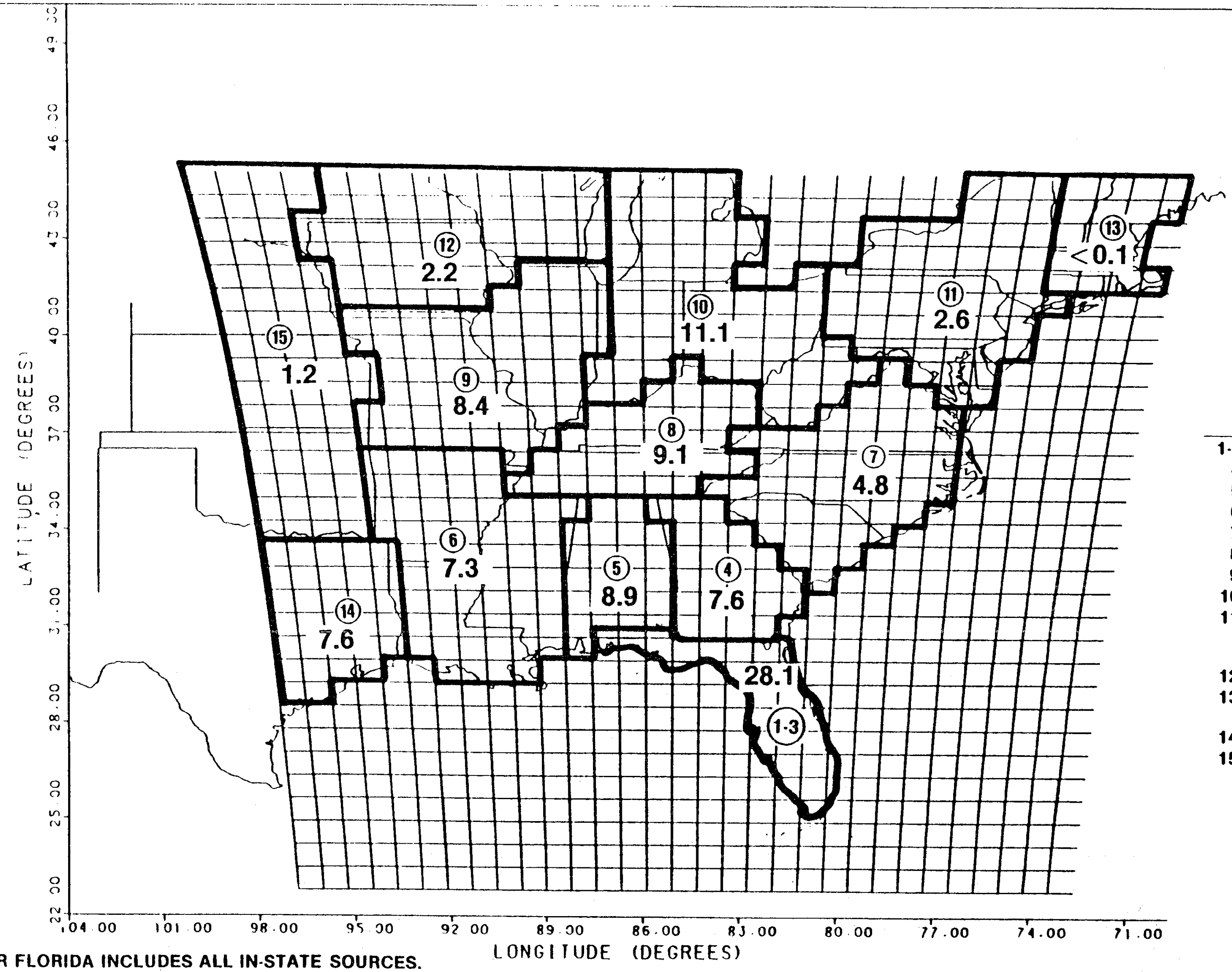

| REGIONS | |
|---|---|
| 1-3 | FL |
| 4 | GA |
| 5 | AL |
| 6 | AR, LA, MS |
| 7 | VA, NC, SC |
| 8 | KY, TN |
| 9 | IL, MD |
| 10 | MI, IN, OH |
| 11 | NY, PA, NJ, MD, DA, D.C. |
| 12 | IA, MN, WI |
| 13 | VT, NH, ME, MA, CT, RI |
| 14 | TX |
| 15 | SD, NB, KS, OK |

NOTE: VALUE FOR FLORIDA INCLUDES ALL IN-STATE SOURCES.

Figure 3.3-11
PERCENT CONTRIBUTION OF SOURCE REGIONS TO $SO_4^{-2}$ CONCENTRATIONS IN FLORIDA

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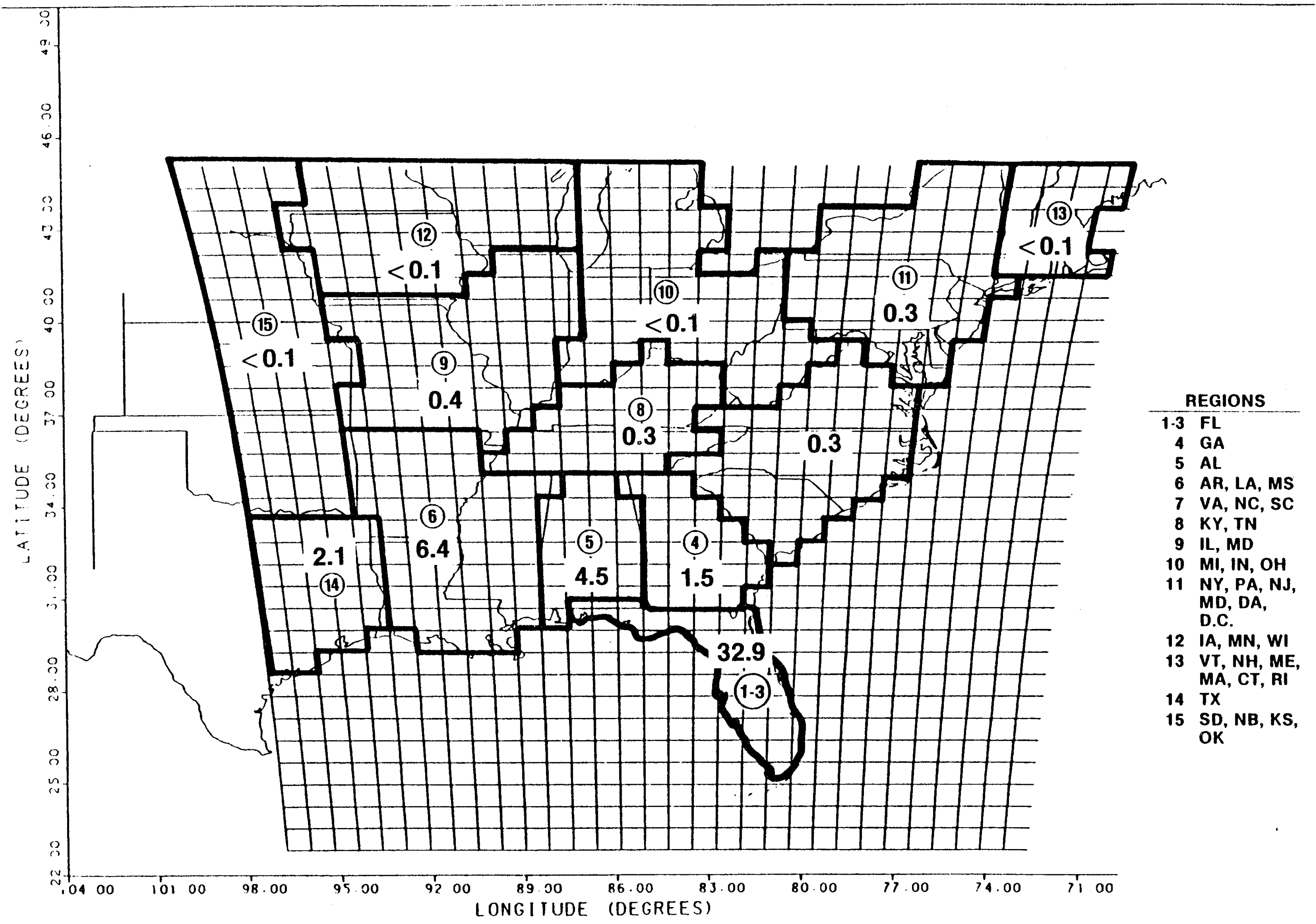

Figure 3.3-12
PERCENT CONTRIBUTION OF ALL FLORIDA SOURCES TO ATMOSPHERIC $SO_4^{-2}$ CONCENTRATIONS IN RECEPTOR REGIONS

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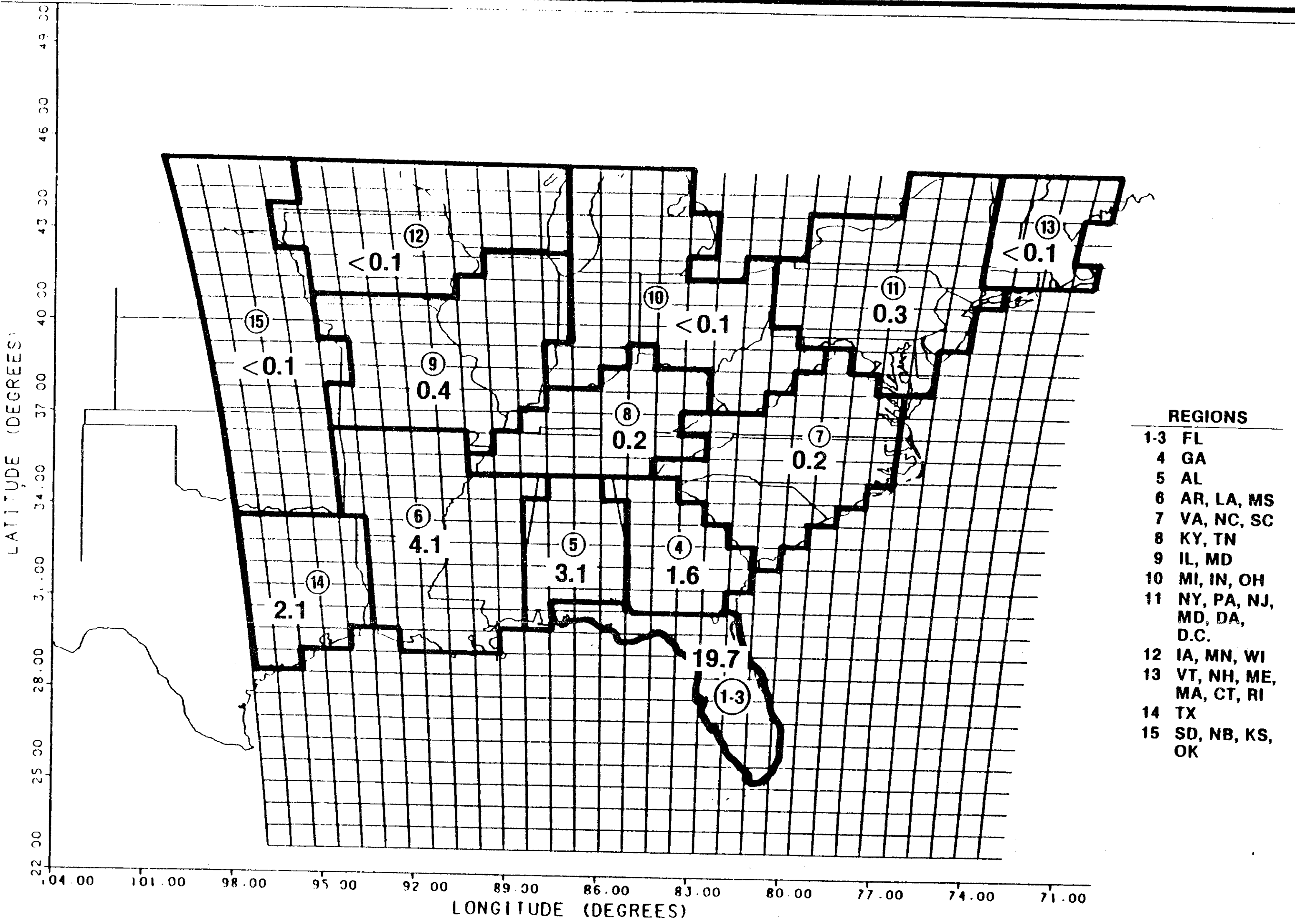

Figure 3.3-13
PERCENT CONTRIBUTION OF FLORIDA UTILITIES TO $SO_4^{-2}$ CONCENTRATIONS IN RECEPTOR REGIONS FOR 6-MONTH SIMULATION PERIOD

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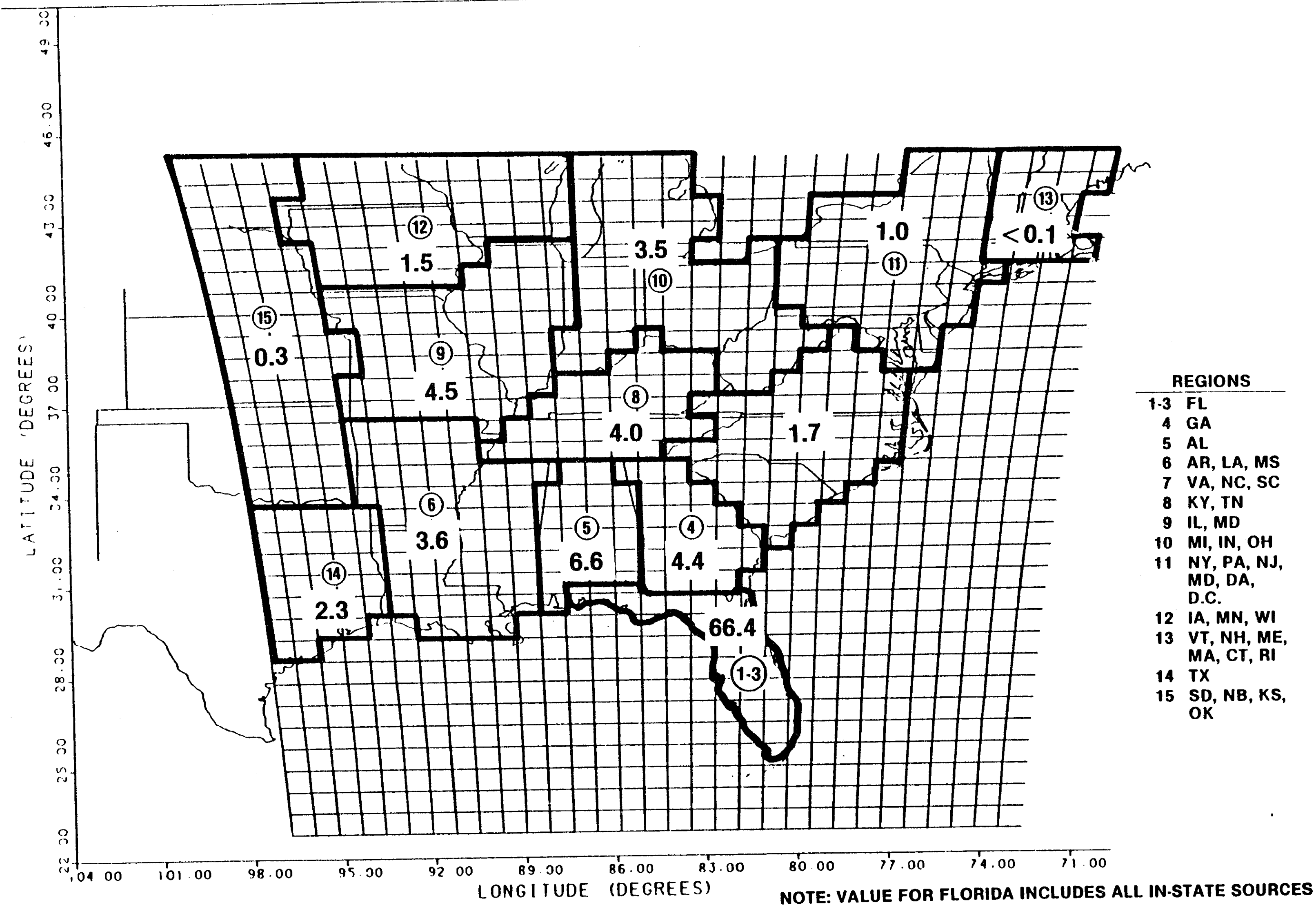

NOTE: VALUE FOR FLORIDA INCLUDES ALL IN-STATE SOURCES

Figure 3.3-14
PERCENT CONTRIBUTION OF SOURCE REGIONS TO TOTAL SULFUR DEPOSITION IN FLORIDA

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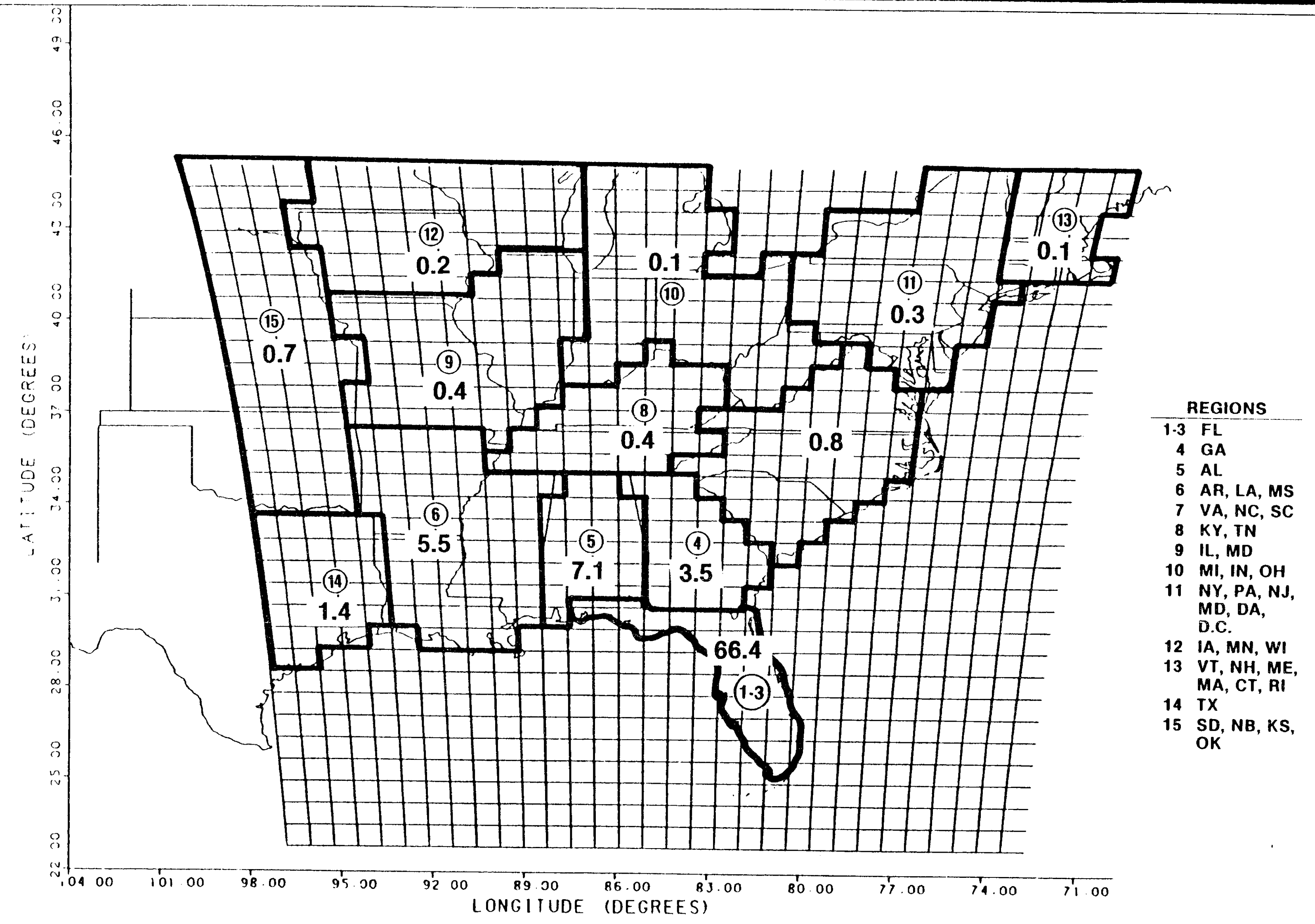

Figure 3.3-15
PERCENT CONTRIBUTION OF ALL FLORIDA SOURCES TO TOTAL DEPOSITION IN RECEPTOR REGIONS FOR 6-MONTH SIMULATION PERIOD

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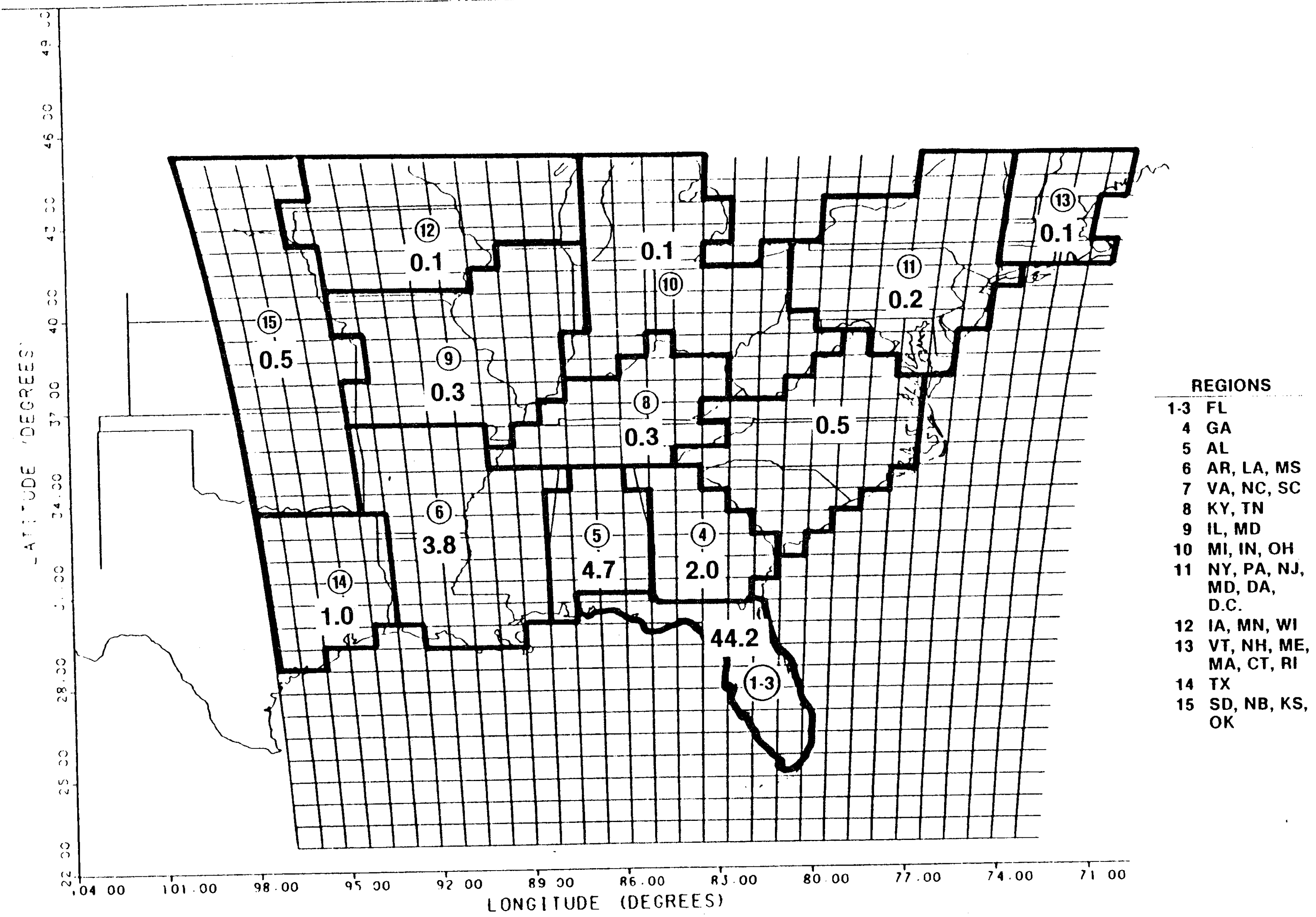

Figure 3.3-16
PERCENT CONTRIBUTION OF FLORIDA UTILITIES TO TOTAL SULFUR DEPOSITION IN RECEPTOR REGIONS

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Mass balances over the eastern United States for the 6-month simulation period are presented in Table 3.3-12. Results show that wet and dry deposition over the terrestrial portion of the ENAMAP domain are roughly comparable and together account for slightly less than 50 percent of emissions. Wet deposition over the region is dominated (75 percent) by $SO_4^{-2}$ scavenging, while dry deposition is dominated (90 percent) by $SO_2$ removal. Average wet and dry deposition over the region correspond to roughly 3.0 and 3.6 kilograms of sulfur per hectare (kg-S/ha) for the 6-month period.

Comparison of the ENAMAP balance for 1983 with that of Galloway and Whelpdale (1980) shows distinct similarities. In both cases dry-deposition estimates slightly exceed wet-deposition estimates and together total about 50 percent of emissions. The 1983 mass balance is for 6 months only; the annual percentage may deviate strongly from those shown. Across Florida, for example, rainfall during the 6-month simulation period amounted to 64 percent of the annual total for October 1982 to September 1983. Thus, direct scaling of deposition values may be misleading. Despite general agreement in dry deposition estimates, these results are not subject to verification.

The model performance results for the 6 months evaluated are presented in Table 3.3-13. Model performance appears to be related to the representation of emissions in regions surrounding monitoring sites. Agreement between observed versus predicted wet deposition is best for Florida sites, poorest for sites within nongridded emission regions, and in between for sites in southeastern states with gridded emissions. The average absolute error of wet deposition prediction increases from 18 milligrams of sulfur per square meter (mg-S/$m^2$) to 25 mg-S/$m^2$ to 49 mg-S/$m^2$ for Florida, southeastern, and non-southeastern sites, respectively. This finding suggests that the representation of emission could impose a bias on overall model performance. However, in the absence of detailed model validation studies, the magnitude and direction of such an effect is unknown.

Table 3.3-12. Calculated Mass Balances Over Terrestrial Portion of ENAMAP Domain

| Month | Percent of Total Sulfur Emitted | | | | | | |
|---|---|---|---|---|---|---|---|
| | Wet Depostion | | | Dry Deposition | | | Export* |
| | $SO_2$ | $SO_4^{-2}$ | Total | $SO_2$ | $SO_4^{-2}$ | Total | |
| 1983 | | | | | | | |
| February | 4.7 | 7.7 | 12.4 | 38.3 | 4.3 | 42.6 | 48.1 |
| March | 6.6 | 15.5 | 22.1 | 24.8 | 3.8 | 28.6 | 43.9 |
| April | 8.6 | 15.1 | 23.7 | 21.2 | 2.2 | 23.4 | 40.5 |
| June | 6.7 | 26.3 | 33.0 | 22.2 | 2.7 | 24.9 | 33.8 |
| July | 3.9 | 14.6 | 18.5 | 22.1 | 2.4 | 24.5 | 47.0 |
| August | 4.8 | 20.5 | 25.3 | 21.8 | 2.6 | 24.4 | 42.2 |
| All | 5.8 | 16.7 | 22.5 | 25.1 | 3.0 | 28.1 | 42.6 |
| 1980† | — | — | 17.9 | — | — | 23.6 | 42.0 |

*Export = Percent of sulfur that crosses model boundaries; as a result of the model's structure, sulfur that crosses the boundary cannot return, nor can sources outside the model domain contribute to the sulfur mass balance within the domain.

†From Galloway and Whelpdale, 1980.

Source: ESE, 1986.

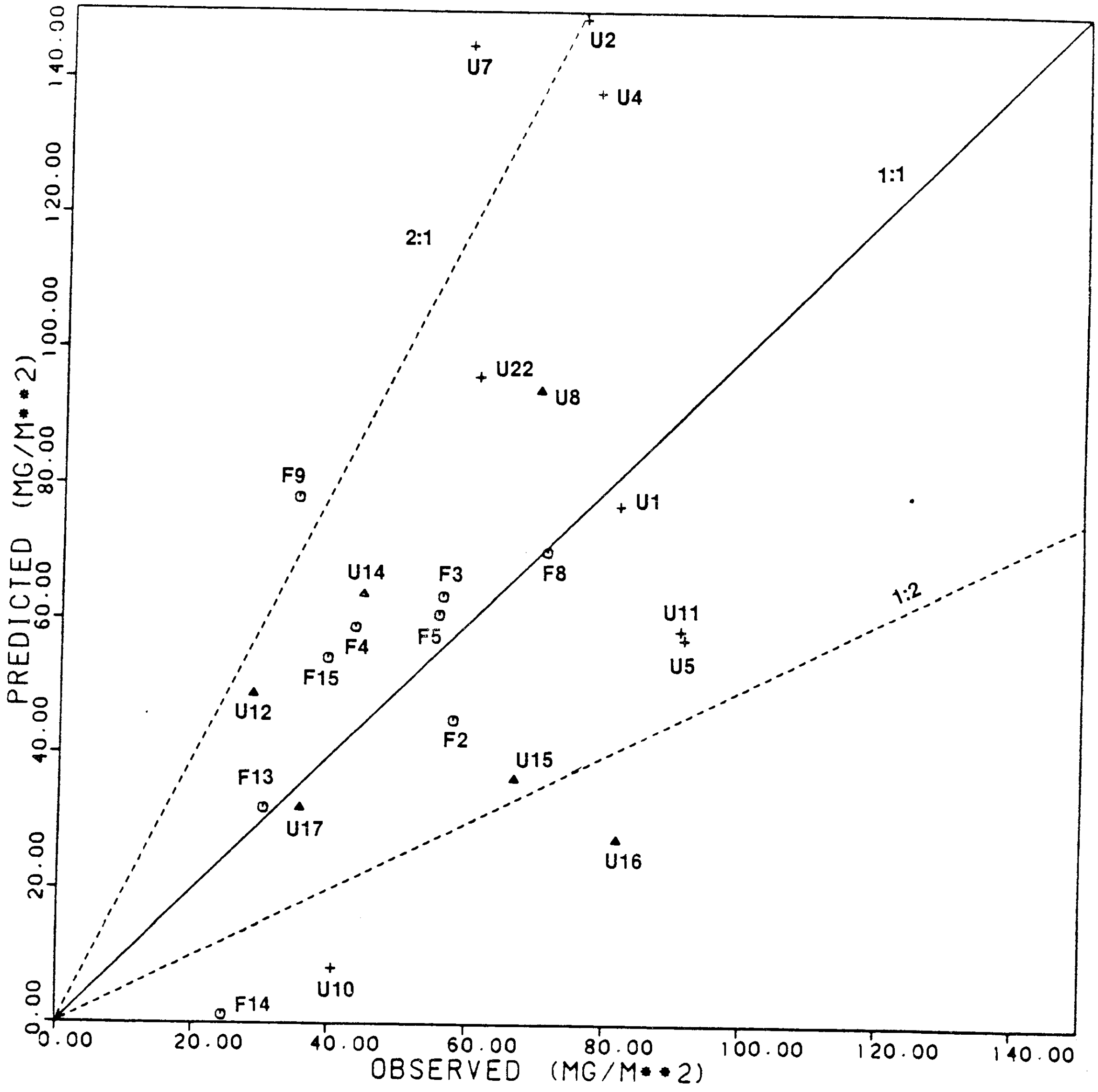
Table 3.3-13. Observed Versus Predicted Sulfur Wet-Deposition Rates, $SO_2$ Concentration, and $SO_4^{-2}$ Concentration for the 6-Month Simulation Period

| Parameter | Sites Considered | Observed ($C_o \pm \sigma C_o$) | Predicted ($C_s \pm \sigma C_s$) | Residual ($d \pm \sigma d$) |
|---|---|---|---|---|
| Wet Deposition (mg-S/$m^2$) | All (n=23) | 57.3 ±39.4 | 61.7 ±63.5 | -4.4 ±57.0 |
|  | Florida | 45.7 ±22.4 | 42.6 ±37.8 | 3.1 ±35.5 |
| $SO_2$ (μg/$m^3$) | Florida | 2.5 ±1.4 | 2.0 ±1.8 | 0.5 ±1.2 |
| $SO_4^{-2}$ (μg/$m^3$) | Florida | 4.6 ±2.2 | 7.5 ±4.8 | -2.9 ±3.6 |

Source: ESE, 1986.

Mean monthly observed versus predicted wet depositions for the 6-month simulation period are illustrated in Figure 3.3-17. Results for individual sites show that the quality of predictions generally decreases in the following order: Florida sites (circles) > southeastern sites (triangles) > non-southeastern sites (crosses). Except for Sites 9 and 14, Florida predictions agree with observations within ±50 percent.

Interestingly, wet deposition of sulfur at Florida Sites 5 and 8, which appear to be affected by local sources (see Section 2.2) was estimated adequately by the model. The initial, automatic mixing of source emissions over the 80-km x 80-km cells does not appear to have adversely affected model performance at these sites relative to other sites that are more isolated from sources. In general, the model estimates of average wet deposition were in better agreement than either $SO_2$ or particulate concentrations. This result is similar to that found by the United States-Canada Work Group 2 (1982) and may be due in part to the more localized influence of localized sources especially for $SO_2$. The differences between observed and predicted depositions and concentrations are not statistically significant (see Table 3.1-13). Mean residual (i.e., observed minus predicted) concentration is generally less than 10 percent of the observed concentration; however, the variability in the residuals is about the same or higher than the observed concentrations.



NOTES: SEE FIGURE 3.3-1 FOR STATION LOCATIONS.
UAPSP(u) AND FLORIDA(F) SITE NUMBERS
SHOWN NEXT TO DATA POINTS.

Figure 3.3-17
OBSERVED AND PREDICTED MEAN MONTHLY WET DEPOSITION FOR 6-MONTH SIMULATION PERIOD

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### 3.3.2.4. Limitations of Model Findings

Results of the previous section indicate that ENAMAP can be adjusted to produce reasonable agreement between predicted and observed long-term (i.e., 6-month) averaged wet sulfur deposition on a regional scale. Mass balances calculated for the terrestrial portion of the model domain also appear to be consistent with independently derived estimates of sulfur deposits to and flux from the eastern United States. Despite the apparent consistency of these general findings, the uncertainty in specific source receptor relationships is unknown, but possibly large (i.e., order of magnitude). The purpose of this subsection is to briefly discuss several of the major limitations and uncertainties inherent to ENAMAP. NAS (1983), Bhumralker (1984), and Schnoor (1984) present more information on this generation of atmospheric transport and deposition models. These reviews unanimously conclude that ENAMAP and related models are inadequate for examination of source-receptor relationships.

As noted previously, a major limitation of trajectory models such as ENAMAP is the paucity of the database used to simulate atmospheric transport of emissions. Analysis of upper air data collected at widely separated locations (i.e., hundreds of kilometers) and 12-hour time intervals can yield a misleading interpretation of atmospheric phenomena. Precipitation events, for example, are frequently short-lived (e.g., thunderstorms) and characterized by abrupt changes in wind speed and direction (e.g., frontal events). Recent comparison of various methods of trajectory calculation indicate that uncertainty is greatest during periods of precipitation (Artz et al., 1985; NCAR, 1985). Unless this uncertainty is of a random nature (unlikely for frontal events), long-term simulations may have major systematic biases.

A related source of uncertainty in ENAMAP is the duration of trajectory calculations. If the mass of an emission puff exceeds its threshold value, the puff will be tracked for as many as 100 3-hour time steps, or

12.5 days. Given the initial deficiencies in the upper-air database, 12.5 days is a long time. In addition, the source configuration used in the present simulation compounds this difficulty because of the high number of sources consolidated into emission centroids.

Despite the multi-layered nature of ENAMAP, atmospheric structure and vertical transport are poorly represented. Loss of pollutants out of the uppermost model layer is permitted and is accounted for well below 1 percent of the sulfur flux during model simulation. This result conflicts with observation of dense aerosol layers at high altitudes (Shipley, 1983) and calculations of pollutant transport via cloud venting (Stull, 1983), which suggest significant convective transport above the boundary layer. Similarly, the inability to treat mesoscale atmospheric processes (e.g., land and sea breezes) limits model applicability. This may be an especially critical limitation for Florida because of its extensive boundaries along the Atlantic Ocean and the Gulf of Mexico.

Probably the most severe limitation of ENAMAP is the treatment of transformation and deposition processes. In all cases, these are simulated as simple, first-order mechanisms. Diurnal seasonal and latitudinal factors are used as simple expedients to modulate tranformation and deposition rates; however, the effects of co-pollutants (e.g., oxidants, catalysts, neutralizing agents, and inhibitors) are not considered. Absence of chemistry is inherent to Lagrangian transport models and is a principal reason for the computational economy of ENAMAP versus most Eulerian models.

Much of the uncertainty embodied in ENAMAP is merely a reflection of limited information on complex natural process. Dry deposition is a good example. At present, observational data for simulation and evaluation of dry deposition are extremely limited. Technological constraints limit measurement of deposition to highly restrained and perhaps unrepresentative environments (i.e., uniformly smooth surfaces). If, however, it is assured that deposition rates are directly proportional to ambient concentrations, then the modeler is confronted with a serious deficiency in available data for $SO_2$ and aerosol $SO_4^{-2}$.

### 3.3.3 AIR MASS TRAJECTORY FINDINGS

Results of the air mass trajectory studies and their implications for Florida are presented in five subsections. The first subsection (3.3.3.1) discusses 5-year climatologies of backward trajectories for three Florida locations: a panhandle site (Site 2, located near Caryville); a north-central site (Site 5, located near Gainesville); and a southern site (Site 9, located near Archbold). The chief objective of studying climatology is to define the general pattern of atmospheric transport to Florida and its variation from location to location within the state. Another objective of the climatology is to compare the general picture of atmospheric transport during 1983 with that for the years 1979 through 1982. Calendar Year 1983 is of particular interest because this year is primarily used as the reference period for subsequent construction of a mass-balance sulfur and nitrogen model for the Florida atmosphere as well as the LRT modeling.

The second subsection (3.3.3.2) compares 1983 trajectories produced using NAMER-WINDTEMP data only and NAMER-WINDTEMP plus ATOLL data as inputs to the ATAD model (refer to Subsection 3.2.4.3). The latter dataset extends trajectories over oceanic areas, thus providing additional information on atmospheric transport. Because ATOLL data covering the entire climatological period (i.e., 1979 through 1983) are not available, trajectories with and without ATOLL data were compared for only a single year. This comparison shows the influence of data completeness on the directional frequency distribution of trajectories for Caryville, Gainesville, and Archbold.

The relationship between atmospheric transport and precipitation/air chemistry data across Florida is investigated in two ways in the third subsection (3.3.3.3). First, trajectories are sorted into directional sectors and the associated precipitation/air chemistry data are compared across sectors. Second, trajectory segments for 6-hour time-steps are used to calculate the air mass residence time in numerous regions (see Table 3.2-5) across North America. Residence time data are then used to infer likely sources of atmospheric pollutants for a variety of synoptic meteorological classes (e.g., continental high) and episodes of low-pH and high-pH precipitation. Finally, regional residence times are compared for the upper and lower quartile ambient concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$.

Air chemistry and trajectory data are combined in the fourth subsection (3.3.3.4) to estimate the import of atmospheric $SO_x$ and $NO_x$ into Florida. Imports are calculated for the northern, southern, eastern, and western boundaries of the state and then compared to infer the relative strength of out-of-state anthropogenic and natural sources of $SO_x$ and $NO_x$.

A mass-balance $SO_x$ and $NO_x$ model for the Florida atmosphere is presented in the final subsection. Included in this model are Calendar Year 1983 estimates of the following components: in-state anthropogenic and biogenic emissions, out-of-state anthropogenic and biogenic imports, wet deposition, dry deposition, and export. Results of the 1983 model are compared with Edgerton's (1981) mass-balance model and then used to infer probable source-sink relationships for atmospheric $SO_x$ and $NO_x$.

### 3.3.3.1 Five-Year Climatology of Trajectories for Florida

Trajectory calculations for Caryville, Gainesville, and Archbold show that 1-day backward trajectories can be calculated successfully (i.e., $\geq$90 percent of the total number of trajectories calculated) using NAMER-WINDTEMP data. However, because trajectories for Florida are calculated for 2 through 5 days, the percentage of undetermined trajectories increases due to lack of data coverage over the Atlantic Ocean and Gulf of Mexico. This result is illustrated in Table 3.3-14 which shows the trajectory sector classifications of 1-day through 5-day trajectories for Caryville for the period 1979 through 1983. (Note: The undetermined category refers to those trajectories which go beyond the trajectory horizon of the ATAD model and result in the model not calculating a trajectory for that time period.) For 1-day trajectories, the frequency distribution is relatively flat with transport maxima from the northwest (NW) and southeast (SE) and minima from the south (S) and southwest (SW). Undetermined trajectories account for 6.8 percent of the 1-day population which is less than the trajectories calculated from any single sector, indicating that the distribution shown is unlikely to change radically if all trajectories could be calculated.

This conclusion is much less plausible for 2-day through 5-day backward trajectories. The frequency distribution for 2-day trajectories shows a distinct minimum in the S sector and reduced frequencies (relative to 1-day) for the east (E) through west (W) sectors. Undetermined trajectories represent the most abundant category, accounting for more than 17 percent of the total populations. For 3-day, 4-day, and 5-day trajectories, the undetermined fraction becomes increasingly dominant, while all directional sectors [except north (N) and NW] decrease markedly. The undetermined category for 5-day trajectories, for example, represents nearly 60 percent of the population and appears to have increased at the expense of all but the N and NW sectors. This effect is largely due to the lack of NAMER-WINDTEMP data over water, which prevents calculations beyond the trajectory horizon (see Figure 3.2-2). The

Table 3.3-14. Frequency Distribution (%) of 1-Day Through 5-Day Backward Trajectories for Caryville for the Period 1979 Through 1983

| Duration (days) | Trajectory Sector | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | N | NE | E | SE | S | SW | W | NW | Undetermined |
| 1 | 12.3 | 10.5 | 11.6 | 14.2 | 9.0 | 9.7 | 11.2 | 14.8 | 6.8 |
| 2 | 12.0 | 11.3 | 8.8 | 10.8 | 5.5 | 8.0 | 9.0 | 17.1 | 17.7 |
| 3 | 13.2 | 9.4 | 5.1 | 7.0 | 3.6 | 6.0 | 6.7 | 16.0 | 33.0 |
| 4 | 12.9 | 6.9 | 2.9 | 4.4 | 2.6 | 4.3 | 5.0 | 13.4 | 47.6 |
| 5 | 10.5 | 5.0 | 1.9 | 2.9 | 1.5 | 3.3 | 3.6 | 12.1 | 59.3 |

Source: ESE, 1986.

trajectory horizon is closest to Caryville in the S sector, the category displaying the most dramatic loss of trajectories in any category. The frequency of N and NW sectors, in contrast, remains essentially constant through at least the 4-day backward trajectories. This suggests that the 1-day frequency distribution may approximate the distributions of 2-day through 5-day trajectories. On the basis of this observation, 1-day trajectory data will be used to describe the 5-year climatologies for Caryville, Gainesville, and Archbold.

Annual frequency distributions of 1-day backward trajectories for 1979 through 1983 are shown in Table 3.3-15. Results for Caryville indicate relatively flat distribution of atmospheric transport among sectors for most years. Slight maxima in the distribution occur in diametrically opposite directions (NW and SE) and appear to persist from year to year. Over the entire period, NW and SE trajectories account for 14.8 percent and 14.3 percent of the total population, respectively. Corresponding values for 1983 are 15.3 percent and 14.2 percent, indicating a fairly typical year for trajectory-assisted interpretation of precipitation and air chemistry. Transport minima in the Caryville frequency distribution vary from year to year, but are generally found in either the S or SW sectors, which average less than 10 percent of the 5-year distribution. Inspection of NWS surface and upper-air weather charts for dates with NW and SE sector trajectories typically shows the influence of continental and maritime high-pressure systems, respectively, of which the former predominate during winter and the latter during summer. Charts for S and SW sector trajectories, however, usually show a transitional situation just prior to the passage of a warm or cold front.

Undetermined trajectories for Caryville average 6.6 percent of the total population and, except for 1981, represent the least important category of trajectories. As noted previously, this suggests that truncation of 1-day trajectories is unlikely to strongly influence the Caryville

Table 3.3-15. Frequency Distribution (%) of 1-Day Backward Trajectories (NAMER-WINDTEMP only) for Caryville, Gainesville, and Archbold

| Year | Trajectory Sector | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | N | NE | E | SE | S | SW | W | NW | Undetermined |
| **Caryville** | | | | | | | | | |
| 1983 | 10.7 | 12.6 | 11.0 | 14.2 | 9.3 | 5.7 | 13.3 | 15.3 | 7.9 |
| 1982 | 12.4 | 9.9 | 14.2 | 14.0 | 10.4 | 10.5 | 8.8 | 12.4 | 7.4 |
| 1981 | 11.1 | 10.6 | 9.1 | 12.4 | 6.8 | 11.7 | 9.7 | 16.5 | 12.2 |
| 1980 | 14.6 | 10.1 | 11.6 | 14.1 | 7.0 | 12.4 | 12.1 | 14.0 | 4.1 |
| 1979 | 12.7 | 9.2 | 12.0 | 16.8 | 11.7 | 8.4 | 12.0 | 15.8 | 1.4 |
| All | 12.3 | 10.5 | 11.6 | 14.3 | 9.0 | 9.7 | 11.2 | 14.8 | 6.6 |
| **Gainesville** | | | | | | | | | |
| 1983 | 7.0 | 13.3 | 11.5 | 14.1 | 8.2 | 6.4 | 12.8 | 18.6 | 8.1 |
| 1982 | 8.0 | 12.1 | 15.1 | 14.6 | 10.1 | 9.5 | 10.4 | 12.0 | 8.2 |
| 1981 | 7.6 | 13.3 | 10.0 | 14.6 | 7.6 | 7.2 | 10.2 | 19.1 | 10.3 |
| 1980 | 11.4 | 9.9 | 12.9 | 13.4 | 9.0 | 7.6 | 16.0 | 15.4 | 4.4 |
| 1979 | 7.1 | 8.4 | 14.1 | 17.2 | 10.5 | 6.9 | 14.5 | 17.0 | 4.3 |
| All | 8.2 | 11.4 | 12.7 | 14.8 | 9.1 | 7.5 | 12.8 | 16.4 | 7.1 |
| **Archbold** | | | | | | | | | |
| 1983 | 7.1 | 8.7 | 13.9 | 15.8 | 8.8 | 7.2 | 8.7 | 15.3 | 14.4 |
| 1982 | 6.1 | 12.8 | 12.8 | 16.4 | 12.3 | 6.2 | 7.9 | 8.3 | 17.2 |
| 1981 | 9.0 | 10.0 | 12.0 | 13.0 | 8.5 | 5.3 | 6.4 | 12.4 | 23.4 |
| 1980 | 10.3 | 9.7 | 14.5 | 14.2 | 10.3 | 7.9 | 13.3 | 13.7 | 8.4 |
| 1979 | 6.4 | 10.0 | 16.4 | 17.2 | 8.4 | 5.3 | 10.3 | 10.5 | 15.4 |
| All | 7.8 | 10.2 | 13.9 | 15.3 | 9.7 | 6.4 | 9.3 | 12.0 | 15.8 |

Source: ESE, 1986.

frequency distribution. The validity of this assumption is evaluated in Subsection 3.3.3.2 using trajectories calculated with NAMER-WINDTEMP plus ATOLL data.

Annual frequency distributions for Gainesville were generally similar to Caryville; however, there was a general increase in the W and NW sectors as well as a decrease in the N and SW sectors relative to Caryville. The NW and SE sectors were the predominant trajectory directions for Gainesville as they were for Caryville.

The difference between trajectory classifications as well as the increase in the numbers of undetermined trajectories observed in Gainesville relative to Caryville was even more apparent for trajectories calculated for Archbold. For this site, undetermined trajectories were often a major percentage of the total. This observation is reflected by the general increase in trajectories for the E, SE, and S sectors, which suggests that many trajectories originate over the Atlantic Ocean and the Caribbean Sea.

Although the frequency distributions for Gainesville and Archbold were somewhat different than Caryville, there were similarities. Given the spatial distribution of upper-air meteorological observations, this finding is not surprising. Previous investigations have shown that these three receptors rely heavily, but to varying degrees, on data from five upper-air stations for calculation of the initial time-step of all trajectories (ESE, 1983b). The 1983 trajectory distributions for all sites are similar to their respective 5-year averages, suggesting that subsequent evaluation of 1983 trajectories can reasonably reflect atmospheric transport over the past 5 years.

Despite the general similarity of frequency distributions among sites, the observed differences are important for several reasons. First, atmospheric transport from N through W sectors decreases from Caryville to Archbold, suggesting that out-of-state emission sources are more likely to influence the precipitation chemistry and air quality at Caryville relative to Archbold. Second, transport from E and SE, presumably regions of low pollutant emissions, increases from Caryville to Archbold, which indicates that precipitation chemistry and air quality at Archbold are influenced more frequently by trajectories from low source regions (i.e., southern Atlantic Ocean). Finally, the importance of the undetermined trajectory classification increases marginally from Caryville to Gainesville but dramatically from Gainesville to Archbold. This later observation may be important in evaluating the potential for trajectory recurvature over the Atlantic Ocean. Taken together, these three observations in trajectory distribution suggest that out-of-state emission sources (i.e., eastern United States) are more likely to influence the chemical climate of Caryville than either Gainesville or Archbold, but that recurvature of trajectories may be important and will be explored in the following subsection. Nevertheless, in spite of the large percentage of undetermined trajectories at Archbold, the trajectory horizon is relatively nonexistent from the N and NW sectors, indicating that out-of-state source contributions at this site are lower than those relative to other sites.

Atmospheric transport for 1983, when compared to the mean transport over the 5-year period, indicates that 1983 would be generally representative of transport to Florida. With the exception of the NE and SW sectors for the Caryville site, the frequency of occurrence for all 1983 trajectory sectors was not significantly different (95-percent confidence interval) from the mean 5-year trajectory sector.

### 3.3.3.2 Comparison of Trajectories Calculated Using NAMER-WINDTEMP and NAMER-WINDTEMP Plus ATOLL Data

Results of 1983 1-day trajectory calculations using NAMER-WINDTEMP plus ATOLL data are shown in Table 3.3-16 for Caryville, Gainesville, and Archbold. Trajectories are also shown for Site 13, located in the Everglades. Annual frequency distributions for Caryville, Gainesville, and Archbold are generally quite similar to the NAMER-WINDTEMP-only trajectories, despite the fact that the undetermined category has been reduced from an average of approximately 10 percent to approximately 2 percent. This indicates that the overall picture of atmospheric transport, as suggested by the NAMER-WINDTEMP trajectories, is little affected by the lack of a complete population.

The difference between NAMER-WINDTEMP and NAMER-WINDTEMP plus ATOLL trajectories does vary, however, as a function of receptor. For Caryville, the frequency of undetermined trajectories was reduced from 7.9 percent for NAMER-WINDTEMP data to 1.2 percent with NAMER-WINDTEMP plus ATOLL data, and the additional trajectories appear to be more or less uniformly distributed across all sectors. Archbold trajectories, however, exhibit a substantial increase in the E and SE sectors (over a 20-percent combined increase) for the NAMER-WINDTEMP plus ATOLL trajectories, indicating that the relative proximity of the trajectory horizon in the E sector has caused truncation of the equivalent of 2 weeks of trajectories. This latter observation is reinforced by the Everglades trajectories for the E and SE sectors, which amount to 40 percent of the total calculated trajectories.

The combined NAMER-WINDTEMP plus ATOLL trajectories generally confirm the frequency distribution indicated by NAMER-WINDTEMP trajectories alone. However, numerous cases have been identified in which the trajectories give conflicting results. This generally occurs when a trajectory calculated from NAMER-WINDTEMP is truncated over water (usually the Atlantic Ocean) while the corresponding NAMER-WINDTEMP plus ATOLL

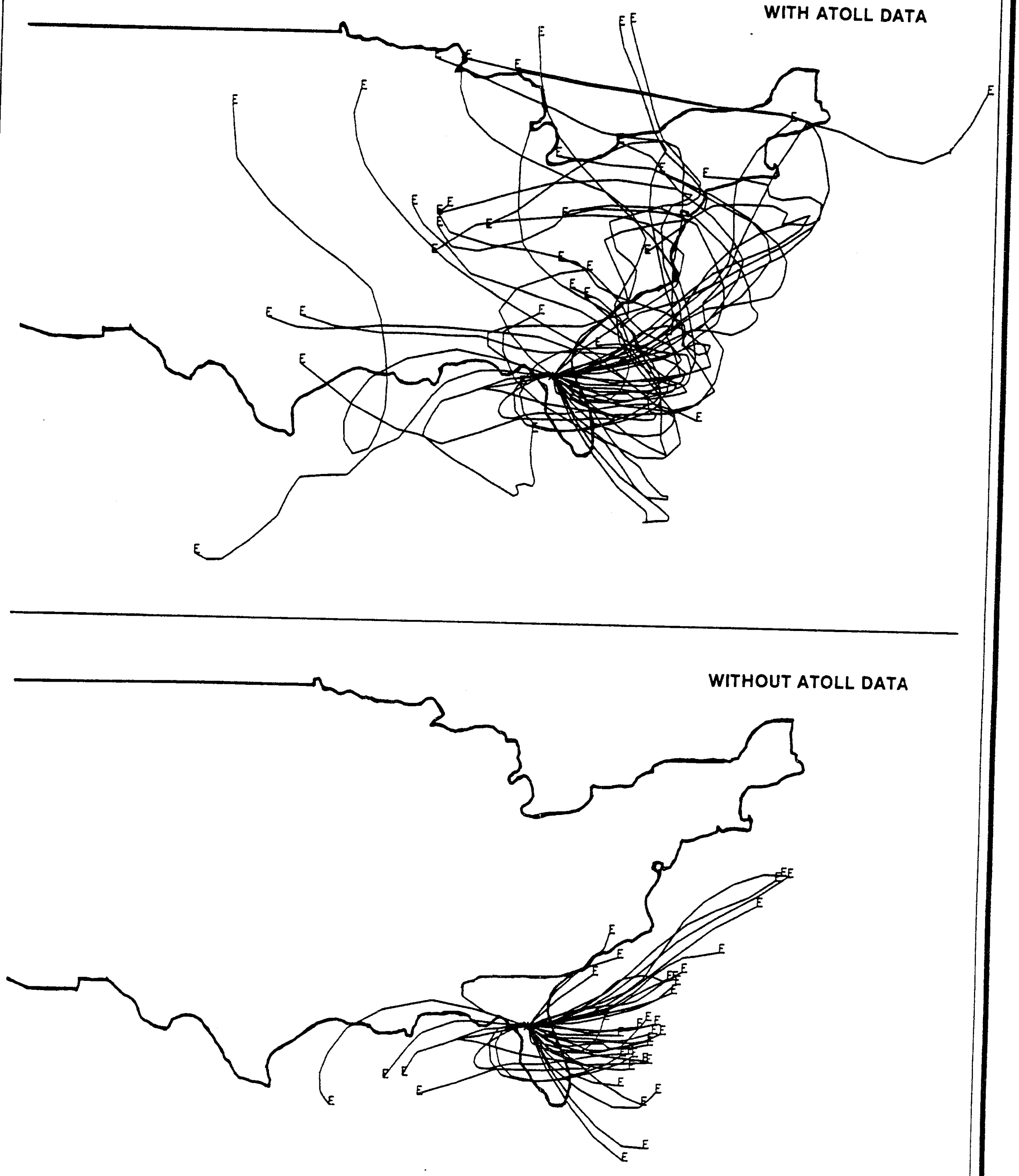
Table 3.3-16. Annual and Seasonal Frequency Distributions (%) of 1-Day Backward Trajectories for 1983 Using NAMER-WINDTEMP Plus ATOLL Data

| Site | Trajectory Sector | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | N | NE | E | SE | S | SW | W | NW | Undetermined |
| Annual | | | | | | | | | |
| Caryville | 11.2 | 13.6 | 11.9 | 14.8 | 10.0 | 6.4 | 14.7 | 16.0 | 1.4 |
| Gainesville | 7.6 | 14.0 | 12.5 | 15.1 | 9.4 | 7.6 | 14.0 | 17.5 | 2.2 |
| Archbold | 7.2 | 10.4 | 18.8 | 17.3 | 9.9 | 8.2 | 10.2 | 15.8 | 2.2 |
| Everglades | 8.4 | 9.6 | 20.7 | 20.1 | 10.3 | 6.5 | 8.4 | 13.2 | 2.7 |
| Winter | | | | | | | | | |
| Caryville | 12.6 | 15.9 | 11.8 | 5.8 | 5.7 | 4.7 | 14.6 | 22.6 | 2.0 |
| Gainesville | 10.7 | 14.3 | 11.0 | 9.5 | 7.3 | 5.5 | 12.6 | 25.6 | 3.6 |
| Archbold | 9.3 | 9.7 | 16.5 | 11.1 | 8.7 | 8.0 | 11.3 | 21.9 | 3.5 |
| Everglades | 9.3 | 8.9 | 16.5 | 13.7 | 8.8 | 7.6 | 11.1 | 19.3 | 4.8 |
| Summer | | | | | | | | | |
| Caryville | 9.6 | 11.1 | 11.9 | 19.5 | 14.1 | 7.9 | 14.6 | 10.5 | 0.8 |
| Gainesville | 5.3 | 13.4 | 13.0 | 20.4 | 10.7 | 8.5 | 14.9 | 13.1 | 0.8 |
| Archbold | 4.9 | 11.9 | 20.8 | 23.2 | 10.9 | 8.2 | 8.9 | 10.3 | 0.9 |
| Everglades | 7.4 | 10.3 | 24.9 | 26.5 | 11.8 | 5.3 | 5.7 | 7.1 | 1.1 |

Source: ESE, 1986.

calculates trajectories that recurve over the eastern United States or Canada. An example of this recurvature effect is illustrated in Figure 3.3-18, which presents 5-day backward trajectories for Gainesville calculated with and without ATOLL data. For 1983, recurvature occurred for 37 of the 5-day trajectories calculated for Gainesville. As shown in Figure 3.3-18, calculations using NAMER-WINDTEMP data alone show reasonably straight trajectories, of which all but three belong to the E, SE, S, or SW sectors. Results of the NAMER-WINDTEMP plus ATOLL calculations, in contrast, indicate a more complicated pattern of transport. Of the trajectories shown, all but four exhibit 5-day endpoints located in the W, NW, or NE sectors. Similar results were obtained for Caryville and Gainesville, but the recurvature effect had more of a north-south influence. For these sites, Caryville had 27 cases of recurvature while Archbold had 47 cases. These results suggest that recurvature occurs about 10 percent of the time. Thus, the NAMER-WINDTEMP plus ATOLL trajectories define a mode of atmospheric transport not readily discernible from trajectories using NAMER-WINDTEMP data only and provide additional information for interpretation of atmospheric chemistry.

This additional mode of transport, which is not readily apparent from the NAMER-WINDTEMP trajectory calculations, can be classified as continental recurvature and, in most cases, appears to follow a clockwise circulation pattern indicative of continental high-pressure systems. The overall effect of recurvature trajectories is a direct transport mechanism between Florida and the eastern United States or Canada along a path that crosses the eastern Atlantic Ocean. This recurvature of trajectories generally decreased from south to north, i.e., recurvature episodes were observed at Caryville, Gainesville, and Archbold on 27, 37, and 47 dates, respectively, during 1983. This observation may have significant implications for Florida as well as the eastern United States as a whole, since it implies frequent continental reentry of well-aged pollutants.



MERCATOR PROJECTION — NOT TO SCALE

Figure 3.3-18
BACKWARD TRAJECTORIES FOR GAINESVILLE PRODUCED WITH AND WITHOUT ATOLL DATA FOR PERIODS OF RECURVATURE OVER LAND (n = 37)

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#### 3.3.3.3 Precipitation and Air Chemistry Versus Trajectory Data

This subsection addresses the variability of precipitation and air chemistry data as a function of atmospheric transport. Two approaches are used to evaluate relationships between chemical and trajectory data. The first approach, sectoral classification, uses a sorting routine to calculate volume-weighted average precipitation chemistry and average air chemistry within eight directional sectors. Sector averages are then compared to infer likely source regions of atmospheric contaminants observed at four sites across Florida. This approach has two major drawbacks. First, because sectors are centered on receptors, the regions designated for each receptor are unique to that receptor. For example, the north sector for Caryville does not correspond to the north sector for Gainesville or Archbold. Second, sector analysis requires the analysis of a preselected trajectory time interval (e.g., 1-day or 3-day backward trajectories). This selection, unfortunately, is always arbitrary and represents a subjective estimate of transport time relevant to the issue of atmospheric deposition.

The second method of evaluating chemistry versus trajectory data is residence time analysis. In this approach, the location of all trajectory segments is determined for a variety of regions including state, groups of states, and major water bodies (e.g., Gulf of Mexico). Residence times for 5-day backward trajectories (NAMER and ATOLL) are computed by summing trajectory segments by region and assuming that each segment represents, on the average, 6 hours of residence time. Residence time analyses are performed for various classes of precipitation and air quality. Variability in residence time, as a function of precipitation and air quality, is then used to infer likely source regions of atmospheric pollutants. In contrast to the sector analysis, the residence time analysis employs regions (e.g., states) that apply universally to all receptors. Thus, comparisons across receptors are more easily presented than in the sector analysis.

It should be noted that sector analysis and residence time analysis are two methods of evaluating a common database. Therefore, the limitations inherent to the ATAD model apply to both techniques, and neither approach should be construed as independent confirmation of the other.

## Sectoral Analysis

Results of the precipitation chemistry classification by 3-day trajectory sector are shown for Caryville, Gainesville, Archbold, and the Everglades in Table 3.3-17. In general, concentration data show a unique relationship with trajectory sector for each site. At Caryville, VWM laboratory $H^+$ concentrations are highest for the north and south trajectories, and lowest for west, northeast, and southeast trajectories. Laboratory $H^+$ concentrations increase by a factor of two or more from the northeast to north sectors and from the southeast to south sectors, indicating relatively high sensitivity of precipitation chemistry to transport direction (or related factors). Excess $SO_4^{-2}$ concentration at Caryville generally follow the pattern described for laboratory $H^+$. In contrast, nitrate concentrations are relatively invariant from sector to sector, exhibiting a range over all sections of 6.6 μN to 11.6 μN. Differences in excess $SO_4^{-2}$ and $NO_3^-$ as a function of sector result in considerable variability of south-to-north ratios. For the north and south sectors, south-to-north ratios (mass basis) were 1.4 and 1.5, respectively, while, for the northeast and southeast section south-to-north ratios are 0.9 and 0.7, respectively. Thus, south-to-north ratios decrease from sections with high laboratory $H^+$ to those with low laboratory $H^+$, suggesting that excess $SO_4^{-2}$ is an increasingly dominant ion with increased acidity in precipitation acidity.

Precipitation chemistry at Gainesville exhibits considerably more variability from sector to sector than that at Caryville. In this case, VWM laboratory $H^+$ concentrations are highest in the north and east sectors, lowest in the south and southwest sectors and vary, over all

Table 3.3-17. VWM Precipitation Chemistry by Trajectory Sector

| Site | Analyte | Trajectory Sector | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | N | NE | E | SE | S | SW | W | NW |
| 2 (Caryville) | Laboratory $H^+$ | 33.0 | 12.1 | 18.3 | 13.9 | 27.0 | 17.1 | 5.5 | 20.5 |
| | Excess $SO_4^{-2}$ | 28.1 | 13.9 | 14.5 | 14.0 | 22.8 | 14.1 | 24.6 | 24.3 |
| | $NO_3^-$ | 10.2 | 7.9 | 9.0 | 9.7 | 7.7 | 6.6 | 8.6 | 11.6 |
| | $NH_4^+$ | 5.4 | 4.9 | 3.5 | 6.7 | 5.6 | 4.3 | 6.7 | 10.4 |
| | Number of Events | 7 | 10 | 9 | 16 | 9 | 11 | 1 | 9 |
| 5 (Gainesville) | Laboratory $H^+$ | 74.5 | 27.0 | 49.6 | 23.1 | 17.0 | 15.0 | 35.4 | 26.8 |
| | Excess $SO_4^{-2}$ | 62.3 | 22.9 | 32.5 | 16.3 | 12.9 | 11.7 | 30.6 | 24.3 |
| | $NO_3^-$ | 21.0 | 8.4 | 23.6 | 11.3 | 5.8 | 11.3 | 12.8 | 11.1 |
| | $NH_4^+$ | 18.9 | 3.3 | 4.6 | 1.7 | 0.6 | 3.4 | 14.9 | 4.1 |
| | Number of Events | 7 | 7 | 1 | 24 | 11 | 4 | 11 | 11 |
| 9 (Archbold) | Laboratory $H^+$ | 10.3 | 16.5 | 15.8 | 10.1 | 16.7 | 9.5 | 53.7 | 12.8 |
| | Excess $SO_4^{-2}$ | 11.6 | 10.1 | 8.8 | 14.7 | 26.8 | 9.7 | 52.8 | 16.2 |
| | $NO_3^-$ | 5.3 | 12.2 | 10.7 | 8.2 | 14.8 | 5.4 | 18.4 | 7.1 |
| | $NH_4^+$ | 2.3 | 4.9 | 4.5 | 6.1 | 11.5 | 3.1 | 9.4 | 6.4 |
| | Number of Events | 15 | 3 | 6 | 19 | 9 | 7 | 1 | 9 |
| 13 (Everglades) | Laboratory $H^+$ | 3.9 | 31.6 | 23.8 | 8.0 | 15.3 | 3.8 | 18.8 | 9.7 |
| | Excess $SO_4^{-2}$ | 6.5 | 31.4 | 19.5 | 9.8 | 17.8 | 8.4 | 25.7 | 11.2 |
| | $NO_3^-$ | 3.5 | 22.3 | 11.9 | 6.2 | 9.1 | 4.8 | 30.6 | 5.8 |
| | $NH_4^+$ | 1.7 | 8.0 | 4.8 | 5.1 | 2.3 | 4.7 | 10.4 | 5.8 |
| | Number of Events | 5 | 7 | 17 | 22 | 5 | 6 | 2 | 11 |

Note: All concentrations are µN.

Source: ESE, 1986.

sectors, by nearly a factor of 5. The general distribution suggests that transport from areas north of Gainesville is associated with relatively high concentrations of laboratory $H^+$ and that transport from areas south of Gainesville in association with relatively low laboratory $H^+$. High laboratory $H^+$ values for the east and west sectors complicate the distribution; however, the east value is based on data from only a single precipitation event. As was observed for Caryville, south-to-north ratios generally increase with laboratory $H^+$ concentration. Highest and lowest mean south-to-north ratios of laboratory $H^+$ at Gainesville are 1.4 and 0.8, respectively, for the three sectors.

Results for Archbold show a relatively uniform distribution of laboratory $H^+$ across sectors. Contrary to findings for Caryville and Gainesville, VWM concentrations for the north sectors are among the lowest observed. This distinction between Archbold and the north Florida sites appears to be related to the seasonality of precipitation chemistry. Inspection of north sector data for south Florida, shows that these events invariably occur during winter in association with relatively clean, cold front precipitation (see Subsection 2.8). In contrast, many of the north sector precipitation events for Caryville and Gainesville occur during the summertime during continental high or continental-Atlantic low meteorological episodes.

Concentration data for the Everglades site exhibit the greatest relative variability across sectors. Laboratory $H^+$ differs by a factor of 8 from the southwest sector (3.6 μN) to the northeast sector (31.6 μN), whereas excess $SO_4^{-2}$ and $NO_3^-$ differ by factors of 4 and 5, respectively, across these two sectors. VWM concentrations of laboratory $H^+$, excess $SO_4^{-2}$ and $NO_3^-$ are lowest at the Everglades, relative to other sites, for all sectors except the west (n = 2), northeast, and east. In contrast, concentrations for the northeast and east sectors are the highest and second highest across all sites. Given the extensive urbanization to the northeast and east of the Everglades (50 km west of Miami), this concentration pattern suggests a local (i.e., urban) influence on precipitation chemistry. This also is suggested by south-to-north ratios in Everglades precipitation. In contrast with other sites, south-to-north ratios at the Everglades site are invariably below 1.0 and are, in fact, lowest for sectors with the highest laboratory $H^+$. Based on the relatively rapid photochemical oxidation rate of $NO_x$ to $HNO_3$ (Schwartz et al., 1984), this south-to-north signature is consistent with a local source of $NO_3^-$ in precipitation from the northeast and east sectors.

The sectoral distribution of wet deposition also varies considerably from site to site (see Table 3.3-18) and appears to be controlled largely by rainfall amounts for each sector. Rainfall at all four sites is highest in the southeast, south, or southwest sectors, and total rainfall for these sectors ranges from 45 percent (Archbold) to 53 percent (Everglades) of annual precipitation. Rainfall amounts for the north, northeast, and northwest sectors accounts for only 21 to 39 percent of annual totals, suggesting that the opportunity for wet deposition from the northern quadrant is appreciably lower than that from the southern quadrant. Despite differences in rainfall totals for the northern and southern quadrants, wet deposition of laboratory $H^+$, excess $SO_4^{-2}$, and $NO_3^-$ from these quadrants is comparable for all sites except Everglades. This is a direct consequence of generally below-average concentrations for precipitation associated with southern quadrant trajectories.

Results of the sectoral classification of air chemistry data (see Table 3.3-19) show a high degree of similarity between sites and a relatively smooth and uniform increase in concentrations from the southern quadrant to the northern quadrant. This relationship between concentration and trajectory sector is most pronounced at the Everglades, where particulate $SO_4^{-2}$, $SO_2$, and $HNO_3$ increased by factors of 3 or more, from the south sector to the north sector. For all sites and all parameters, minima are observed in the southeast, south, or southwest sectors and maxima (except for $NO_2$ at the Everglades and particulate $SO_4^{-2}$

Table 3.3-18. Percent of Wet Deposition and Rainfall Amount by Trajectory Sector for the Period 10/01/82 Through 09/30/83

| Site | Analyte | Trajectory Sector | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | N | NE | E | SE | S | SW | W | NW |
| 2 | Laboratory $H^+$ | 18.6 | 8.4 | 11.8 | 13.0 | 17.9 | 19.0 | 0.2 | 11.3 |
| | Excess $SO_4^{2-}$ | 17.1 | 10.2 | 10.0 | 14.2 | 13.6 | 16.9 | 0.7 | 14.5 |
| | $NO_3^-$ | 12.7 | 11.9 | 12.9 | 20.2 | 11.4 | 16.2 | 0.5 | 14.2 |
| | Rainfall (cm) | 10.9 | 13.4 | 12.3 | 18.1 | 12.8 | 21.4 | 0.5 | 10.6 |
| | Number of Events | | | | | | | | |
| 5 | Laboratory $H^+$ | 18.1 | 5.7 | 2.2 | 25.4 | 7.4 | 1.5 | 23.8 | 15.8 |
| | Excess $SO_4^{2-}$ | 18.7 | 5.9 | 1.7 | 22.2 | 6.9 | 1.5 | 25.3 | 17.7 |
| | $NO_3^-$ | 13.1 | 4.5 | 2.6 | 31.7 | 6.4 | 2.9 | 22.0 | 16.8 |
| | Rainfall (cm) | 7.2 | 6.2 | 1.3 | 32.4 | 12.8 | 3.0 | 19.7 | 17.4 |
| | Number of Events | | | | | | | | |
| 9 | Laboratory $H^+$ | 16.4 | 3.6 | 12.6 | 18.7 | 6.6 | 9.5 | 20.0 | 12.6 |
| | Excess $SO_4^{2-}$ | 16.6 | 2.0 | 6.3 | 24.5 | 9.5 | 8.8 | 17.9 | 14.4 |
| | $NO_3^-$ | 14.0 | 4.5 | 14.3 | 25.3 | 9.7 | 9.1 | 11.5 | 11.7 |
| | Rainfall (cm) | 22.1 | 3.1 | 11.1 | 25.6 | 5.5 | 13.9 | 5.2 | 13.6 |
| | Number of Events | | | | | | | | |
| 13 | Laboratory $H^+$ | 1.8 | 11.0 | 43.4 | 20.3 | 8.7 | 3.8 | 1.8 | 9.9 |
| | Excess $SO_4^{2-}$ | 2.8 | 10.4 | 33.5 | 23.5 | 9.6 | 7.7 | 2.4 | 9.9 |
| | $NO_3^-$ | 2.4 | 12.0 | 33.1 | 24.4 | 7.9 | 7.2 | 4.6 | 8.3 |
| | Rainfall (cm) | 5.1 | 4.5 | 23.5 | 32.7 | 7.4 | 12.7 | 1.3 | 12.1 |
| | Number of Events | | | | | | | | |

Source: ESE, 1986.

Table 3.3-19. Mean Concentrations* of Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ by Trajectory Sector for 1983

| Site | Analyte | Trajectory Sector | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | N | NE | E | SE | S | SW | W | NW |
| 2 | Particulate $SO_4^{-2}$ | 6.8 | 6.5 | 4.7 | 3.8 | 4.2 | 4.5 | 7.3 | 5.6 |
| | $SO_2$ | 4.6 | 2.4 | 1.9 | 1.4 | 1.7 | 1.9 | 3.8 | 4.5 |
| | $HNO_3$ | 1.6 | 1.3 | 0.94 | 0.85 | 0.97 | 1.3 | 1.5 | 1.3 |
| | $NO_2$ | 8.1 | 6.2 | 4.9 | 3.8 | 7.0 | 5.0 | 6.0 | 8.2 |
| | Number of Events | 12 | 10 | 15 | 25 | 12 | 8 | 13 | 18 |
| 5 | Particulate $SO_4^{-2}$ | 5.9 | 5.0 | 4.4 | 2.9 | 4.0 | 4.2 | 5.1 | 6.4 |
| | $SO_2$ | 4.1 | 3.6 | 2.9 | 1.7 | 1.6 | 2.0 | 2.2 | 4.6 |
| | $HNO_3$ | 1.5 | 1.3 | 1.2 | 0.82 | 0.84 | 0.95 | 1.2 | 1.8 |
| | $NO_2$ | 10.9 | 8.9 | 7.7 | 6.4 | 6.6 | 5.7 | 6.7 | 11.7 |
| | Number of Events | 10 | 12 | 19 | 17 | 11 | 9 | 15 | 24 |
| 9 | Particulate $SO_4^{-2}$ | 5.4 | 3.3 | 2.8 | 2.5 | 3.2 | 2.6 | 3.8 | 4.4 |
| | $SO_2$ | 3.8 | 1.5 | 1.5 | 2.4 | 2.0 | 3.1 | 4.2 | 5.2 |
| | $HNO_3$ | 1.4 | 0.69 | 0.76 | 0.67 | 0.83 | 0.81 | 1.3 | 1.3 |
| | $NO_2$ | 7.1 | 4.6 | 4.0 | 4.4 | 3.6 | 3.8 | 7.1 | 6.5 |
| | Number of Events | 10 | 15 | 21 | 19 | 15 | 7 | 12 | 16 |
| 13 | Particulate $SO_4^{-2}$ | 5.2 | 3.3 | 2.5 | 2.5 | 1.9 | 2.2 | 2.9 | 4.8 |
| | $SO_2$ | 2.2 | 1.3 | 1.1 | 1.1 | 0.71 | 0.70 | 1.4 | 3.1 |
| | $HNO_3$ | 1.6 | 0.87 | 0.65 | 0.43 | 0.34 | 0.40 | 0.94 | 1.6 |
| | $NO_2$ | 3.7 | 2.9 | 3.0 | 2.8 | 2.8 | 1.7 | 4.6 | 3.2 |
| | Number of Events | 8 | 11 | 24 | 25 | 11 | 14 | 9 | 14 |

* All concentrations are $\mu g/m^3$

Source: ESE, 1986.

at Caryville) are observed in the north or northwest sectors. This observation suggests that considerable amounts of $SO_x$ and $NO_x$ may be transported into the state along northern quadrant trajectories. Annual imports of $SO_x$ and $NO_x$ to Florida will be estimated in Subsection 3.3.3.4.

Examination of results from Gainesville, Archbold, and the Everglades suggests that in-state sources also influence concentration patterns. This effect is made apparent by comparison of data for the southeast, south, and southwest sectors across these sites. Note that this is a reasonable comparison only if the sites lie along a common axis (in this case, north to south) and if the contribution of nonlocal sources to southeast, south, and southwest trajectories is assumed constant from site to site. Using the Everglades as a baseline site for the southeast, south, and southwest sectors, data for Gainesville and Archbold indicate increasing concentrations of all parameters from south Florida to north Florida. Increases in $NO_2$ and $SO_2$ are greater than those for particulate $SO_4^{-2}$ and $HNO_3$, both on a relative and absolute basis. However, the north-to-south trend is by no means uniform. $SO_2$ in the southwest sector, for example, increases from 0.7 $\mu g/m^3$ at the Everglades to 3.1 $\mu g/m^3$ at Archbold, then decreases to 2.0 $\mu g/m^3$ at Gainesville. These findings are in general agreement with results of Section 2.8, and suggested greater potential for local contributions to $SO_2$ and $NO_2$ than to their respective oxidation products.

Regional residence times for air parcels arriving at Caryville, Gainesville, and Archbold are shown in Table 3.3-20. Results indicate distinct differences between sites, implying variable influences of source regions with respect to these receptors. This is illustrated, in a broad sense, by comparison of residence times over land and water among sites. For Caryville, 5-day backward trajectories spend approximately 60 percent of the time (3 out of 5 days) over land and about 32 percent over water. Undetermined residence time amounts to a small fraction of

Table 3.3-20. Residence Time Analysis (%) for Caryville, Gainesville, and Archbold for 1983

| Region | Caryville | Gainesville | Archbold |
|---|---|---|---|
| <u>Land</u> | 59.9 | 48.1 | 30.1 |
| Florida | 6.5 | 10.8 | 9.4 |
| North Florida | 1.6 | 8.2 | 3.3 |
| South Florida | 0.8 | 1.2 | 5.4 |
| Florida Panhandle | 4.1 | 1.4 | 0.7 |
| Alabama | 8.7 | 4.0 | 1.8 |
| Arkansas-Mississippi-Louisiana | 7.7 | 3.6 | 2.6 |
| Georgia | 6.6 | 5.4 | 1.8 |
| Tennessee-Kentucky | 3.4 | 2.4 | 1.6 |
| North Carolina-South Carolina-Virginia | 4.9 | 3.8 | 1.9 |
| Missouri-Indiana | 3.7 | 2.6 | 1.8 |
| West Virginia-Michigan-Illinois-Ohio | 3.1 | 3.0 | 1.6 |
| Iowa-Minnesota-Wisconsin | 3.6 | 3.2 | 1.8 |
| Pennsylvania-New York-New Jersey | 1.6 | 1.9 | 0.9 |
| New England | 0.2 | 0.2 | <0.1 |
| Texas | 2.2 | 1.3 | 1.4 |
| Western United States | 5.1 | 3.6 | 2.4 |
| Canada | 2.3 | 2.1 | 0.8 |
| Mexico | 0.3 | 0.2 | 0.2 |
| <u>Water</u> | 31.5 | 41.5 | 53.5 |
| Gulf of Mexico | 19.8 | 16.2 | 18.1 |
| South Atlantic Ocean | 9.4 | 22.2 | 33.7 |
| North Atlantic Ocean | 2.3 | 3.1 | 1.7 |
| <u>Undetermined</u> | 8.6 | 10.4 | 16.4 |

Source: ESE, 1986.

the total (<10 percent). Based upon inspection of individual trajectories, the undetermined component appears to be the result of trajectories leaving the northern or western boundary of the computational domain (i.e., 50°N or 105°W). The residence time over land for Caryville trajectories therefore appears to be somewhat of an underestimate.

Residence times for Archbold, in contrast, show the trajectories spend roughly 30 percent and 53 percent of the time over land and water, respectively. The undetermined component of residence time is well above 10 percent and, in this case, is primarily due to trajectories crossing the eastern boundary of the computational domain (i.e., 65°W). Land and water residence times for Caryville and Archbold thus appear to differ by at least a factor of 2. Residence times for Gainesville trajectories are intermediate between the other sites, suggesting a fairly monotonic decrease in atmospheric transport from the continental land mass to Florida. Given the relative strengths of continental and oceanic emissions of $SO_x$ and $NO_x$, this finding is consistent with observed trends in air and precipitation density throughout the state (see Subsection 2.5).

The residence time in each state or multi-state source region also decreases from Caryville to Archbold. The only noteworthy exception to this trend involves Florida, for which the residence time of Caryville trajectories is lower than either Gainesville or Archbold. For Archbold trajectories, the residence time over Florida is nearly one-third of that over all land masses. This finding suggests that the relative influence of local sources is likely to be stronger at Archbold than at Caryville or Gainesville.

Residence time data for upper and lower quartile concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ at Caryville, Gainesville, and Archbold are listed in Tables 3.3-21, 3.3-22, and 3.3-23. In general, results show marked distinctions between upper and lower quartile data

Table 3.3-21. Residence Time Analysis (%) for Upper and Lower Quartile Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ for Caryville for 1983

| Region | Particulate $SO_4^{-2}$ |  | $SO_2$ |  | $HNO_3$ |  | $NO_2$ |  |
|---|---|---|---|---|---|---|---|---|
|  | Upper | Lower | Upper | Lower | Upper | Lower | Upper | Lower |
| Land | 83.4 | 40.4 | 77.4 | 38.6 | 74.9 | 29.6 | 75.1 | 51.5 |
| North Florida | 1.5 | 0.5 | 0.3 | 2.1 | 1.4 | 1.1 | 0.7 | 1.6 |
| South Florida | 0.1 | 1.1 | <0.1 | 1.5 | 1.2 | 1.0 | 0.2 | 2.5 |
| Florida Panhandle | 7.9 | 2.4 | 1.3 | 4.6 | 5.6 | 3.9 | 1.4 | 6.9 |
| Alabama | 16.3 | 5.9 | 12.3 | 3.5 | 15.1 | 3.8 | 11.5 | 7.4 |
| Arkansas | 11.8 | 6.2 | 12.4 | 2.8 | 10.8 | 4.1 | 9.7 | 9.9 |
| Georgia | 11.0 | 3.0 | 3.3 | 7.6 | 5.4 | 2.6 | 5.7 | 10.1 |
| Tennessee-Kentucky | 4.2 | 0.8 | 6.2 | 1.2 | 5.4 | 0.1 | 4.9 | 0.1 |
| North Carolina-South Carolina-Virginia | 6.9 | 2.0 | 1.7 | 5.8 | 3.3 | 2.1 | 3.7 | 5.9 |
| Missouri-Indiana | 6.0 | 2.5 | 9.1 | 1.2 | 7.5 | 1.2 | 8.4 | 1.1 |
| West Virginia-Michigan-Illinois-Ohio | 6.1 | 0.8 | 7.0 | 1.0 | 5.4 | 0.4 | 3.5 | 0.9 |
| Iowa-Minnesota-Wisconsin | 3.6 | 1.1 | 5.5 | 1.7 | 4.8 | 1.3 | 3.7 | 0.3 |
| Pennsylvania-New York-New Jersey | 2.1 | 1.3 | 1.2 | 1.6 | 0.6 | 1.2 | 2.1 | 2.6 |
| New England | 0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.3 |
| Texas | 1.9 | 2.1 | 3.6 | 0.5 | 2.8 | 0.7 | 3.4 | 1.1 |
| Western United States | 2.0 | 6.6 | 10.2 | 1.7 | 3.8 | 4.8 | 11.5 | 0.7 |
| Canada | 1.8 | 3.3 | 3.1 | 1.8 | 1.5 | 1.3 | 4.1 | 0.1 |
| Mexico | 0.1 | 0.8 | 0.2 | <0.1 | 0.3 | <0.1 | 0.6 | <0.1 |
| Water | 14.3 | 47.9 | 5.0 | 50.6 | 19.0 | 58.5 | 16.3 | 41.2 |
| Gulf of Mexico | 10.2 | 32.9 | 5.0 | 27.8 | 16.0 | 42.8 | 13.8 | 18.2 |
| South Atlantic Ocean | 3.1 | 12.3 | <0.1 | 17.7 | 2.9 | 15.7 | 1.7 | 23.0 |
| North Atlantic Ocean | 1.0 | 2.7 | <0.1 | 5.1 | 0.1 | 0.2 | 0.8 | 1.6 |
| Undetermined | 2.3 | 11.7 | 17.6 | 10.8 | 6.1 | 11.9 | 8.6 | 7.3 |

Source: ESE, 1986.

Table 3.3-22. Residence Time Analysis (%) for Upper and Lower Quartile Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ for Gainesville for 1983

| Region | Particulate $SO_4^{-2}$ | | $SO_2$ | | $HNO_3$ | | $NO_2$ | |
|---|---|---|---|---|---|---|---|---|
| | Upper | Lower | Upper | Lower | Upper | Lower | Upper | Lower |
| Land | 63.2 | 29.5 | 70.6 | 28.1 | 71.0 | 25.5 | 66.3 | 41.5 |
| North Florida | 10.1 | 3.4 | 3.7 | 10.2 | 9.8 | 3.2 | 8.5 | 0.9 |
| South Florida | 1.0 | 1.2 | 0.6 | 1.3 | 0.3 | 1.2 | 0.5 | 0.2 |
| Florida Panhandle | 1.8 | 0.8 | 1.2 | 1.6 | 2.1 | 1.0 | 0.9 | 2.9 |
| Alabama | 6.5 | 2.0 | 5.9 | 1.0 | 9.4 | 1.2 | 5.9 | 4.4 |
| Arkansas | 6.0 | 3.1 | 5.4 | 1.9 | 6.2 | 2.5 | 2.4 | 7.3 |
| Georgia | 8.9 | 2.9 | 7.3 | 1.4 | 9.9 | 1.8 | 9.6 | 0.6 |
| Tennessee-Kentucky | 4.0 | 1.1 | 6.2 | 0.9 | 4.2 | 1.0 | 4.3 | 1.6 |
| North Carolina-South Carolina-Virginia | 5.1 | 4.3 | 4.8 | 1.9 | 3.6 | 1.5 | 4.4 | 2.4 |
| Missouri-Indiana | 5.7 | 0.4 | 7.1 | 0.2 | 4.8 | 2.3 | 5.4 | 3.2 |
| West Virginia-Michigan-Illinois-Ohio | 5.9 | 2.0 | 7.2 | 1.5 | 5.9 | 2.5 | 5.7 | 3.0 |
| Iowa-Minnesota-Wisconsin | 3.5 | 0.1 | 7.9 | <0.1 | 6.2 | 0.6 | 7.1 | 2.8 |
| Pennsylvania-New York-New Jersey | 2.0 | 2.1 | 1.7 | 1.7 | 0.8 | 1.0 | 1.9 | 0.7 |
| New England | <0.1 | <0.1 | <0.1 | 0.1 | 0.3 | 0.2 | 0.5 | <0.1 |
| Texas | 0.6 | 0.9 | 1.4 | 0.5 | 1.4 | 1.7 | 0.7 | 5.3 |
| Western United States | 1.0 | 2.8 | 6.2 | 1.5 | 2.1 | 1.6 | 4.7 | 3.4 |
| Canada | 1.0 | 2.2 | 3.9 | 1.7 | 3.8 | 1.4 | 3.8 | 0.7 |
| Mexico | <0.1 | 0.2 | <0.1 | 0.7 | 0.2 | 0.8 | <0.1 | 2.1 |
| Water | 35.9 | 50.4 | 19.7 | 55.7 | 24.8 | 57.2 | 24.2 | 50.7 |
| Gulf of Mexico | 17.8 | 21.5 | 3.8 | 18.1 | 13.7 | 20.7 | 4.6 | 38.0 |
| South Atlantic Ocean | 12.6 | 27.3 | 12.5 | 37.6 | 9.9 | 35.4 | 15.2 | 12.4 |
| North Atlantic Ocean | 5.5 | 1.6 | 3.6 | 4.2 | 1.2 | 1.1 | 4.4 | 0.3 |
| Undetermined | 0.9 | 20.1 | 9.7 | 16.2 | 4.2 | 17.3 | 9.9 | 7.8 |

Source: ESE, 1986.

Table 3.3-23. Residence Time Analysis (%) for Upper and Lower Quartile Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ for Archbold for 1983

| Region | Particulate $SO_4^{-2}$ |  | $SO_2$ |  | $HNO_3$ |  | $NO_2$ |  |
|---|---|---|---|---|---|---|---|---|
|  | Upper | Lower | Upper | Lower | Upper | Lower | Upper | Lower |
| Land | 54.8 | 12.1 | 60.5 | 7.7 | 55.3 | 16.8 | 67.0 | 23.9 |
| North Florida | 6.6 | 0.8 | 8.0 | 2.1 | 7.9 | 0.9 | 7.7 | 2.2 |
| South Florida | 4.9 | 5.1 | 2.3 | 4.4 | 6.8 | 3.1 | 3.9 | 1.9 |
| Florida Panhandle | 1.1 | <0.1 | 2.0 | <0.1 | 1.9 | 0.2 | 2.4 | 3.4 |
| Alabama | 3.9 | 0.3 | 5.3 | <0.1 | 4.6 | 0.9 | 6.0 | 0.8 |
| Arkansas | 4.5 | <0.1 | 1.4 | 0.4 | 4.8 | 0.7 | 7.0 | 2.3 |
| Georgia | 3.2 | 0.9 | 4.2 | <0.1 | 3.6 | 0.9 | 4.6 | 0.5 |
| Tennessee-Kentucky | 5.9 | 0.3 | 3.7 | <0.1 | 3.9 | 0.2 | 3.7 | 2.3 |
| North Carolina-South Carolina-Virginia | 2.6 | 1.4 | 1.9 | <0.1 | 1.5 | 3.0 | 1.7 | 2.2 |
| Missouri-Indiana | 4.9 | 0.1 | 5.6 | <0.1 | 3.5 | 0.2 | 5.3 | 1.3 |
| West Virginia-Michigan-Illinois-Ohio | 3.8 | 0.6 | 2.8 | <0.1 | 3.6 | 1.0 | 2.4 | 1.5 |
| Iowa-Minnesota-Wisconsin | 5.7 | 0.3 | 6.6 | <0.1 | 4.7 | 0.1 | 5.0 | 0.1 |
| Pennsylvania-New York-New Jersey | 2.5 | 0.8 | 0.7 | <0.1 | 0.9 | 1.8 | 0.7 | 0.9 |
| New England | <0.1 | <0.1 | 0 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Texas | 0.5 | 0.1 | 4.1 | 0.2 | 2.7 | 1.3 | 5.1 | 1.5 |
| Western United States | 2.2 | 0.7 | 8.1 | <0.1 | 2.1 | 0.4 | 9.4 | 1.5 |
| Canada | 2.3 | 0.2 | 2.8 | <0.1 | 2.6 | 1.1 | 1.9 | 1.0 |
| Mexico | <0.1 | 0.4 | 1.0 | 0.4 | <0.1 | 0.8 | <0.1 | 0.5 |
| Water | 36.4 | 62.1 | 25.7 | 68.3 | 36.6 | 58.5 | 25.7 | 62.2 |
| Gulf of Mexico | 9.4 | 14.0 | 16.8 | 22.2 | 15.3 | 17.2 | 14.7 | 26.1 |
| South Atlantic Ocean | 25.1 | 47.1 | 8.9 | 44.8 | 20.3 | 39.0 | 11.0 | 34.4 |
| North Atlantic Ocean | 1.9 | 1.0 | <0.1 | 1.3 | 1.0 | 2.3 | <0.1 | 1.7 |
| Undetermined | 8.8 | 25.8 | 13.8 | 24.0 | 8.1 | 24.7 | 7.3 | 13.9 |

Source: ESE, 1986.

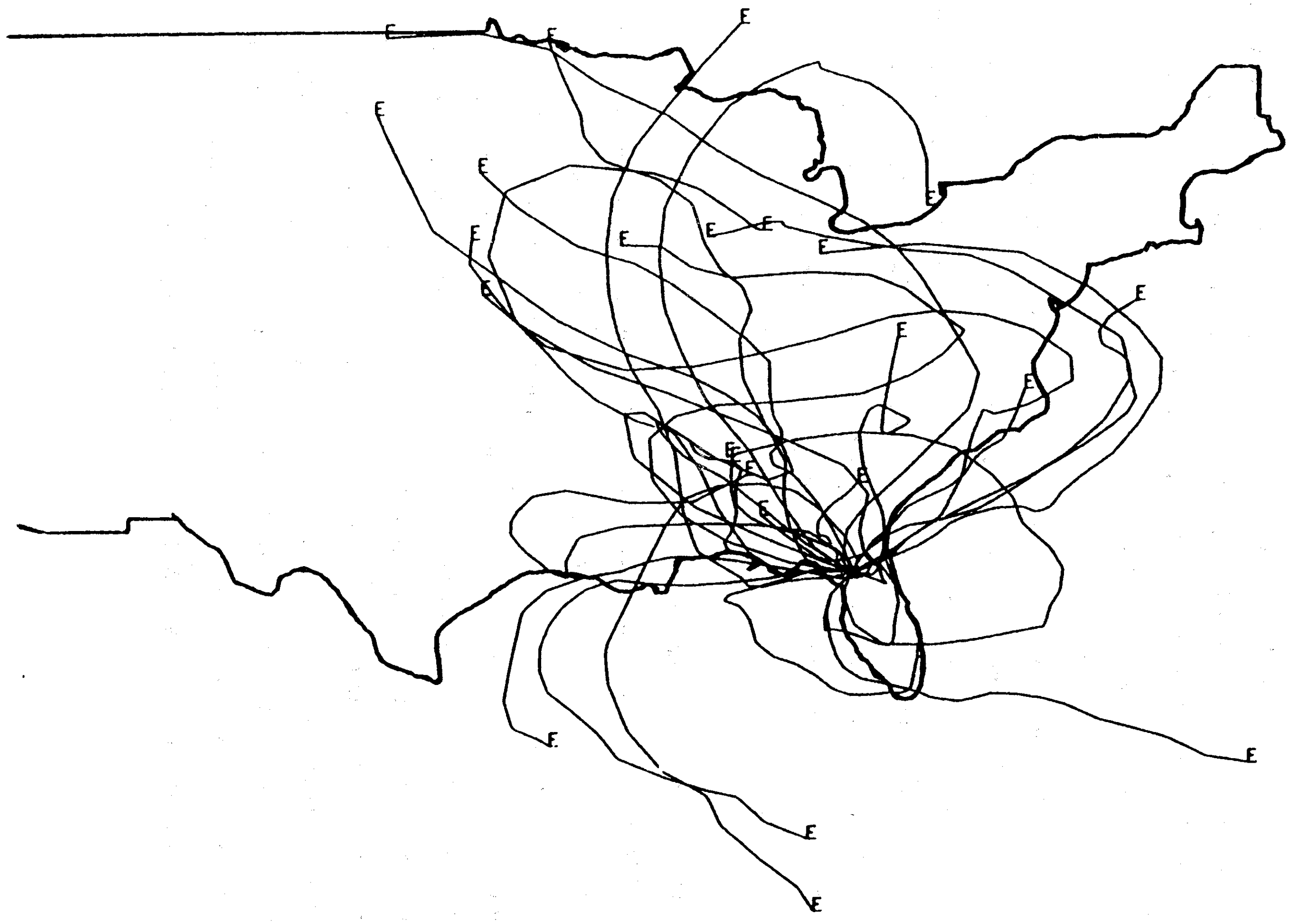
for all sites and all parameters. At Caryville, for example, residence times over land range from 75 to 83 percent and from 30 to 50 percent for upper quartile and lower quartile concentrations, respectively.

Residence times over Florida are uniformly less than 10 percent for upper quartile concentrations, indicating little opportunity for local source contributions. This is especially evident in the case of $SO_2$ and $NO_2$ data which show longer in-state residence times for lower quartile concentrations than for upper quartile concentrations.

Caryville data also show marked contrasts in residence times over southeastern states for upper and lower quartiles concentrations. Particulate $SO_4^{-2}$ data, for example, indicate that total residence times over the southeast (excluding Florida) increase from about 18 percent during low concentration episodes to 50 percent during high concentration episodes. This finding suggests that neighboring states are a significant source of particulate $SO_4^{-2}$ at Caryville.

Gainesville and Archbold show similar differences between episodes of high and low concentration, but with generally higher in-state and over-water residence times. An interesting feature of the data for Gainesville is a significant residence time increase over the North Atlantic Ocean for high particulate $SO_4^{-2}$ episodes. Rather than suggest that the North Atlantic is a source of pollutants, this finding shows that nonsource regions can act as conduits for transport of polluted air masses. This effect is shown in Figure 3.3-19 for Gainesville high particulate $SO_4^{-2}$ episodes. Of the 32 trajectories displayed, 6 show extensive transport over the Atlantic Ocean, followed by recurvature over land. Relatively frequent transport of this nature was observed in comparison between NAMER-only and NAMER-plus-ATOLL trajectories.

UPPER QUARTILE
MEAN CONCENTRATION = —ug/m³



MERCATOR PROJECTION — NOT TO SCALE

Figure 3.3-19
TRAJECTORY ENSEMBLES FOR UPPER QUARTILE PARTICULATE $SO_4^{-2}$ EPISODES AT GAINESVILLE, 1983

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### 3.3.3.4 Transport of $SO_x$ and $NO_x$ into Florida

Data used to calculate import of $SO_x$ and $NO_x$ into Florida are shown in Table 3.3-24. Total annual ventilation of the state during 1983 was 18.8 x $10^7$ cubic kilometers ($km^3$), which corresponds to a mean transport speed of approximately 18 kilometers per hour (km/hr) [11 miles per hour (mph)]. Ventilation was highest across the eastern and southern boundaries of the state, which accounted for 30 percent and 28 percent of total transport, respectively, and lowest for the northern and western boundaries, which accounted for 22 percent and 20 percent of total transport, respectively. Wind speed across the northern and western boundaries was slightly greater than that across the northern and eastern boundaries (14 versus 12 km/hr); however, this was offset by greater mixing depths for the southern and eastern boundaries (approximately 1.5 km versus 1.0 km). The mean mixing depth for all boundaries over the entire period was 1.3 km.

Whereas ventilation varied moderately across boundaries, concentrations of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ varied dramatically. Mean concentrations of all pollutants were highest for the northern and western boundaries and lowest for the southern and eastern boundaries. The northern boundary concentrations of particulate $SO_4^{-2}$ and $SO_2$ calculated from data obtained at Sites 2 and 3 correspond to 4.5 $\mu g/m^3$ of $SO_x$ [as sulfur (S)] which is approximately 75 percent of the value Galloway and Whelpdale (1980) used for rural eastern United States in their mass-balance sulfur model for eastern Northern America. Southern boundary concentrations of particulate $SO_4^{-2}$ and $SO_2$ (0.5 $\mu g/m^3$, as S) calculated from data obtained at Sites 2 and 14 approach background values observed over remote portions of the northern hemisphere (Granat et al., 1976; Meszaros, 1978). Mean $HNO_3$ and $NO_2$ concentrations in air crossing the southern boundary are significantly (i.e., by a factor of 10) lower than those calculated for other boundaries. Chameides (1983) used concentrations of 0.05 $\mu g/m^3$ and 0.04 $\mu g/m^3$, for $HNO_3$ and $NO_2$, respectively in his cloudwater chemistry model for the remote marine

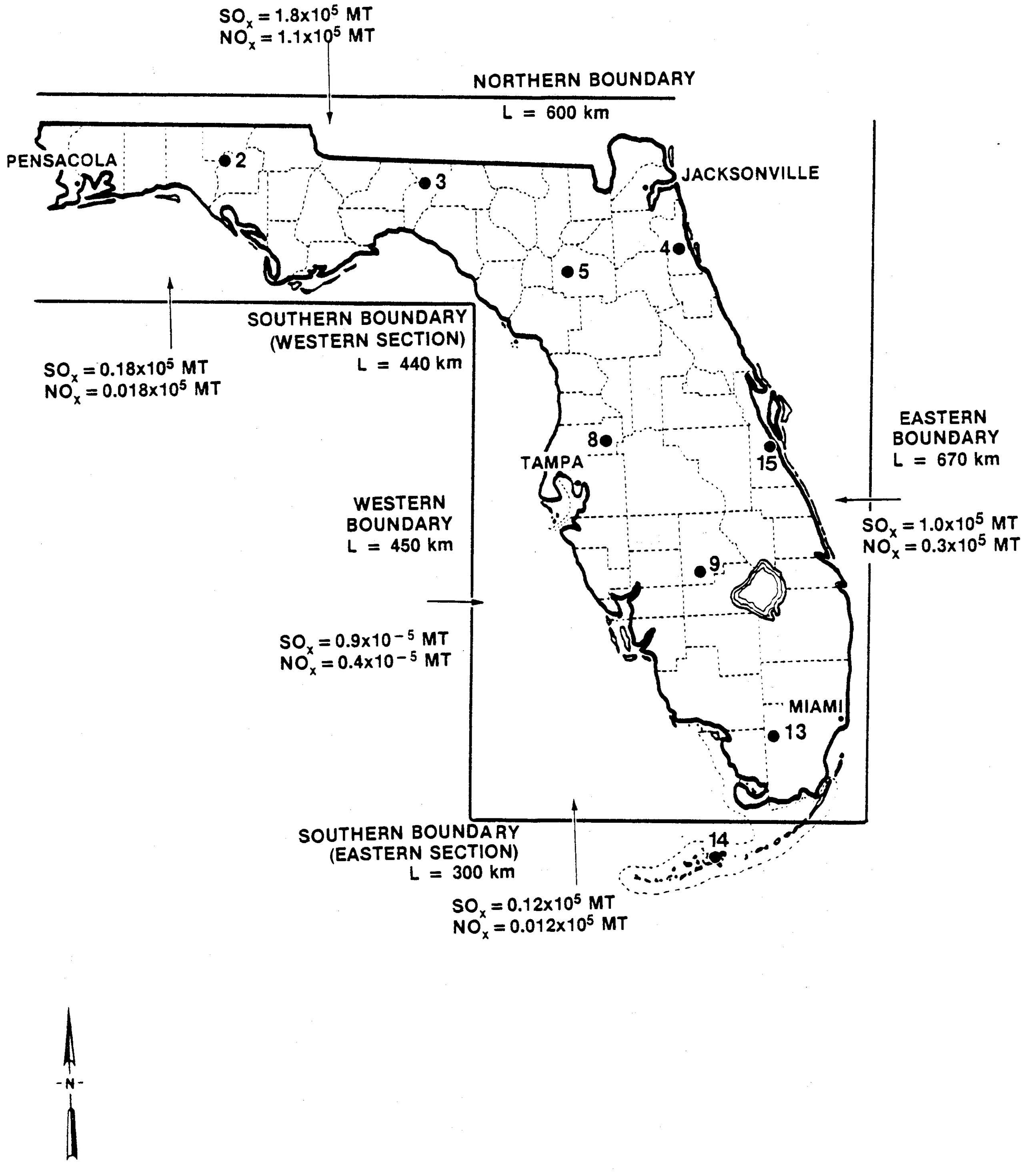

Figure 3.3-20
BOUNDARIES AND AIR MONITORING SITES USED TO ESTIMATE IMPORT OF $SO_X$ AND $NO_X$ TO FLORIDA

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the 5-year climatology, the overall nature of atmospheric transport within Florida appears to have been relatively constant for the period 1979 through 1983. The present estimate of ventilation appears to be more representative than the 1980 estimate for two reasons. First, the method of calculating transport winds (i.e., trajectory analysis) during 1983 employs observational data through the transport layers, whereas Edgerton (1981) applied an empirical correction factor to surface-wind data. Second, trajectory analysis provides an estimate of daily mixing depths for the 1983 ventilation calculations. In contrast, an annual average mixing depth, independent of season and transport direction, was used in the 1980 model.

Lacking observational data for particulate $SO_4^{-2}$ and $SO_2$ as well as the capability to classify these pollutants by wind direction, literature values were used for the concentration term in the 1980 sulfur model. For the northern and southern boundaries, concentration estimates in the 1980 model and 1983 observations agrees quite well. Edgerton (1981) assumed ranges of 3.0 to 6.0 $\mu g/m^3$ (as S) and 0.5 to 1.0 $\mu g/m^3$ for transport across the northern and southern boundaries of the state, respectively. Observational data used in the 1983 model suggest values of 4.5 $\mu g/m^3$ and 0.5 $\mu g/m^3$ for the northern and southern boundaries, respectively. For the eastern and western boundaries, in contrast, concentrations of 0.5 to 1.0 $\mu g/m^3$ (i.e., background values) were assumed in the 1980 model, whereas values of 1.9 $\mu g/m^3$ and 2.6 $\mu g/m^3$, respectively, were suggested by the 1983 observations. This disparity in concentration estimates accounts for roughly 0.8 x $10^5$ MT of sulfur, or about one-third the difference between the 1980 and 1983 models. Given the frequent curvature of trajectories from the eastern United States over the waters of the Atlantic Ocean or Gulf of Mexico and then across Florida (see Subsection 3.3.3.2), Edgerton's assumption of background concentrations for the eastern and western boundaries appears to be incorrect.

Comparison of mean concentrations of imported particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ with observed values suggests that a substantial portion of the measured $SO_x$ and $NO_x$ originates from out-of-state sources. The mean concentration of particulate $SO_4^{-2}$ across the state during 1983 was 4.1 $\mu g/m^3$, or approximately 110 percent of the mean import concentration. This contrasts with results for $HNO_3$, which indicate that statewide observations were approximately 200 percent of imports. This finding implies that in-state sources account for about 10 percent and 50 percent of the observed particulate $SO_4^{-2}$ and $HNO_3$, respectively, over the monitoring network. This apparent contrast in local contributions of particulate $SO_4^{-2}$ and $HNO_3$ may be at least partially attributable to the overall design of the monitoring network, which could be more successful in excluding local sources of $SO_x$ than $NO_x$. However, the relative oxidation rates of $SO_2$ and $NO_2$ to their respective oxidation productive may be a more plausable explanation. Although tropospheric oxidation rates and mechanisms for $NO_2$ and especially $SO_2$ are not clearly known, the results of laboratory chamber experiments suggest that the oxidation of $NO_2$ should be 2 to 3 times faster than that of $SO_2$ (Calvert, 1984; Schwartz et al., 1984). Thus, the local effects of $SO_2$ and $NO_x$ emissions appear to differ insofar as the air monitoring network is concerned. This finding suggests that network-wide precipitation chemistry might also be influenced to a variable extent by local $SO_2$ and $NO_x$ emissions.

### 3.3.3.5 Mass-Balance Model for Florida

The results of the mass-balance model for $SO_x$ and $NO_x$ are presented in Table 3.3-25. These results were developed from several analyses presented in previous sections. Specifically, anthropogenic emissions of $SO_2$ and $NO_x$ were developed for the period of September 15, 1982, through September 15, 1983 (refer to Subsection 3.3.1). Biogenic $SO_x$ emissions were estimated from recent results of field experiments performed by the FIU/University of Miami research team. Biogenic $NO_x$ emissions were taken from Messer (1981), who developed a nitrogen budget for Florida. Import of $SO_x$ and $NO_x$ were estimated through trajectory analysis and ambient air monitoring (see Subsection 3.3.3.4). Wet deposition and dry deposition were obtain from Subsection 2.3.1.5; wet deposition was developed from that observed in wet buckets, whereas dry deposition was calculated from deposition velocities and ambient air concentrations. The export term was derived as the difference between sources and sinks.

In simple terms, the results suggest that anthropogenic sources located in Florida contribute 50 percent of the $SO_x$ and 53 percent of the $NO_x$ deposition. Utility sources in Florida would contribute 35 percent and 17 percent of the $SO_x$ and $NO_x$ deposition, respectively. There are, however, inherent errors associated with each model component which would directly translate to uncertainties in the calculated contributions. As previously discussed, the exact magnitude of individual errors is often not known and their cumulative effect may be quite large, but an understanding of their qualitative significance is important to put the mass-balance results in perspective.

Of the source terms, the estimated import of $SO_x$ and $NO_x$ has the highest degree of uncertainty and is especially important because of its magnitude. The uncertainties are associated with three areas. First, the errors associated with trajectory analysis could influence both the categorization of ambient concentrations as well as the estimated annual ventilation. Because of the magnitude of this term (i.e., import

Table 3.3-25. Florida Mass-Balance Model for $SO_x$ and $NO_x$

| Parameter | $SO_x$ (x 1,000 MT) | $NO_x$ (x 1,000 MT) |
|---|---|---|
| Sources: | | |
| Anthropogenic[1] | 425 | 224 |
| Biogenic | 20[2] | 17[3] |
| Imports[4] | 400 | 180 |
| Sinks: | | |
| Wet Deposition[5] | 73 | 28 |
| Dry Deposition[5] | 40 | 45 |
| Export[6] | 732 | 348 |

[1] From Table 3.3-1.
[2] Estimated from ongoing Biogenic Emissions Study (Cooper, 1986).
[3] Messer (1981).
[4] From Table 3.3-24
[5] From Table 2.3-9.
[6] Exports = $\sum$sources - $\sum$sinks.

Source: ESE, 1986.

estimated to be 47 percent of the total), a small error in trajectory assignments and estimated ventilation can translate into large errors in import estimates. Second, any errors in the ambient concentrations would directly translate to errors in the import term. Such errors would include analytical errors as well as measurement errors for $SO_2$ and $NO_x$ originating from sources in Florida rather than outside the state. In addition, the ambient measurements were obtained from height of 10 m which may not accurately represent the concentrations through the mixing depth. Third, import is calculated using air quality data collected every third day. At best, these measurements (n = 120 per site per year) can serve only to approximate transport across state boundaries. Finally, the difference between the ambient sampling duration (24 hours) and the trajectory analysis periods (3 hours) could exacerbate the uncertainties associated with both.

The anthropogenic and biogenic emission estimates also have associated uncertainties. Although the uncertainties in the biogenic emission terms are probably large, their relative signficance to the model is less important since their magnitude is small (<5 percent) compared to the total. The anthropogenic emissions on the other hand have a high relative significance but are probably the most accurate of the source terms. This is especially true for the utility emissions which were developed from an extensive database. While there may be greater errors associated with nonutility point and area sources, the estimated emissions were calculated using data that has undergone extensive review and processing by the state over the last 10 years. In addition, standard procedures were used which would, as a minimum, produce some comparability between the different databases used.

The estimated sinks for $SO_x$ and $NO_x$ are uncertain for several reasons. First, the dry deposition was estimated from calculations using assumed deposition velocities and ambient air concentrations. As a consequence, the error over the state could be quite large; however, the magnitude of such an error is unknown. Second, errors associated with wet-deposition measurements would, to a lesser degree, affect the accuracy of this estimated sink.

## 3.4 RESPONSE TO KEY RESEARCH QUESTIONS

The Source Attribution Program of the Florida Acid Deposition Study involved:

1. Evaluation, collection, and QA checks of emissions inventories for the major acid precursors, $SO_x$, and $NO_x$;
2. Long-range transport and deposition modeling of $SO_x$;
3. Analysis of the trajectories of air masses ending at monitor locations in Florida, and comparison of the residence time of these air masses in different potential source regions as a function of air and precipitation chemistry; and
4. Development of an atmospheric mass balance of $SO_x$ and $NO_x$ for Florida on the basis of these investigations.

This program was conducted with the objective of answering several key research questions; these questions are specifically addressed below.

### 3.4.1 SOURCES

- What are the current anthropogenic and biogenic sources of acid precursors found in Florida's atmosphere?
  - a. From Florida utilities?
  - b. From nonutilities in Florida?
  - c. From sources located outside of Florida?
  - d. From biogenic sources?

Florida's anthropogenic emissions of $SO_x$ (expressed as S) were estimated to be 425,000 MT in study year 1983 (mid-September 1982 through mid-September 1983, see Table 3.3-1) and 460,000 MT in calendar year 1980 (ESE, 1983a). The estimate for 1983 is more reliable than the 1980 estimate because of differences in data acquisition and review procedures, but the difference may also be indicative of interannual fluctuations in emissions. Florida's biogenic sulfur emissions are the subject of an ongoing study conducted by FIU and the University of Miami for the Florida Acid Deposition Study. The results will be published later as an addendum to this study. Preliminary results indicate that biogenic sulfur emissions are from 5,500 to 22,000 metric tons per year (MT/yr) or approximately 1 to 5 percent of anthropogenic emissions. Based on these findings, Florida's current total sulfur emissions are approximately 430,000 to 480,000 MT/yr.

A significant fraction of the acid precursors in Florida's atmosphere is imported from out-of-state sources. Edgerton (1981) had estimated that approximately 30 percent of Florida's atmospheric sulfur was imported. That estimate is less reliable than estimates developed in this study, which are based on much more reliable and appropriate air quality data collected under this study and more sophisticated procedures for estimating transport winds (refer to Subsection 3.3.3.4).

The mass-balance model for $SO_x$ (refer to Subsection 3.3.3.5) and the LRT model (refer to Subsection 3.3.2) yield very similar results pertaining to import of sulfur. The mass-balance model indicates that approximately 45 percent of the sulfur in Florida's atmosphere is imported from out of state, and the LRT model indicates that approximately 55 percent of Florida's atmospheric sulfur is imported. Taken independently, each of these estimates must be considered highly uncertain. It is important to recognize, however, that each estimate is based on a different series of calculations, yet the results are relatively consistent. However, the data sources used in developing the estimates are largely the same, so the similarity in estimates tends to indicate an internal consistency rather than truly independent corroboration. Imported sulfur probably accounts for 45 to 55 percent of the sulfur in Florida's atmosphere. Approximately 780,000 to 1,100,000 MT of sulfur enter Florida's atmosphere per year, either by import or from in-state emissions.

ESE (1983a) estimated that Florida's utilities emitted approximately 340,000 MT of sulfur in Calendar Year 1980. During study year 1983, Florida's utilities were estimated to emit 290,000 MT of sulfur (see Table 3.3-1). Based on these estimates, Florida utilities apparently account for approximately 30 to 40 percent of the sulfur in Florida's atmosphere.

Anthropogenic sources other than utilities were estimated to emit 124,000 MT of sulfur in 1980 (ESE, 1983a), and 135,000 MT of sulfur in 1983 (see Table 3.3-1). Thus, Florida's nonutility anthropogenic sources account for about 10 to 15 percent of the sulfur in Florida's atmosphere.

Estimates of the sources of $NO_x$ to Florida's atmosphere are somewhat more uncertain than the estimate for $SO_x$, as a result of two limitations of this study:

1. The monitoring program has accounted for a smaller proportion of all nitrogen species than sulfur species; and
2. The ENAMAP model was not applied for $NO_x$ because of the additional complexities and greater uncertainty of $NO_x$ transformations and deposition rates.

Nonetheless, estimates of the sources of $NO_x$ to Florida's atmosphere are possible. Anthropogenic emissions of $NO_x$ were estimated to be 214,000 MT as nitrogen in 1980 (ESE, 1983a) and 224,000 MT as nitrogen in Study Year 1983 (see Table 3.3-1). The 1983 estimates are considered more reliable, but the difference may also be indicative of interannual fluctuations.

Florida's biogenic nitrogen oxide as nitrogen ($NO_x$-N) emissions have been estimated from the literature to be 17,000 MT/yr, or about 8 percent of anthropogenic emissions in the state. Florida's total $NO_x$-N emissions are the sum of anthropogenic and biogenic emissions and, thus, are approximately 230,000 to 240,000 MT/yr.

The mass-balance model results (refer to Subsection 3.3.3.5) indicate that approximately 180,000 MT of $NO_x$-N is imported into Florida's atmosphere from out-of-state sources per year, resulting in approximately 420,000 MT of $NO_x$-N entering Florida's atmosphere per year, either as in-state emissions or import. Approximately 45 percent of Florida's $NO_x$ is imported.

ESE (1983a) estimated that Florida's utilities emitted approximately 90,000 MT of $NO_x$-N in Calendar Year 1980. During Study Year 1983, Florida's utilities were estimated to emit 70,000 MT of $NO_x$-N. Based on these estimates, Florida's utilities apparently account for approximately 15 to 20 percent of the $NO_x$ in Florida's atmosphere.

Anthropogenic sources other than utilities were estimated to emit 120,000 MT of $NO_x$-N in 1980 (ESE, 1983a) and 150,000 MT of $NO_x$-N in 1983 (see Table 3.3-1). Thus Florida's nonutility anthropogenic sources account for approximately 30 to 35 percent of the $NO_x$ in Florida's atmosphere. Nonutility anthropogenic sources of $NO_x$ are predominantly attributable to vehicle exhaust (90 percent of nonutility anthropogenic sources).

### 3.4.2 UNCERTAINTY OF SOURCE ATTRIBUTION RESULTS

- What is the uncertainty in estimating the predicted impact of Florida anthropogenic emission sources on current levels of acidic deposition?

This broad question can best be addressed after consideration of several corollary (although more limited) questions that relate closely to specific modeling tasks. The corollary questions (a through f below) relate to the ENAMAP model application and adjustment presented in detail in Subsection 3.3.2.1.

a. How do initial model results compare to observational data?

Initial ENAMAP model results using the best initial estimate for all model parameters did not compare closely to observational data. Monthly average wet-deposition rates over the eastern United States exceeded the observed wet-deposition rates by a factor of roughly 3. Similarly averaged atmospheric $SO_2$ and $SO_4^{-2}$ concentrations in Florida were underpredicted by approximately 30 percent.

b. What changes were evaluated to improve model comparison with observational data?

As presented in Table 3.3-8, the following parameter changes were evaluated to determine their effect in improving model performance:

1. The $SO_2$ to $SO_4^{-2}$ transformation rate was decreased in an attempt to reduce $SO_4^{-2}$ wet deposition.
2. The $SO_2$ and $SO_4^{-2}$ dry-deposition velocities were increased in an attempt to increase dry deposition and reduce wet deposition.
3. The height of the lowest model mixing layer was increased in an attempt to increase dry deposition.
4. Wet scavenging rates of $SO_2$ and $SO_4^{-2}$ were reduced to reduce wet deposition.

c. What is the sensitivity of such changes to model results?

The model sensitivity analysis indicates that there are a variety of alternatives in parameter adjustment that could affect model/data comparisons. The model's response was relatively sensitive to the height of the lowest atmospheric layer. A change in this parameter directly affects the dry-deposition rate, since contaminants are dry deposited only from the lowest layer. The predicted dry-deposition rate increased by approximately 80 percent when the height of the lowest layer was increased from 200 m to 350 m.

The model's response was also sensitive to the wet-scavenging coefficients, although variations in the wet-scavenging coefficients produced less-than-proportionate changes in wet-deposition rates. Reducing the wet-scavenging coefficient by a factor of 8 reduced wet-deposition rates by a factor of approximately 3 and slightly increased dry-deposition rates. Considering the offsetting increase in dry deposition, total sulfur deposition was reduced by a factor of only 2 in response to reducing the wet-scavenging coefficient by a factor of 8.

Most individual parameter changes tested caused a shift between the relative importance of the dry- and wet-deposition processes but had minor effects on (1) the total amount deposited, and (2) the amount of $SO_2$ transformed to $SO_4^{-2}$. The change in the mixing layer from 200 m to 350 m increased dry-deposition at the expense of wet-deposition; total sulfur deposition increased by only 11 percent, and the fraction of emitted $SO_2$ that was transformed to $SO_4^{-2}$ decreased from 56 percent to 46 percent. Decreasing the wet-scavenging coefficients by a factor of 8 increased the fraction transformed from 46 percent to 57 percent. Increasing the deposition velocity by a factor of 2 had a nearly proportionate effect on dry-deposition rates but resulted in a slight reduction in wet-deposition and less than a 10-percent change in total deposition and in the percent transformed. The most direct and obvious way to change the percent transformed would be to change the transformation rate, but a 40-percent reduction in the transformation rate resulted in only a 14-percent reduction in the fraction transformed. This lack of direct proportionality is presumably due to $SO_2$ transformation at a greater distance from sources, but still within the model domain.

d. Can such changes be supported?

The ENAMAP model, like other models of its type, has significant limitations because of its simplified representation of complex atmospheric processes. Its ability to reproduce observational results is also adversely affected by the quality of the meteorological and emissions data used as input. Finally, comparisons with observational data will exhibit some degree of inappropriateness insofar as model estimates designed to characterize an 80-km by 80-km grid cell must be compared with observations from a wet-deposition bucket collector having an area of only 0.65 square meter ($m^2$). In this context, the model practitioner is left with considerable latitude in selection of acceptable and defensible values for model parameters. In practice, parameter values are typically adjusted, within some realistic range of values to improve comparisons with observational data.

The "base case" (initial model application Run 1) represented a "best estimate" of all parameter values consistent with the broader technical literature and in the context of earlier experimentation with ENAMAP by the model developers (Endlich et al., 1983). To achieve better comparisons with the data, it was necessary to increase the height of the lowest model layer from 200 to 350 m. Within a model layer, atmospheric sulfur concentrations are well mixed vertically. This lowest layer is a feature of the model's construction that has little or no counterpart in the real atmosphere. The sensitivity of the model's response to changes in such an ill-defined parameter must be viewed as a weakness of the model.

It was also necessary to reduce wet scavenging coefficients by a factor of 8 to produce reasonable estimates of wet-deposition rates. The resulting wet-scavenging coefficients are well below those that have been determined by field studies (see, e.g., Scott and Laulainen, 1979) as well as the already relatively low coefficients that were used by Endlich et al. (1983) in earlier experimentation with the ENAMAP model. For the same reasons that it is inappropriate to compare the wet-deposition observations with ENAMAP results, so too is it inappropriate to compare small-scale observations of the scavenging coefficient with the value that must be applied by the model for use in 80-km by 80-km grid cells. When ENAMAP simulates precipitation, it simulates uniform rainfall over a grid cell. This is a simplified and unrealistic representation of actual smaller-scale processes. The fact that wet-scavenging coefficients needed to make the model work are lower than those observed in the field is an interesting finding, but a mechanistic explanation would be purely speculative and could not be supported by the model results per se.

e. How did the adjusted model compare with observational data?

Table 3.3-13 illustrates the performance of the adjusted model over a 6-month simulation. Within Florida, the statewide average sulfur wet-deposition rate has been reproduced to within 7 percent (3.1 mg-S/m$^2$). In the southeast, excluding Florida, the 6-month average, areally averaged wet-deposition rate was reproduced to within 8 percent (4 mg-S/m$^2$). Outside the southeast, emissions were consolidated by state and emitted from a single cell. This simplified approximation was made to conserve computational resources and was consistent with the Florida emphasis of this study. Correspondingly, ENAMAP results were less accurate in the northern part of the United States, with the 6-month spatial average deposition exceeding the observed by 25 percent.

Long-term average wet-deposition rates at individual monitor locations were reproduced considerably less accurately than broad areal averages. Point-by-point predicted and observed deposition rates were significantly correlated ($R = 0.59$) only for the nine monitoring sites in Florida. The average absolute error of wet-deposition prediction was 18 mg-S/m$^2$ for Florida; 25 mg-S/m$^2$ in the gridded southeastern emission zone; and 49 mg-S/m$^2$ at nonsoutheastern sites. These point-by-point errors can be compared with the areally averaged errors of 3 mg-S/m$^2$, 4 mg-S/m$^2$, and 19 mg-S/m$^2$, respectively. No comparisons to short-term average deposition rates have been made, although they would be expected to differ substantially from the observed rates.

Within the state of Florida, the air concentrations estimated by the model were compared with the air chemistry network data over the 6-month average. Florida average $SO_2$ concentrations were underestimated by about 20 percent, whereas $SO_4^{-2}$ was overestimated by about 60 percent. Point-by-point comparisons were similarly less reliable than broad areal averages for air chemistry estimates as for wet-deposition.

f. Can further adjustment of the model be supported?

Wet-deposition rates are underestimated by the model by about 10 percent. Model sensitivity studies (see Subsection 3.3.2.2) indicate that model wet-deposition could be increased by 10 percent by increasing the precipitation scavenging coefficient for both $SO_2$ and $SO_4^{-2}$ by about 10 to 20 percent compared to the value used. A change of this magnitude would lead to corresponding, though muted, percentage changes in a variety of other model outputs. Air concentrations of $SO_x$ would be reduced, which would improve the comparison of atmospheric sulfate concentrations with observed concentrations but would adversely affect the comparison of observed and calculated $SO_2$ concentrations. In consideration of this effect, it may be appropriate to increase the $SO_4^{-2}$ wet-scavenging coefficient by 20 to 30 percent and not change the $SO_2$ scavenging coefficient.

Several results suggest that the amount transformed in the model is slightly too high in comparison with observational data. The change suggested above to increase scavenging coefficients for both forms of $SO_x$ would reduce the amount transformed slightly (probably less than 1 percent) by depositing more $SO_2$ before it is transformed. An increase in the scavenging coefficient of $SO_4^{-2}$ only would not be expected to have any effect on the amount transformed. The most direct approach to reducing $SO_4^{-2}$ concentrations (63 percent too high) while increasing $SO_2$ concentrations (20 percent too low) would be to decrease the transformation rate.

Reduction of the $SO_2$ dry-deposition velocity would increase the $SO_2$ and $SO_4^{-2}$ concentrations and would not be recommended since $SO_4^{-2}$ concentrations are already 63 percent too high.

The ENAMAP model is based on a simplification of actual atmospheric processes, attempting to represent potentially nonlinear processes with linear relationships. For example, a variety of research results indicate that scavenging of $SO_x$ exhibits nonlinear characteristics; however, ENAMAP, like most other models of its type, treats scavenging as a linear process. Depending on the strength of the nonlinearity, minor adjustments in a linearized parameter, such as the scavenging coefficient, cannot be supported.

Errors in estimating the spatial variability of deposition rates (see Subsection 3.3.2) appear to be dominated by errors in the model's input data characterizing the spatial variability of precipitation. This suggests that additional improvements in reproducing spatial patterns of deposition are unlikely in the context of the existing meteorological database.

Any comparison of the predictions of models like ENAMAP with observational data available at the state of the art will exhibit some element of inappropriateness; i.e., an "apples and oranges" problem. For example, model results applying over an 80 km x 80 km area are compared with observations from a wet-deposition bucket collector having an area of 0.65 $m^2$. Section 2.4 presents information that $SO_4^{-2}$ deposition varies by approximately 8 percent over only a few meters. The uncertainty of a point observation as an estimate of deposition over 6,400 $km^2$ is difficult to estimate but probably substantial.

For these reasons, further refinement and "calibration" of a model having the characteristics of ENAMAP beyond the extent pursued here is probably fruitless and misleading. More precise comparisons would not reveal further insights. Such refinements would demonstrate neither additional realism in the simulation nor reliability in the parameter values (e.g., deposition velocities) that would be used to achieve more "precise" comparisons.

- What is the uncertainty in estimating the predicted impact of Florida anthropogenic emission sources on current levels of acidic deposition?

Both the mass-balance model (refer to Subsection 3.3.3.5) and the ENAMAP LRT model (refer to Subsection 3.3.2) provide information on the contribution of various categories of sources and source regions to current levels of acid deposition in Florida. Although the series of calculations made was different in arriving at estimates based on these models, both ultimately rely on wind fields analyzed from NWS stations, supplemented in the case of the mass-balance model by oceanic wind estimates from the ATOLL database. Furthermore, both are based either implicitly (mass-balance model) or explicitly (ENAMAP) on assumptions of linear transformation and removal processes. Finally, each relies on the same emissions database. Consequently, although the series of calculations is substantially different and in some way complementary and independent, it should not be surprising that the results of the two approaches are similar. The similarity should not be used to imply reliability or accuracy, only consistency.

The mass-balance model for Florida relies partially on the air mass trajectory calculations of the ATAD model. Although Pack et al. (1978) and Mueller (1983) found that individual trajectory directions were reliable only to ±15° or ±20°, the ensemble of many trajectories, as used in this application, would be expected to be more reliable. The import estimates are also based on the assumption that ground-level air concentrations are representative of the average concentration through the mixing layer.

A quantitative evaluation of the precision of the mass-balance model based on observational data is virtually impossible since the estimated quantities are not directly observable. The LRT model ENAMAP, however, estimates several quantities that have been measured directly or calculated from observations. Sulfur deposition rates over the eastern United States have been estimated by Galloway and Whelpdale (1980) for 1980, based on observations of air chemistry, precipitation chemistry, and meteorological data. Galloway and Whelpdale's (1980) estimates of the fractional contribution of wet deposition, dry deposition, and export to the deposition of atmospheric sulfur over the eastern United States correspond to the ENAMAP results for 1983 within ± 25 percent (see Table 3.3-12). Clearly the comparison periods differ. Since substantial annual variations in deposition have been documented, the value of this comparison is extremely limited. It is for this reason that only the relative mass balances (percent of emissions wet-deposited, percent of emissions dry-deposited, percent of emissions transported out of the domain) have been compared as an indication that the ENAMAP results are generally consistent with the findings of other investigations. Actual meteorological differences between the two periods could cause the mass balances to differ considerably between the two periods, in which case the observed "consistency" would actually result from prediction errors. Available data are not adequate to define the value of this comparison.

ENAMAP estimates of wet-deposition rates and air concentrations of $SO_2$ and $SO_4^{-2}$ also correspond closely to observations from the Florida monitoring network and wet-deposition rates throughout the eastern United States (see Table 3.3-13). The domain-average, wet-deposition rate is within 8 percent of the observed rate. The Florida average-deposition rate is within 7 percent of the observed rate. Average $SO_2$ concentration in Florida is reproduced to within 20 percent and $SO_4^{-2}$ to within 60 percent. These are results from a model which has been adjusted to improve agreement between observations and predictions over a limited time period. Model results for different time periods may not show similar agreement between observations and predictions.

Comparisons of average deposition rates over broad areas (Florida, eastern United States) are encouraging. Point-by-point comparisons are considerably less faithful. Insofar as the model was adjusted to faithfully reproduce domain-average deposition rates and concentrations of $SO_2$ and $SO_4^{-2}$, the successful comparison should not be interpreted to imply that subdomain transports are similarly reliable. Available data are not adequate to evaluate the interregional transports estimated by ENAMAP, and a variety of compensating errors could fortuitously lead to accurate reproduction of air quality and deposition totals based on inaccurate transport rates. Nonetheless, the variety of successful observational data comparisons and the similarity of results between ENAMAP and the mass-balance model suggest that ENAMAP LRT calculations are reasonably faithful. Confidence in ENAMAP results should only extend to its ability to reproduce existing deposition patterns. The various simplifications of ENAMAP, particularly its linearization of transformation and transport processes, limit its ability to predict the pattern that might result from altered source emission scenarios.

In the context of the preceding discussion, it should be clear that the number of factors leading to uncertainty and the potential to be misled by any simple quantitative analysis demands that the answer to this question remain qualitative. Estimates of the percentage contribution of various source regions and source categories to total sulfur and nitrogen deposition that appear in Subsection 3.4.3 should be considered semiquantitative. To avoid misrepresenting the precision of these results, percentage contributions will be expressed only to the nearest 5 percent.

### 3.4.3 CONTRIBUTION OF FLORIDA SOURCES TO DEPOSITION RATES

- How do Florida's current anthropogenic emission sources contribute to current levels of acidic deposition in Florida and neighboring states?

The results of ENAMAP and the mass-balance model permit this question to be addressed semiquantitatively for sulfur deposition rates. The contribution of in-state sources to nitrogen deposition rates must rely on a more qualitative discussion because less information is available on the transformation and deposition processes for atmospheric $NO_x$. Consequently, ENAMAP was not used to model the long-range transport and deposition of $NO_x$.

Out-of-state emission sources appear to be a major source of sulfur wet-deposition in Florida, and more sulfur is deposited by wet than dry processes, implicating out-of-state sources as major contributors to current levels of sulfur deposition. This conclusion is derived principally from ENAMAP model results, but is supported by related findings of the mass-balance model and the monitoring network.

Figure 3.3-14 indicates that approximately 35 percent of total sulfur deposition in Florida is attributable to out-of-state sources. This result cannot be directly verified, but several intermediate ENAMAP results that contribute to this overall result can be corroborated by other findings of the study. ENAMAP calculated that about 30 percent of the $SO_2$ and about 70 percent of $SO_4^{-2}$, and, thus, about 55 percent of Florida's atmospheric sulfur is attributable to out-of-state sources. The mass-balance model results indicate that approximately 45 percent of Florida's atmospheric sulfur is imported. The difference in these two results is well within the uncertainty bounds that should be ascribed to them. ENAMAP's results indicate that out-of-state sources contribute predominantly to atmospheric $SO_4^{-2}$ rather than $SO_2$. This finding is supported in part by the air mass trajectory findings that imported air exhibits 86 percent of the monitor network average $SO_4^{-2}$ concentration. In ENAMAP, this predominantly out-of-state $SO_4^{-2}$ tends to be scavenged by precipitation more efficiently than the $SO_2$, which tends to be attributed relatively more to in-state sources. The comparison of air chemistry and precipitation chemistry data from the monitoring network (see

Subsection 2.7.5) tends to confirm the validity of this aspect of ENAMAP's internal processes. Excess sulfate in precipitation was found to be significantly correlated with ambient in $SO_4^{-2}$, but not with atmospheric $SO_2$ concentrations. This suggests that precipitation excess $SO_4^{-2}$ is more likely to be derived from scavenging of particulate $SO_4^{-2}$ than by scavenging of gaseous $SO_2$ and subsequent aqueous phase transformation to $SO_4^{-2}$. This result is also consistent with findings of Scott and Laulainen (1979). Thus, ENAMAP results indicate that out-of-state sources contribute substantially (65 percent) to atmospheric $SO_4^{-2}$ concentrations in Florida and that these $SO_4^{-2}$ particles are scavenged effectively by precipitation. The results also imply a major contribution (55 percent) to wet sulfur deposition by out-of-state sources. These results can be corroborated by a broader base of results from the monitoring network, the mass-balance model, and other investigations.

Dry deposition, on the other hand, is the predominant removal mechanism for $SO_2$, and Florida $SO_2$ concentrations are predominantly attributable to in-state sources, yielding the result that approximately 90 percent of dry deposition in Florida is attributable to Florida sources (see Figure 3.3-4). Integrating these results indicates that 65 percent of total sulfur deposition in Florida is attributable to in-state sources (Figure 3.3-16) and approximately 45 percent of the total deposition of sulfur in Florida is attributable to Florida utilities (Figure 3.3-18).

The contribution of Florida utilities to out-of-state sulfur deposition is estimated to be less than 5 percent of total sulfur deposition in any out-of-state receptor region and less than 1 percent of total deposition in regions that include potentially sensitive receptors in the Appalachians and Adirondacks (refer to Subsection 3.3.2.2). All Florida anthropogenic sources combined contribute less than 10 percent of total sulfur deposition in any out-of-state region and less than 1 percent in regions that include potentially sensitive receptors in the Appalachians and Adirondacks.

For $NO_x$, the contribution of current anthropogenic sources to current levels of deposition is best estimated by reference to the mass-balance model results, which indicate that in-state anthropogenic sources account for about 50 percent of Florida's atmospheric $NO_x$. Florida utilities account for only about 20 percent of Florida's atmospheric $NO_x$.

Dry-deposition rates for $NO_x$ are highly uncertain--certainly one of the more unreliable results developed as part of the Source Attribution Program. The estimates are based on only a few measured deposition velocities. Furthermore, the monitoring network, designed to represent regional air chemistry patterns by avoiding major local sources, does not provide the capability to estimate the total mass of $NO_x$ deposited in the state. Automotive exhaust, a major contributor (approximately 40 percent) of anthropogenic emissions, is emitted at ground level in urban areas and along major highways and can be expected to deposit by dry processes near the source. This dry deposition of $NO_x$ cannot be accounted for by the Florida network. As mentioned previously, the monitoring network also does not analyze all relevant species of $NO_x$. Nitrous acid, PAN and particulate nitrate, among others, are currently unquantifiable contributors to the atmospheric $NO_x$ budget.

In consideration of these uncertainties, the contribution of Florida anthropogenic sources to Florida's $NO_x$ deposition rate must be estimated by assuming that it is proportional to their contribution to Florida's atmospheric $NO_x$. This assumption is probably invalid because local (Florida) sources and particularly local ground-level sources would be expected to contribute relatively more to dry-deposition rates. Thus, local ground-level sources such as vehicle exhaust would be expected to contribute significantly more than 30 percent to total $NO_x$ deposition in the state, and utility sources could contribute somewhat more than 20 percent to total deposition.

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# 4.0 ECOLOGICAL EFFECTS

## 4.1 INTRODUCTION AND OBJECTIVES

### 4.1.1 HISTORICAL OVERVIEW

Research regarding the possible ecological effects of acidic deposition in Florida began with a survey of 20 softwater lakes in north- and south-central Florida conducted by Brezonik and co-workers from the University of Florida (Brezonik et al., 1983). This survey, which was performed in 1978 and 1979, examined the distribution of major ions, pH, and aluminum (Hendry, 1983), and characterized the planktonic (phytoplankton and zooplankton) and benthic invertebrate communities of these lakes (Schulze, 1980). Results from this survey showed that the lakes could be segregated into two statistically distinct groups based on pH. The acid lakes characteristically had lower concentrations of dissolved salts and nutrients, and higher aluminum concentrations. Generally lower densities of phytoplankton and zooplankton also were observed in the acidic lakes, supporting the hypothesis that lake acidification is accompanied by declines in productivity. However, as Brezonik (1983) observed, the trends in trophic state and acidity may only be correlative rather than causative--distinctions which cannot be resolved in the absence of more data.

Subsequent to the initial studies of Brezonik and his co-workers, the Ecological Effects Program of the Florida Acid Deposition Study was initiated with the ultimate objective of determining the sensitivity of Florida's resources (terrestrial, aquatic, and manmade) to acidic deposition. The study began in January 1981 and initially focused on defining the state-of-the-art of acidic deposition research and the applicability as well as the implications of the results regarding Florida's resources. These objectives were realized by implementing a comprehensive review and evaluation of the existing literature, and included an analysis of the limitations of the various published approaches towards defining sensitivity.

The initial review of the literature indicated that the applicablity of the available sensitivity indices to Florida was ambiguous and in certain cases yielded contradictory results. In the absence of acceptable tools to define sensitivity, subsequent FADS research focused on delineating the geographical distribution of lakes and lake districts with similar buffering capacities. As a corollary objective, groups of soils with equivalent buffering characteristics were defined using a refined index. Assuming an appropriate sensivity index could be developed, these groupings of lakes and soils ostensibly could be used to define the distribution of sensitive systems. A final objective was to evaluate the influence of soil characteristics on the buffering capacity of receptor aquatic ecosystems.

Sensitivity presupposes a dose-response relationship has been established which would allow a prediction of system response given a certain acidic deposition rate, and that the chemical changes induced by this perturbation yield a known biological response. Prior to the Florida Acid Deposition Study, such responses had not been established for terrestrial and aquatic ecosystems within Florida, although preliminary work was begun in 1981 in Lake McCloud (Baker, 1984; Ogburn, 1984) and the soils within its watershed (Volk and Byers, 1983; Byers, 1984). Consequently, a series of studies was initiated to examine processes believed to control ecosystem response to acidic deposition. These process-oriented studies included the following:

1. Examined the magnitude of sulfate adsorption in poorly buffered soils, and how this mechanism influences soil sensitivity.
2. As an extension of the original Lake McCloud watershed study, evaluated the influence of artificially acidified lakewater on the microbiology and chemistry of a very poorly buffered and acidic soil.

3. Evaluated the contribution of lake sediments to overall lake buffering capacity, and examined how this capability is influenced by sediment type.
4. Determined the magnitude of aluminum release as a function of pH and evaluated the mineral phases control aluminum solubility as softwater lake sediments buffer overlying lakewater against changes in pH.
5. Through the use of sediment-water microcosms,evaluated both the fate of sulfate in softwater Florida lakes and its role in alkalinity production.

With the exception of the McCloud Lake research which was conducted _in situ_, these studies were addressed largely through a series of laboratory experiments designed to isolate the components of interest.

Studies other than the process oriented research listed above were included in the Florida Acid Deposition Study program. These included an examination of the acid-induced oligotrophication hypothesis in softwater Florida lakes using the original database compiled by Brezonik _et al_. (1983) and an analysis of the geographical distribution of freshwater fish in Florida with respect to ambient geochemical and physical factors and pH in particular. In addition, the Florida Acid Deposition Study program included experimental studies on the direct effects of simulated acidic deposition on several terrestrial resources of great economic significance in Florida (_viz_., slash pine, citrus, and tomato). A final component of the Florida Acid Deposition Study involved the development of a diagnostic model in order to describe softwater lake response to acidification.

### 4.1.2 OBJECTIVES

The synthesis phase represents an integration of the results derived from each phase of the Florida Acid Deposition Study. Implicit in this integrative approach is the evaluation and incorporation of results from studies conducted by other researchers both within Florida and in other geographical areas. This approach is centered around the overall program objective of defining sensitivity and the resources potentially at risk to acidic deposition within Florida. Within this overall framework, more specific objectives can be defined:

1. At current levels of acidic deposition, what are the likely effects?
2. How are soils and lake systems likely to respond to changes in acid inputs?
3. What are the chemical and physical relationships between deposition and sensitivity of soils and lake systems?
4. What soils and lakes are potentially sensitive to current levels of acidic deposition?
5. What are the potential effects of current levels of acid deposition to agricultural crops or terrestrial systems? In addition, what are the responses of agricultural crops and terrestrial systems to changes in deposition?
6. What are the long-term trends of soil and lake chemistry in Florida?
7. What are the potential effects of acidic deposition and precurser emissions to manmade materials in Florida?
8. How are changes in acidic deposition levels and precursor emissions likely to influent manmade materials?

Within the context of these specific questions, the focus of the Final Report is to present the support as well as the limitations or lack of support defining the effects of acidic deposition. From this analysis, conclusions are drawn regarding sensitivity of aquatic, terrestrial, and manmade resources within Florida.

### 4.1.3 ORGANIZATIONAL OVERVIEW

The framework of the final report incorporates a structure based on discipline; chapters are segregated using the fundamental disciplines of this study (i.e., terrestrial, aquatic, and manmade effects) as the focal points. A principle component of the final report is to critically evaluate the existing results describing the effects of acidic deposition developed during the previous phases of the Florida Acid Deposition Study. Rather than recapitulate the specific methodologies of the various efforts studies, the reader is directed as follows for detailed descriptions of each study:

- Effects literature review--ESE, 1982c.
- Geophysical distribution of soils and lakes with equivalent buffering characteristics--ESE, 1983a.
- Sulfate adsorption in soils--ESE, 1984.
- Geographical distribution of fish--ESE, 1984.
- Lake sediment buffering characteristics--ESE, 1984.
- Aluminum solubilization from sediments in response to pH--ESE, 1984.
- Effects of simulated acidic deposition on slash pine, citrus, and tomato--ESE, 1984.
- Lake McCloud soil chemistry and microbiological studies--ESE, 1985.
- Examination of productivity and pH relationships in Florida softwater lakes--ESE, 1985.
- Analysis of sulfate dynamics and its role in alkalinity production--ESE, 1985.
- Development of a diagnostic model for lake acidification in Florida--ESE, 1985.

In addition, the nature of each study is briefly described in subsequent sections which are devoted to presenting the results of the Florida Acid Deposition Study in relation to other, current research.

### 4.1.3.1 Terrestrial Ecosystems

Effects of acidic deposition in terrestrial ecosystems are described in Subsection 4.2. This chapter begins with an overview of soil chemical, physical, and microbiological properties and their relationship or role in soil response to acid inputs (Subsection 4.2.1). The distribution of soils with respect to their buffering capacity and the chemical response to acidity are discussed in Subsection 4.2.1 as well.

Response of vegetation, including both forested and cropland resources, and the biological components of the soil are presented in Subsection 4.2.2. Effects mediated by the chemical response of the soil, otherwise known as indirect effects, and direct effects of acidic deposition to members of the soil community (e.g., soil bacteria and fungi), vegetation, and crops are the focus of this section. In addition, the synergistic effects of other airborne contaminants, notably ozone, are discussed.

#### 4.1.3.2 Aquatic Ecosystems

The discussion of the effects of acidic deposition on aquatic ecosystems in Florida is presented in Subsection 4.3. Historically, the major concern for the potential effects of acidification has centered on aquatic systems. Although concern about terrestrial effects has perhaps supplanted aquatic sensitivity as a major issue, the issue of aquatic sensitivity in general (and Florida in particular) is not resolved. This section is divided into two subsections: chemical or abiotic response (Subsection 4.3.1) and effects on aquatic biota (Subsection 4.3.2). Subsection 4.3.1 details the principal limnological processes that influence lake acidification and analyzes the linkage between watersheds and receptor aquatic systems (Subsection 4.3.1). Another issue of uncertainty that assumes significance in Florida concerns the potential sensitivity of clear softwater lakes and softwater lakes highly colored by organic acids. Subsection 4.3.1 also reviews recent developments in model approaches used to describe and/or predict the acidification process in lakes and evaluates their applicability to Florida.

The section on potential effects to aquatic biota (Subsection 4.3.2) incorporates results of recent bioassays on fish indigenous to Florida.

The section reviews the available literature on potential effects and the role of organic acids characteristic of colored lakes in mediating biological responses to acidification. The distribution of fish in Florida in relation to pH is also discussed.

### 4.1.3.3 Material Effects

As is the case for terrestrial and aquatic resources, damage to man-made materials may be induced from indirect and direct exposure to acidic deposition. Consequently Subsection 4.4, which discusses effects on materials, is divided into two main subsections (Subsections 4.4.1 and 4.4.2) describing direct and indirect effects, respectively. Relative to the other disciplines included in the Ecological Effects Program, the state of the art regarding materials effects is not particularly well advanced and reflects both the limited research performed in this area and the inherent difficulty in isolating the effects of acidic deposition apart from other environmental factors. This section reviews the results and limitations of current research on material effects including corrosion. In addition, the economic implications of damage attributable to acidification are discussed in conjunction with the uncertainty implicit in the damage functions used to derive these estimates.

### 4.1.3.4 Response to Key Research Questions

The final two chapters in the synthesis report develop the specific responses and the conclusions regarding the various objectives or key research questions presented in the Introduction. Subsection 4.5, which presents the response to the identified key research questions, is derived explicitly from the information presented in the earlier chapters for each major discipline. Within the framework of each response is an analysis of the inherent limitations and uncertainty.

## 4.2 EFFECTS ON TERRESTRIAL SYSTEMS

In this section, the potential effects of acidic deposition on terrestrial systems including soils and vegetation are summarized. This discussion is based on the technical literature and several experimental studies performed under the auspices of the Florida Acid Deposition Study. To the extent possible, reported results having generic applicability are interpreted in the context of Florida conditions.

### 4.2.1 RESPONSE OF SOILS TO ACIDIC INPUT

The characteristics of both terrestrial and aquatic systems are profoundly influenced by the physical, chemical, and biological attributes of soils. Soils in conjunction with climate define the character and extent of productivity in terrestrial systems. In addition, the soils comprising a particular lake or stream watershed play an important role in regulating the chemical characteristics (and ultimately, the biological characteristics as well) of the receptor aquatic system. Because of the central role assumed by soils in most ecosystems, considerable interest has focused on the effects of acidic deposition on soils. Potential effects in soils have been reviewed at length during Phase I (ESE, 1982c) and more recently by McFee *et al.* (1984). Potential and hypothesized effects of acidic deposition on the nonliving portion of the soil matrix include:

1. Increased soil acidification;
2. Alteration in cation exchange capacity (CEC);
3. Loss of base cations (i.e., $Ca^{+2}$, $Mg^{+2}$, $K^{+}$, $Na^{+}$); and
4. Mobilization of trace elements.

These effects and associated research that has particular relevance for describing or inferring the response of terrestrial systems within Florida to acidic deposition are detailed in the sections following.

### 4.2.1.1 Overview of Soil Properties in Relation to Acidification

#### Soil Physical Properties

The sensitivity or response of soils to acid inputs is fundamentally affected by the physics of the soil matrix governing water flow. The ability of a soil to conduct water vertically through the soil profile is perhaps the most important physical property influencing the interaction of soils with acidic deposition. Soils with a porous structure such as- the coarse, sandy soils typically found in Florida permit water to flow evenly through the profile, allowing a rather large fraction of deposited rainfall to infiltrate and come into contact and potentially react with soil particles. However, if the rate of infiltration and percolation is extremely rapid, water migrating through the soil profile may have little time to react, and the water will be altered to only a small extent (McFee et al., 1984). Soils with poorly developed structure tend to conduct water through a relatively small series of cracks or root channels resulting in exposure and interaction of only small fractions of infiltrating rainwater and soil (Bache, 1980). Soil porosity and hydraulic conductivity in turn are influenced by particle size, shape, and the uniformity of the grain-size distribution. In general, porosity is greater in soils with uniform distributions (Yariv and Cross, 1979).

#### Soil Chemical Properties

Resistance of soils to changes induced by acidic deposition are typically measured in terms of soil pH and soil CEC. Soil pH is indicative of the intensity of acidification, but as a parameter it provides little information as to the magnitude of response a soil is likely to exhibit when exposed to changes in acidic deposition. CEC in turn is a capacity parameter; it indicates the total quantity of cations (including protons and aluminum) that a particular soil can retain by adsorption. CEC among different soils varies widely and is related to both the amount of organic matter and types and amount of clay minerals present in the soil. Organic matter characteristically has a high CEC (approximately 200 meq/100 g; Bolt and Bruggenwert, 1978) which is pH dependent; as soil pH decreases, the number of sites available for cation exchange decreases. Lerman (1979) summarized the CEC of various clays and natural materials (Table 4.2-1). Because adsorption occurs at the surface of soil particles, CEC tends to increase with decreasing particle size because of corresponding increases in the ratio of surface area to mass. The amount of CEC actually available for neutralization of acid inputs is a function of base saturation [i.e., the fraction of cation exchange sites occupied by base cations ($Ca^{+2}$, $Mg^{+2}$, $K^{+}$, and $Na^{+2}$)]. Soil pH is closely related to base saturation; Peech (1941) for example has developed such a relationship from a theoretical perspective and verified it empirically for a series of Florida soils. The relationship between soil pH and base saturation differs between different soils, however.

Several other chemical properties may also influence soil response to acid deposition. These include the type of weatherable minerals and the ability of a particular soil to adsorb sulfate. $SO_4^{-2}$ adsorption affects cation migration in accordance with the principle of electroneutrality; in order for ion leaching to occur, each cation must be accompanied by an equivalent quantity of anions. By removing $SO_4^{-2}$ from solution, adsorption thus can retard cation migration. Furthermore, $SO_4^{-2}$ adsorption can result in increases in CEC. Weathering rates are highly variable depending on the type and age of material. For example, ion exchange reactions occur within a few seconds for expanding clay minerals such as montmorillonite as contrasted with micas which require several weeks to undergo ion exchange. Quartz sands and feldspars also are more resistant to weathering than silicate clays with high oxygen-to-silicon ratios (Yariv and Cross, 1979). For dissolution reactions which are diffusion-controlled, the rate of flow through the soil can control the rate of weathering (see Berner, 1969 for a detailed discussion).

### Soil Microbiology

The soil microbial community is largely responsible for the recycling of nutrients in terrestrial ecosystems. In systems such as forests that are

Table 4.2-1. CEC of Natural Materials, Arranged in a Decreasing Order of Upper-Limit Values

| CEC (meq/100 g) | Material |
|---|---|
| 350-130 | Organic matter |
| 300-100 | Zeolites |
| 260 | Hydrous manganese oxide |
| 150-100 | Vermiculite |
| 100-70 | Montmorillonites (typical) |
| 60-20 | Micas from soils |
| 50-40 | Halloysite ($4H_2O$) |
| 47-4 | Chlorite |
| 40-10 | Illite |
| 30-20 | Palygorskite |
| 20-11 | Glauconite |
| 15-3 | Kaolinite |
| 10-5 | Halloysite ($2H_2O$) |
| 4 | Pyrophyllite |
| 1 | Feldspra, quartz |
| 0.5 | Basalt (Snake River) |

Note: meq/100 g = milliequivalents per 100 grams.

Source: Lerman, 1979.

not managed by man in the sense of receiving artificially imposed nutrient amendments, productivity and continued growth is particularly dependent on the release and recycling of nutrients via microbial decomposition of dead leaves, roots, and other material. Should acidic deposition result in reduced rates of organic decomposition, nutrient availability for plant uptake is affected. Enhanced rates of decomposition in turn can lead to increases in productivity in systems limited by nutrient availability. However, if the rate of nutrient mineralization exceeds the uptake rate by plants, the net effect of acidic deposition may be accelerated rates of nutrient leaching from the soil (Kelly and Strickland, 1984).

The role of soil microorganisms is perhaps most critical with regard to regulation of the nitrogen cycle in forested systems. Soil microorganisms are the only organisms capable of fixing or converting atmospheric nitrogen to a form that is usable by higher plants (nitrogen fixation). In addition, microorganisms convert organic nitrogen to inorganic forms plants require for uptake. Finally, microorganisms mediate the oxidation of ammonia to nitrate, a species of nitrogen which is readily leached in the soil environment. Because forest productivity in the southeastern United States is typically limited by the availability of nitrogen, effects on the microbial community induced by acidic deposition could be significant.

#### 4.2.1.2 Distribution of Soils in Florida

A series of different methods has been used to delineate the spatial distribution of Florida soils with respect to soil buffering characteristics and potential sensitivity to acidic deposition. An initial evaluation of these indices conducted during Phase I (ESE, 1982) indicated that various investigators have used different approaches and achieved different results for Florida. The most finely delineated regional indicator was constructed by McFee (1980) who mapped the distribution of CEC in surficial soils as a function of soil association.

However, as McFee mentioned in his analysis, his model was somewhat arbitrary in the development of sensitivity criteria and can be criticized for his exclusion of base saturation as a model variable.

Based on this initial evaluation, a more refined index incorporating base content was developed and applied to Florida to model of McFee (1980). A database comprising 465 samples collected previously by Calhoun et al. (1974) and Carlisle et al. (1978, 1981) was used to calculate soil buffering capacity which was defined by integrating CEC, base saturation, and bulk density over the surficial 25 cm of the soil column. Other physical and geochemical factors, such as the rate of infiltration and sulfate adsorption, which can influence soil response to acidic deposition were not included.

Average buffering capacity of Florida soils was calculated as a function of soil order, suborder, and soil great group (Note: these classes represent groupings of increasingly finer resolution and greater homogeneity). The results, which are presented in Table 4.2-2, demonstrated a broad range of values, although several distinct trends emerged. Of the four orders that dominate Florida soils (entisols, ultisols, spodosols, and histosols), the greatest average buffering capacity was observed in the highly organic histosols. Buffering capacities of the other principal orders were considerably lower and reflect the fact that surficial soils in Florida are dominated by acidic sands. Ultisols, which generally are found in the Western Highlands region of the panhandle and the north-central portion of Florida, were the most weakly buffered order with an average buffering capacity of 54 kiloequivalents per hectare (keq/ha). Entisols, which dominate the central Florida Ridge, are characterized by highly weathered quartz sands, acidic and depleted in both CEC and base content. Similarly, the surficial horizon of spodosols in Florida characteristically are quite acidic (pH <5) and contain small quantities of exchangeable base cations.

Table 4.2-2. Summary of Available Buffering Capacity of Florida Soils

| Order | Average Buffering Capacity (keq/ha) | Suborder | Average Buffering Capacity (keq/ha) | Great Group | Average Buffering Capacity (keq/ha) |
|---|---|---|---|---|---|
| Entisol | 203 | Psamment | 63 | Quartzipsamment | 52 |
| | | | | Udipsamment | 240 |
| | | Aquent | 686 | Psammaquent | 307 |
| | | | | Hydraquent | 2,930 |
| | | | | Haplaquent | 2,790 |
| | | | | Sulfaquent | 2,510 |
| Ultisol | 54 | Udult | 54 | Paleudult | 55 |
| | | | | Hapludult | 34 |
| | | Aquult | 54 | Ochraquult | 60 |
| | | | | Paleaquult | 52 |
| Spodosol | 68 | Aquod | 78 | Halaquod | 78 |
| | | Humod | 25 | Haplohumod | 25 |
| Alfisol | 206 | Aqualf | 228 | Albaqualf | 222 |
| | | | | Glossaqualf | 323 |
| | | | | Ochraqualf | 193 |
| | | | | Umbraqualf | 218 |
| | | Udalf | 107 | Hapludalf | 130 |
| | | | | Paleudalf | 65 |
| Histosol | 765 | Saprist | 765 | Medisaprist | 540 |
| | | | | Medifibrist | 439 |
| | | | | Medihemist | 167 |
| | | | | Sulfhemist | 2,780 |
| Mollisol | 565 | Aquoll | 565 | Argiaquoll | 393 |
| | | | | Haplaquoll | 757 |
| Inceptisol | 134 | Aquept | 78 | Humaquept | 78 |
| | | Ochrept | 294 | Dystrochrept | 186 |
| | | | | Eutrochrept | 510 |
| | | Umbrept | 151 | Haplumbrept | 151 |

Sources: ESE, 1983a.
Calhoun _et al._, 1974.
Carlisle _et al._, 1978, 1981.

### 4.2.1.3 Chemical Response to Acid Inputs

#### pH

The acidification of soils is a natural consequence of soil development and reflects continual acidification and leaching due to the formation of organic and carbonic acids, cation uptake by vegetation, and other processes such as nitrification (cf. Brady, 1974; Bache, 1980; Overrein *et al*., 1980; Van Breemen *et al*., 1983; and McFee *et al*., 1984). In ecosystems where rainfall exceeds losses of water due to runoff and evapotranspiration, leaching can result in base cation depletion and further acidification of the soil profile (Van Breemen *et al*., 1983 and 1984; McFee *et al*., 1984). Soil hydrologic processes strongly control soil acidification. Flow paths and rates coupled with the kinetics of weathering reactions control the extent to which acidic deposition interacts and is changed by the soil.

Soil acidification will occur within a particular soil only if the input rate of acid exceeds the buffering capacity of the soil and the cation contributions from weathering are exceeded by cation losses due to leaching (Johnson *et al*., 1982). For most soils, the buffering capacity greatly exceeds acidic deposition rates (Richter and Johnson, 1983; Johnson, 1985). Even soils relatively depleted in base cations may contain large reservoirs of exchangeable base cations compared to acid inputs. For example, Roof (1985) has calculated a total base cation reservoir equivalent to 129 keq/ha (to a depth of 75 cm) for the typic quartzipsamment soil found within the Lake McCloud (Florida) watershed; this is over two orders of magnitude in excess of the annual proton wet deposition rate of approximately 0.3 keq/ha. This particular soil is very poorly buffered with a CEC of only 1.22 meq/100 g of soil and base saturation less than 6 percent. In soils with even lower reservoirs of exchangeable base cations, acidic deposition rates constitute a correspondingly greater fraction and greater concern may be expressed regarding further soil acidification attributable to acidic deposition.

However, as base saturation decreases, the ability of protons to displace adsorbed base cations decreases (Wiklander, 1974).

Evidence supporting recent soil acidification by current levels of acidic deposition is not strong (McFee et al., 1984). Nilsson (1983) reviewed studies detailing increases in soil acidification in Swedish forest soils and concluded that evidence implicating acidic deposition as the principal cause does not exist; ion uptake by vegetation and tree species replacement appear to be the most important causes instead. Johnson and Richter (Johnson, 1985; Richter and Johnson, 1983) have concluded that current levels of acidic deposition are unlikely to induce measurably rapid increases in soil acidification. Their conclusion is based in part on the magnitude of the base cation reservoir available for ion exchange relative to acid inputs. Johnson and Richter point out that leaching of base cations is just one of several processes contributing to soil acidification (e.g., net uptake of cations by vegetation and humus formation). Johnson and Richter also argue that rates of weathering and base cation replenishment may increase with increasing rates of acid inputs. As discussed later, enhanced rates of weathering with increasing input acidity have been observed at experimental sites in Norway (Stuanes, 1980) and at Lake McCloud, which were exposed to artificially high rates of acidic deposition. Finally, annual acid inputs are substantially less than reservoirs of total acidity typically observed in soils. For example, total exchangeable acidity at the heavily polluted Solling site in West Germany approximates 400 keq/ha in the surficial 50 cm of the soil profile; this is contrasted with an annual proton loading rate of 1.6 keq/ha (Richter and Johnson, 1983).

The relative importance of acidic deposition compared with internal or natural sources of acidity generation as factors in soil acidification has been the subject of considerable interest (e.g., Rosenquist et al., 1980; Seip, 1980). Van Breemen et al. (1984) used proton budgets developed from several ecosystem studies to evaluate the relative contribution of acidic deposition to soil acidification. The budgets were quantified with respect to a variety of proton sources and sinks. Proton sources in the budgets included:

1. Atmospheric inputs of free protons and $SO_2$,
2. Proton loading associated with nitrogen transformations (e.g., nitrification of $NH_4^+$ to $NO_3^-$),
3. Deprotonation of $CO_2$ or organic acids,
4. Anionic mineralization and net assimilation of non-nitrogenous cations by biomass, and
5. Weathering of anionic species.

Proton sinks or mechanisms contributing to acid neutralization considered in the budgets included:

1. Cationic weathering,
2. Biological assimilation of non-nitrogenous anions,
3. Proton consumption associated with nitrogen transformations, and
4. Hydrologic export of free protons.

As a measure of the capability of an ecosystem to withstand ambient rates of acidic deposition, Van Breemen _et al_. (1984) defined the external-internal proton ratio (EIPR) as the ratio of atmospheric inputs of mineral and potentially mineral acids such as $SO_2$ to the internal proton loading. Systems with low rates of soil acidification such as Birkenes, Norway (which is characterized largely by podzolic or spodosolic soils) are according to Van Breemen _et al_. (1984) "extremely proton sensitive." In these systems, external inputs of acids are comparable to internal rates of acidity generation and soil acidification in part proceeds through the dissolution of aluminum and the retention of sulfate. This situation results in export of both protons and dissolved aluminum through the soil profile. Systems characterized by low EIPR values ($<0.3$) are capable of assimilating acidic inputs; soil acidification in turn proceeds through the displacement or dissolution of base cations.

The only field research within Florida to evaluate the effects of acidic deposition on soil acidification was a series of three studies conducted within the Lake McCloud watershed (Volk and Byers, 1983; Byers, 1984; ESE, 1985; and Roof, 1985). In these experiments, a series of transects were irrigated with acidified lakewater to simulate the effects of acidic deposition on soil acidification and nutrient flux. The relatively higher ionic concentration in the McCloud lakewater (compared to ambient precipitation) also served to simulate ionic inputs from rain percolating through the forest canopy (i.e., throughfall) (Byers, 1984). Treatment pH levels and total irrigation amounts for each study are summarized in Table 4.2-3.

Byers (1984) reported soil pH values at 15- and 75-cm depths at the conclusion of the 1982 irrigations. After 100 cm of irrigation, soil pH at 15 cm in plots receiving the pH 3.0 and 3.7 treatments was 4.63 and 4.83, respectively, compared to pH 5.00 for the control transect. At the 75-cm depth, differences in soil pH between the control and experimental transects were substantially lower; soil pH for the plots receiving pH 3.0 and 3.7 treatments was 4.53 and 4.63, respectively, compared to pH 4.73 for the plots receiving pH 4.6 treatments.

As part of the irrigation studies conducted during 1984, soil samples were collected at several different depths to evaluate changes in soil pH after cumulative additions of 100 and 200 cm of simulated acidic precipitation (Table 4.2-4). Prior to any irrigations in 1984, measurements of soil pH at each depth interval indicated statistically no difference in soil pH, indicating that soil pH in the experimental transects had recovered essentially to control levels. After application of 100 cm of simulated acidic deposition, soil pH in the surficial 2.5 cm of the soil profile was significantly reduced in the experimental transects. At lower depths in the profile, significant reductions in soil pH were observed only for the pH 3.0 treatment.

Table 4.2-3. Summary of Lake McCloud Simulated Acidic Deposition Field Irrigation Studies

| Irrigation Period | Treatment pH | Total Irrigation Amount per Irrigation Period (cm) | Appliation Amount Per Event (cm) |
|---|---|---|---|
| 3/81 to 8/81 | 3.7, 4.6 | 50 | 2.5 |
| 3/82 to 8/82 | 3.0, 3.7, 4.6 | 100 | 5.6 |
| 2/84 to 8/84 | 3.0, 3.6, 4.6 | 200 | 10.0 |

Source: ESE, 1986.

Table 4.2-4. Soil pH Values for a Typic Quartzipsamment Soil (Lake McCloud, Florida) After Cumulative Applications of Simulated Acidic Precipitation

| Depth (cm) | Treatment pH | Cumulative Application (cm)* | | |
|---|---|---|---|---|
| | | 0 | 100 | 200 |
| 0 to 2.5 | 4.6 | 4.67$^{a}$ | 4.99$^{b}$ x | 4.93$^{b}$ x |
| | 3.6 | 4.59 | 4.69 y | 4.61 y |
| | 3.0 | 4.51$^{a}$ | 4.16$^{c}$ z | 4.29$^{b}$ z |
| 7.5 to 15 | 4.6 | 5.14 | 5.11 x | 5.11 x |
| | 3.6 | 5.07 | 4.94 x | 4.86 x |
| | 3.0 | 5.02$^{a}$ | 4.61$^{b}$ y | 4.44$^{b}$ y |
| 15 to 75 | 4.6 | 5.18 | 5.20 | 5.10 x |
| | 3.6 | 5.17 | 5.05 | 4.81 xy |
| | 3.0 | 5.10$^{a}$ | 5.04$^{a}$ | 4.46$^{b}$ y |

* Means followed by the same letter are not significantly different ($p = 0.05$) by the Duncan/Waller multiple range test. Letters a, b, and c refer to comparisons of differences between sampling periods for a particular treatment and depth interval; letters x, y, and z refer to comparisons of differences between pH treatments for a particular depth and time period.

Sources: Roof, 1985.
ESE, 1986.

These results suggest that progressive acidification of soils similar to the acidic, poorly buffered typic quartzipsamment of the Lake McCloud watershed is not likely to occur, at least within a relatively short timeframe (decades). Total proton deposition for the pH 3.7 transect over the approximately 4 years of research at Lake McCloud exceeded deposition on the control (pH 4.6) transect by 6.1 keq/ha. This excess deposition equates to approximately 7 to 14 years of total acid deposition [wet deposition ($H^+$ plus $NH_4^+$) = 0.42 kiloequivalents per year (keq/yr); dry deposition assumed to equal wet deposition]. Furthermore, base inputs equivalent to 7 to 14 years of dry deposition were not included in the experiments at Lake McCloud. Finally, the reservoir of acidity in these soils is so large that further soil acidification attributable to acidic deposition is likely to be unmeasurable (refer to Subsections 4.5 and 5.3.2).

### Base Cation Effects

The exchangeable base cation reservoir of a soil represents the integrated effect of a series of processes including cation leaching through the soil profile, weathering, cation uptake by vegetation, mineralization, throughfall, and atmospheric inputs. In principle, acidic inputs will accelerate base cation depletion rates; accordingly a fundamental issue related to acidic deposition is the magnitude and location within the soil profile that associated base cation losses and acid accumulation occur (Ulrich, 1983).

Some perspective on the likelihood of cation depletion induced by acidic deposition is offered by some calculations developed by McFee et al. (1984). In their analysis, McFee et al. (1984) evaluated base cation losses for three different types of soil, of which two are representative of the highlands of the Florida panhandle (southeastern ultisol) and the central Florida Ridge (entisol). Buffering capacity considered only CEC and was restricted to the surficial 15 cm of the soil profile (Table 4.2-5); other factors such as atmospheric inputs of base cations, anion adsorption capacity, and hydrologic characterics were not included

Table 4.2-5. Estimates of Time Required to Effect a 50-Percent Change in Base Saturation in the Top 15 cm of Soil*

| Soil | CEC (meq/100 g) | Assumption† 1 | Assumption† 2 | Assumption† 3 |
|---|---|---|---|---|
| | | Number of Years | | |
| Midwestern Alfisol | 15 | 75 | 110 | 220 |
| Southeastern Ultisol | 9 | 45 | 67 | 125 |
| Quartzipsamment with low organic matter | 3 | 15 | 22 | 45 to 90 |

* Time required for significant acidification of uncultivated soils that are slightly acid or nearly neutral under high rates of acidic deposition--100 cm of pH 4.0 precipitation plus 16 kg/ha/yr of sulfur in dry deposition (total acid input of 2 keq/ha/yr of $H^+$.

† Assumption 1: All incoming $H^+$ exchanges for (replaces) basic cations on the soil exchange complex. There are no accompanying basic cations and no weathering or other input of basic cations. This is the worst-case situation and cannot exist in nature.

Assumption 2: The incoming $H^+$ is accompanied by 0.3 to 0.5 keq/ha/yr of basic cations $Ca^{+2}$, $Mg^{+2}$, and $K^+$ (Cole and Rapp, 1981); the replacing efficiency of $H^+$ for basic cations drops below 1.0 as the base saturation of the soil drops (Wiklander, 1975). No additional formation of CEC from weathering is assumed.

Assumption 3: Same as under 2 except that acidification is further slowed by release of basic cations from weathering 1 keq/ha-yr [for example, 20 kg/ha of $Ca^{+2}$ or 15 kg/ha-yr of $Ca^{+2}$ plus 3 kg/ha/yr of $Mg^{+2}$ within range calculated for Hubbard Brook (Likens _et al_., 1977)] and the cycling of basic cations back to soil surface by plants. No additional formation of CEC from weathering is assumed.

Source: McFee _et al_., 1984.

from the analysis. Total deposition of acid was assumed to be 2 kiloequivalents per hectare per year (keq/ha-yr) compared to annual wet-only deposition rates of 0.3 to 0.4 keq/ha in the panhandle and north-central Florida.

Assuming that all proton inputs exchange efficiently (i.e., 1:1) for base cations adsorbed on cation exchange sites, base saturation will be depleted by 50 percent in 15 and 45 years for the entisol and ultisol soils, respectively. As McFee _et al_. (1984) observed, this particular scenario is extremely unlikely. For example, annual wet-deposition rates for base cations (excluding $Na^+$) approximated 0.15 to 0.17 keq/ha in north and north-central Florida between September 13, 1983, and September 11, 1984 (ESE, 1985) and Brezonik _et al_. (1983) report base cation deposition rates (excluding $Na^+$) equivalent to 0.56 keq/ha-yr in bulk deposition. Furthermore, consideration of leaching of only those cations adsorbed to the soil matrix neglects a larger reservoir that can become exchangeable through weathering, apparently even in highly leached soils (Richter and Johnson, 1983). This hypothesis is supported by measurements of changes in base content within the surficial 75 cm of soil in the Lake McCloud watershed which show essentially no net losses of $Ca^{+2}$, $Mg^{+2}$, and $K^+$ (combined) after irrigation of experimental transects with 100 cm of lakewater acidified to pH 3.0 and 3.7 (Byers, 1984). Ion budgets constructed from Byers' data suggest that weathering contributed approximately 4.5 and 4.8 keq/ha of $Ca^{+2}$, $Mg^{+2}$, and $K^+$ at pH 3.0 and 3.7, respectively.

### Trace Elements

In acidic soils, exchangeable base cations are not easily displaced by acid inputs, and toxic trace elements such as aluminum and manganese may be mobilized as a result of acidic deposition. Ulrich (1980, 1983) hypothesized that aluminum dissolution will supplant proton exchange for base cations as a buffering mechanism for acidic deposition in strongly acid soils (pH <4.2). Below pH 5.0, the solubility of manganese oxides may reach toxic levels (Ulrich, 1983). Foy (1981, cited in McFee et al., 1984) indicated that aluminum toxicity is a primary factor limiting crop root development in many acidic soils characteristic of the southeastern United States.

Analysis of the effects of acidic deposition on trace element mobilization in Florida has been confined primarily to the Lake McCloud studies and studies (ESE, 1984) designed to evaluate the role of sulfate adsorption in controlling base cation and aluminum mobilization in poorly buffered soils. The field studies conducted at Lake McCloud indicate that aluminum mobilization does not become important until input pH levels drop below pH 3.6. In both the 1982 and 1984 studies, aluminum was solubilized in the surficial 15 cm of the soil by pH 3.0 treatments. At this pH level, aluminum mobilization was the principal acid neutralization mechanism; at higher pH treatments (pH 3.6 and 4.6), aluminum mobilization was minor and base cation leaching was the predominant contributor to neutralization. Surficial soil solution aluminum concentrations ranged as high as 7.2 mg/L for the most acidic treatment. The 1982 experiment (100 cm total irrigation) showed that solubilized aluminum from the upper soil profile became rapidly immobilized deeper (15 to 75 cm) within the profile (Byers, 1984). Further additions of acid (pH 3.0) during experiments in 1984, however, resulted in elevated aluminum concentrations at the 75-cm depth. Consequently, a potential effect of prolonged exposure of this particular soil to highly acidic deposition (pH <3.6) is the mobilization and transport of aluminum through the watershed.

### Sulfate

The principle of electroneutrality requires that the transport or leaching of cations can proceed only if the cations in solution are accompanied by an equivalent quantity of anions (Johnson et al., 1979a;

Johnson and Cole, 1980). Because $SO_4^{-2}$ is the predominant anion in precipitation in Florida, processes contributing to the immobilization of sulfate may strongly retard cation leaching and help mitigate potential effects of soil acidification. $SO_4^{-2}$ adsorption generally is believed to proceed through ligand exchange for aquo and hydroxyl groups, resulting in neutralization of soil solution acidity (Rajan, 1978). As a result, soils containing large quantities of iron and aluminum sesquioxides typically adsorb $SO_4^{-2}$ (e.g., Johnson et al., 1979b; Singh, 1980; Wiklander, 1980).

Anion adsorption increases as solution pH decreases and approaches the pKa (acid dissociation constant) of the acid (Hingston et al., 1967 and 1972). For $H_2SO_4$, the second pKa is 1.92; therefore, as solution pH becomes increasingly acidic and approaches pH 1.92, the magnitude of $SO_4^{-2}$ adsorption should increase as well (assuming all other factors remain constant). In addition, soil surfaces are amphoteric, containing both negative and positive charges, the magnitude of which is pH- dependent. As solution pH decreases, protonation reduces the negative charge of the soil surface; electrostatic repulsion of anions in turn is reduced, thereby facilitating anion adsorption. In a study of a gravelly outwash soil from western Washington, Johnson and Cole (1977) observed that anion ($SO_4^{-2}$, $NO_3^-$, $PO_4^{-3}$, and $Cl^-$) adsorption was strongly pH-dependent with greater adsorption at lower pH values. Johnson and Cole hypothesized that the apparent functional dependency on pH was apparently due to protonation of hydroxyl surfaces and a reduction in concentration of competing hydroxyl ions.

$SO_4^{-2}$ adsorption dynamics, and the influence of $SO_4^{-2}$ adsorption on cation mobilization and solution pH change, have been studied for three poorly buffered soils (typic quartzipsamment, plinthic paleudult, and ultic haplaquod) from northern Florida (ESE, 1984). Calculated adsorption maxima derived from adsorption isotherms were quite low [<1.5 microequivalents per gram (μeq/g) of soil] and inversely related to pH.

Assuming a bulk density of 1.5 grams per cubic centimeter ($g/cm^3$) infers $SO_4^{-2}$ adsorption capacities for the surficial 15 cm of the soil profile ranging from 0.15 keq/ha (typic quartzipsamment, pH 5.0) to 3.1 keq/ha (ultic haplaquod, pH 3.0).

$SO_4^{-2}$ budgets, based on lysimeter measurements in conjunction with infiltration and vertical flow data collected by Byers (1984) for the Lake McCloud experimental site, do not correlate well with $SO_4^{-2}$ adsorption isotherm results. $SO_4^{-2}$ adsorption isotherms indicate adsorptive capacities (within the surficial 15 cm) ranging from 0.15 keq/ha (pH 5.0) to 2.8 keq/ha (pH 3.0) for the typic quartzipsamment soil characteristics of the Lake McCloud site. Budget results, however, show net $SO_4^{-2}$ uptake as high as 6.1 keq/ha within the surficial 15 cm of the soil. Most of the sulfate retention occurred in the uppermost 15 cm, with the magnitude and relative loss (i.e., the amount of $SO_4^{-2}$ retained relative to the input) increasing as the treatment pH became more acidic. $SO_4^{-2}$ retention was insignificant as pH 4.6 and did not become important as a mechanism for acid neutralization until the treatment pH was equal to or less than pH 3.6. At pH 3.0, $SO_4^{-2}$ retention was second only to aluminum mobilization as the mechanism removing protons from solution. Removal of $SO_4^{-2}$ from soil solution has been attributed to $SO_4^{-2}$ adsorption (Byers, 1984), but it seems likely, based on the experiment isotherms, that uptake is a combination of vegetative uptake and adsorption. Losses due to $SO_4^{-2}$ reduction, which occurs only under anaerobic conditiosn, are highly unlikely because of the high rates of infiltration characteristic of the Lake McCloud soils (cf. Byers, 1984).

## 4.2.2 RESPONSE OF VEGETATION (FORESTS AND CROPS) AND SOIL BIOLOGY TO ACIDIC INPUTS

### 4.2.2.1 Microbiological Responses (Nutrient Recycling)

The biota of soils are of fundamental importance in maintaining the functional integrity of terrestrial ecosystems. The biota can be segregated roughly into two components: soil microorganisms which include bacteria, fungi, actinomycetes, algae, protozoans, and viruses; and soil animals which, among others, include nematodes, annelid worms, and a host of arthropods such as ants, centipedes, and mites. Soil animals may feed directly on dead plant material (e.g. annelids) or predate upon soil fungi and bacteria (e.g. mites) and are critical in the transfer of energy to aboveground communities (cf. Engelmann, 1968) and nutrient cycling. Soil microorganisms in turn perform several vital functions in terrestrial systems (Alexander, 1980):

1. Soil microrganisms are responsible for the mineralization of organic matter into inorganic forms of nitrogen, phosphorus, and sulfur requisite for plant growth.
2. Through humification of soil organic matter and the formation of soil aggregates, soil microorganisms create and maintain soil structure critical for root development and proper aeration.
3. Microbial decomposition acts against accumulation of excessive amounts of organic matter that can result in anaerobiosis and subsequent toxicity arising from partial decomposition.

Abrahamsen *et al*. (1980) evaluated the effects of simulated acidic deposition on soil biota at two experimental field sites in southern Norway. Ground water acidified with sulfuric acid to varying levels (pH 2 to 6) was applied at rates of 25 or 50 millimeters per month (mm/month) over approximately a 2-year period. Collembola and Enchytraeidae abundance increased significantly with increasing acidity, although the dominant enchytraeid species was almost eliminated from the most acidified plots (pH 2.5). With the exception of predatory species, Acarina (mites) were largely unaffected by acidification; predatory mites tended to exhibit reduced abundances at the highest acidity level. Liming to increase soil pH appeared generally to reduce abundance of collembols, mites, and enchytraeids. Abrahamsen et al. (1980) hypothesized that increased animal abundance with acidity may reflect either increases in food reserves or reduction in predation as a result of declines in predatory mite abundance.

Baath et al. (1980) conducted a six year study in a Scots pine forest in northern Sweden to examine the effects of acidification on soil biota. Dilute sulfuric acid solutions were applied to field plots at rates of 1.0 or 3.1 keq/ha-yr. Similar to results obtained by Abrahamsen et al. (1980), reductions in the enchytraeid Cognettia sphagnetorum were observed in plots receiving the most acid treatment. Collembola abundance generally increased with acidity while Acarina appeared to be relatively unaffected by the acid treatments. In a review of acidic deposition effects on soil biota, McFee et al. (1984) noted that the soils studied by Abrahamsen et al. (1980) and Baath et al. (1980) are strongly acid and concluded that acidic deposition effects on animals in such soils are not significant. However, McFee et al. (1984) observe that inherent experimental limitations such as failure to account for synergistic effects of associated pollutants (e.g. trace elements) restrict the weight of their conclusion.

### Microbiological Effects

The literature regarding the potential effects of acidic deposition on microbial activity is mixed and conflicting. Roberts et al. (1980) observed little effect of acidic solutions (pH 2.7 and 3.1) on total respiration (as determined by weight loss of detritus) or the ratio of fungal to bacterial respiration in samples removed the from the organic layer of a pine forest. Similarly, Abrahamsen et al. (1980) observed minimal effects of extended treatments of simulated acid rain (pH 2 and

3) relative to control plots (pH 5.6) on spruce needle decomposition. More recently, Kelly and Strickland (1984) evaluated the effects of simulated acidic deposition (annual average pH 3.5 to 5.7) on microbial activity in microcosms established in an oak stand in Alabama. The treatments were applied weekly over a 30-month period. Using $CO_2$ evolution as an indicator of microbial activity, Kelly and Strickland (1984) found no statistically significant effect of treatment on decomposition in the field studies. Subsequent laboratory analysis, however, indicated significant reductions in $CO_2$ evolution in the dioxide ($O_2$) horizon and because many plants derive a large portion of their nutritional demands from the $O_2$ layer, Kelly and Strickland (1984) concluded further study was required.

Bewley and Stotzky (1983) acidified various mixtures of soil and clay with sulfuric acid to evaluate the effects of acidification on soil respiration and glucose metabolism. $CO_2$ evolution was unaffected by acidification until the soil pH was depressed below 3.0; further reductions of soil pH to 2.0-0.7 arrested $CO_2$ evolution completely. Growth of the fungal species Aspergillum niger, A. flavipes, Trichoderma viride, and Penicillium brefeldianum was reduced or completely inhibited in soils acidified below pH 3.5. Although soil acidification to below pH 3 has been observed in soils exposed to ambient levels of acidic deposition, Bewley and Stotzky suggest that the "microhabitat" concept is relevant for their results. This reflects the preponderance of microbial activity in the relatively thin, surface layers of the soil and correspondingly greater exposure to acidic deposition than suggested by bulk soil pH. In circumstances where acidic deposition is severe, Bewley and Stotzky hypothesized that microbial activity may be adversely affected despite little or no effects on bulk soil pH. It should be noted that Bewley and Stotzky's conclusions are based on changes observed as a function of soil pH; although actual treatment solution pH levels were not reported, their experimental protocol infers treatment pH levels ranging as low as -0.6.

Within Florida, acidification effects research on microbial activity was initially performed by Boylan (1982). Boylan conducted a series of long term experiments on three types of Florida soils. Soil columns containing either a psammentic paleudult (Eustis fine sand), typic quartzipsamment (Candler fine sand), or hemic medisaprist (Okeechobee muck) were acidified with $H_2SO_4$ and $H_2SO_4/HNO_3$ mixtures (pH 4.0 and 3.7) with 1 inch irrigations applied weekly over a 23-month period. Microbial response relative to control cores receiving ambient rainwater (pH 4.4 to 5.2) was monitored for a variety of parameters (Table 4.2-6). Microbial abundance (bacteria, fungi, and actinomycetes), adenosine triphosphate (ATP) concentrations, and nitrogen fixation rates were not significantly influenced by the acidic treatments. Respiration in the Candler soil, which was characterized by the lowest initial or pretreatment pH (pH 4.48), was significantly enhanced by the acidic treatment; conversely, respiration was significantly reduced in the Okeechobee soil which had the highest initial pH (pH 7.65) of the three soils evaluated. In a similar manner, enzymatic response was variable, both as a function of soil and as a function of each particular enzyme (Table 4.2-6).

A series of short-term (16-week) experiments using the Candler soil, a grossarenic paleudult (Apopka), and a ultic haplaquod (Pomona) was conducted by Boylan (1982). In a departure from the long-term experimental protocol, the treatments were expanded to include pH 3.0 by acidifying Lake McCloud water with 70:30 [volume-to-volume (v/v)] $H_2SO_4:HNO_3$. This approach was consistent with concurrent soil acidification experiments in the Lake McCloud watershed coducted by Byers (1984). Results from the short-term studies demonstrated that soil respiration, ATP levels, and enzymatic activities were not adversely affected by the simulated acidic deposition, although a significant reduction in nitrogen fixation in response to treatment acidity was observed for the Apopka soil.

Table 4.2-6. Summary of Long-Term Acidification Effects on Microbial Activity in Related Florida Soils

| | Soil* | | |
|---|---|---|---|
| Parameter | Eustis (psammentic paleudult) | Candler (typic quartzipsamment) | Okeechobee (hemic medisaprist) |
| Microbial plate count | ND† | ND | ND |
| ATP | ND | ND | ND |
| $N_2$ fixation | ND | ND | ND |
| $CO_2$ evolution | ND | + | - |
| Dehydrogenase | ND | + | - |
| Urease | ND | - | ND |
| Phosphatase | - | ND | - |
| Protease | + | ND | ND |

*Undisturbed columns of Eustis and Okeechobee soil were treated with rainwater acidified to pH 4.0 with $H_2SO_4$ for 11 months followed by 12 months acidification with rainwater acidified to pH 3.7 with 70:30 (v/v) $H_2SO_4$:$HNO_3$. The Candler soil received the pH 3.7 treatment for 23 months [2.5 centimeters per week (cm/week)]. Control columns received equivalent volumetric loadings of unacidified rainwater.

†ND = no significant difference, + = significant increase and - = significant reduction ($p < 0.05$) relative to control columns

Source: Boylan, 1982.

*In situ* studies evaluating the effects of simulated acidic deposition on microbial activity were conducted March through July, 1981 (Boylan,1982) and February through August 1984 (ESE, 1985) in the Lake McCloud watershed in conjunction with soil chemistry experiments. Experimental plots were irrigated with acidified lakewater (1981-pH 3.7; 1984-pH 3.0 and 3.6) and response was compared to control plots receiving unacidified lakewater (pH 4.6). Application of 50 cm pH 3.7 lakewater during 1981 had no effect on total bacterial population abundance or $CO_2$ evolution. Similarly, ATP levels, nitrogen fixation rates, and enzymatic activity were not significantly influenced by the acid treatment in the bulk surficial (0 to 2.5 cm) soil (Boylan, 1982). However, Boylan (1982) did observe some apparent depth dependent effects. Nitrogen fixation rates and dehydrogease activity appeared to be substantially reduced (an approximately sevenfold reduction) in the uppermost 1 cm of the soil profile relative to the control plot. Conversely, protease activity appeared to be stimulated by acidic inputs in the surificial 1 cm.

In 1984, the Lake McCloud experimental plots were irrigated with a total of 200 cm of simulated acidic deposition (ESE, 1985). Soil samples were collected from the surficial 2 cm before the irrigation program was started and after cumulative application of 100 and 200 cm and were analyzed for $CO_2$ evolution, enzymatic activity, and soil pH. In addition, nitrogen mineralization rates were examined at the conclusion of the study. After the application of 200 cm of acidic treatments, there was no discernible difference in soil pH related to treatment; correspondingly, largely minimal effects on soil microbial activity were observed. No statistically significant difference was observed for soil respiration for acid treatments as low as pH 3.0. Dehydrogenase activity (which, like $CO_2$ evolution, is an indicator of net microbial activity) was stimulated by pH 3.6 but not by pH 3.0 treatments. Enzymatic response was variable, suggesting that processes such as the nutrient addition effects of nitrogen and sulfur in the simulated acidic deposition may be confounding the results. Phosphatase activity was adversely affected by the most acidic treatment (pH 3.0), whereas arylsulfatase activity was unaffected by treatment pH. Urease activity in turn was stimulated by the pH 3.7 treatment. Mineralization of organic nitrogen (using N as a tracer) after 200 cm of simulated acidic deposition was also unaffected by treatment pH; these results differ somewhat from Boylan (1982) who observed a reduction in mineralization after 100 cm of pH 3.7 treatment but no reduction at pH 3.0 during irrigation studies conducted at the same site in 1982.

### 4.2.2.2 Vegetation (Forest) Effects

#### Definitions

Effects of acidic deposition on vegetation that have been reported in the technical literature are reviewed in this section in order to evaluate the potential effects of current levels of acidic deposition on vegetation in Florida. Three categories of effects are considered: direct effects, indirect effects, and synergistic effects.

Direct effects are those which result directly from the deposition of acidic substances on plant surfaces. They include visible macroscopic and microscopic injury to plant tissue as well as a variety of yield and growth responses. They may also include changes in the allocation of carbon to different organs of the plant which can in turn affect yield or resistance to stress.

Indirect effects are the effects of acidic deposition on agents which influence vegetation. These include, for example, effects on the ability of pathogens or mycorrhizal fungi to infect plant hosts or impacts on nitrogen-fixing organisms which change the availability of soil nitrogen to higher plants.

Synergistic effects are interactive effects of acidic deposition with stress factors such as drought, insect defoliation, frost, or other air pollutants causing injuries that are more severe than the additive effect from each stress factor alone.

Adverse impacts of acidic deposition on forests in the eastern United States and West Germany have been inferred by some scientists from reports of widespread declines in tree productivity in the past 20 to 30 years. Three types of forest decline are recognized, according to Cowling (1984). Type 1 is a "widespread, rapidly developing, and synchronous decrease in diameter growth" with few, if any, other visible symptoms.

Type 2 and Type 3 declines are widespread decreases in diameter growth followed by synchronous occurrence of other visible symptoms often leading to death of trees. Type 2 decline is rapidly developing and synchronous over 1 to 5 years. Type 3 decline develops progressively over 3 to 15 years. Symptoms of the Type 2 and Type 3 declines include reduction in diameter growth, loss of vigor, dieback (i.e., death of portions of the canopy), death of branches, and eventual death of the tree. Declines usually have multiple causes.

No pathogens have been identified as being associated with most of the Type 1 and Type 2 declines being reported, and airborne pollutants are suspected as a primary cause. Type 2 declines are more severe than Type 1 declines and are more likely to be reported because symptoms are highly visible. Type 3 declines can be attributed to biotic pathogens such as fungi, insects, bacteria, nematodes, and viruses as well as physical stresses such as drought. Specific examples of forest declines are given in Table 4.2-7.

### Reports of Forest Declines

Type 2 Declines--Type 2 declines in central Europe, particularly West Germany, have been reported for Norway spruce (*Picea abies*) and white fir (*Abies alba*). Symptoms observed in addition to dieback include changes in growth patterns of shoots, reduced number of fine roots, abnormal branching, and occasional shedding of green needles and shoots, according to Schutt and Cowling (1985).

White fir first showed visible symptoms in the 1970s. Symptoms worsened following an unusually severe regional drought in 1976. Decline in Norway spruce was evident in the early 1980s, increasing in 1982 and 1983 (Smith, 1985). Although white fir declines have occurred periodically on the north side of the alps for 250 years, the Norway spruce decline was new (Schutt and Cowling, 1985).

Table 4.2-7. Definitions of Types of Forest Declines

| Type of Decline | Definition | Example | Cause |
|---|---|---|---|
| Type 1 | Widespread, rapidly developing synchronous decrease in diameter growth with few, if any, other visible symptoms | Decrease in diameter growth of pines in New Jersey pinelands | Unknown |
| | | Decrease in diameter growth of fir and spruce in Virginia and West Virginia | Unknown |
| Type 2 | Widespread, rapidly developing synchronous decrease in diameter growth, followed by other visible symptoms over 1 to 5 years leading to high tree mortality | Dieback and mortality in white fir and Norway spruce in West Germany | Unknown |
| | | Dieback and mortality of red spruce in Adirondack Mountains, United States | Unknown |
| | | Injury and death of Ponderosa pine in San Bernardino Mountains, California | Airborne pollutants |
| Type 3 | Widespread decrease in diameter growth followed by other visible symptoms leading to high tree mortality; develops progressively over 3 to 15 years | Beech-bark disease in northeastern United States | Combined action of fungus and insect |
| | | Littleleaf disease of shortleaf pine in southern United States | Pathogens plus low soil fertility |

Sources: Cowling, 1984.
ESE, 1986.

According to Schutt and Cowling (1985), Scots pine (Pinus sylvestris) and beech (Fagus sylvatica) in Europe became similarly affected at this time and the decline now affects additional tree species, shrubs, and herbs. Diameter growth reduction began in approximately 1960 in the silver fir, in 1970 in the Norway spruce, and between 1978 and 1980 in beech.

Schutt and Cowling (1985) report their personal observations that new disease symptoms have appeared on other species, including general loss of foliar biomass, loss of fine root biomass, less abundant mycorrhizae, altered morphology, and excessive seed and cone production. Schutt and Cowling (1985) state that from 1980 to 1984, similar symptoms appeared in spruce and other tree species in central Europe, northern Italy, and southern Scandinavia.

Much of the recent information about German forests has been obtained from annual surveys sent to foresters since 1982. These surveys conclude that damage to West German forests has been increasing each year since 1982. Conclusions are based on subjective estimates by the respondents of percent trees affected and percent foliage loss in their regions. The use of this survey as a research tool has been sharply criticized by Manion (1985) who points out that most of the affected Norway spruce was evaluated as having 10 to 20 percent foliage loss and that 10 to 20 percent foliage loss is well within the limits of "normal healty tree variation." Moreover, the survey procedure evalutes only crown density and does not ask for impacts of weather conditions, biotic agents, cultural practices, and stand history. Smith (1985) also states that the surveys are not scientifically acceptable evidence of the extent of forest decline.

Forest declines in the United States are less severe than forest declines in West Germany. A Type 2 decline has been reported for red spruce (Picea rubens) in high-elevation forests in New England, New York, and

North Carolina, according to Johnson and Siccama (1983) and Burgess (1984). Progressive defoliation culminates in death of affected trees.

Quantitative surveys of red spruce conducted in the northeast in the mid-1960s and early 1970s and repeated a decade later showed a reduction in density and basal area and an increase in mortality and dieback, according to McLaughlin (1985). Further studies to determine the reason for this decline have not identified insect and pathogen infestation as a cause. Tree-ring analysis also showed a sudden shift to abnormally small annual rings during the mid-1960s.

A quantitative study of spruce stands throughout the Appalachians at nine sites from Green Mountain in Vermont to Mount Mitchell in North Carolina indicated greater mortality and dieback in the Northern Appalachians than in the southern Appalachians, according to Johnson and Siccama (1983). The percentage of dead spruce (from all causes) in northern stands ranged from 20 to 55 percent whereas the percentage of dead spruce in southern stands was generally less than 10 percent. The percentage of spruce trees showing dieback symptoms in northern stands ranged from 20 to 65 percent; dieback symptoms affected only 5 to 10 percent of spruce trees in southern stands.

Type 1 Declines--Type 1 declines have been reported for several species in the United States. Reduced diameter growth is the only evidence for these declines which are usually identified by studies of growth rings. Dendroecological techniques are used in measuring tree-ring width to compare historic tree growth with growth in recent decades.

Johnson *et al*. (1981) reported an abnormal decrease in growth rates of pitch pine (*Pinus rigida*) and shortleaf pine (*Pinus echinata*) in southern New Jersey since approximately 1960, based on tree-ring analysis. The authors found no correlation with climate, age, fire, disease, or pests.

Puckett (1982) used response-function analysis of growth-ring widths to determine the relationship of tree growth to precipitation and temperature since 1900 for four species in southeastern New York. Eastern hemlock (Tsuga canadensis) showed no consistent trend, but the climate apparently became more limiting to growth of white pine (Pinus strobus), pitch pine, and chestnut oak (Quercus prinus) after 1954. The number of replicates used to analyze the relationship was not provided, but the reported minimum number of 15 trees per species indicates a small sample size for this type of study.

Vogelmann et al. (1985) reported Type 1 declines between 1965 and 1983 in balsam fir and mountain maple in Vermont, evidenced by reduction of basal area and biomass, based on vegetation sampling. Decreases in reproduction (i.e., number of stems with less than a 2-cm diameter) were reported for mountain maple, sugar maple, and beech.

Forest declines have also been reported for the southeastern United States. According to McLaughlin (1985), the high-elevation stands of red spruce and Fraser fir (Abies fraseri) in Virginia, Tennessee, and North Carolina show similar patterns of annual growth-ring reduction beginning around 1960. Abrupt changes in ring width of shortleaf pine on lower elevation sites in Tennessee were also reported to have occurred at the time.

Adams et al. (1985) reported growth rate declines, using growth-ring data, for balsam fir (Abies balsamea), Fraser fir (Abies fraserii), and red spruce in mountains of West Virginia and Virginia. The declines began in the mid-1960s during a period of unusual drought, and have continued even though the drought period ended in the 1970s.

In 1983, the Southeastern Forest Experiment Station which has conducted forest inventories in the southeast since 1933, reported a suspected growth loss in southern pines. A task force was commissioned to determine if the apparent loss is real and, if so, its extent and probable causes.

After the first year of analysis, the task force reported that net annual growth of pines in the south has decreased after a long upward trend (Sheffield et al., 1985). Although part of the decrease can be attributed to reduced timberland acreage, average annual radial growth of existing trees has declined and pine mortality has increased. Species measured in the inventory include loblolly, slash, longleaf, pond, Virginia, and shortleaf pine.

Reductions are not uniform among species, states, ownership categories, or between regions within states [i.e., coastal plain versus upland (piedmont and mountains)]. Moreover, timber inventory methodology was not designed to determine causes of productivity changes. Methodologies differ between survey periods and important tree, stand, and site parameters that would have aided in distinguishing between potential causes of decline were not measured.

Mortality of all pine species increased in the past decade (Table 4.2-8). Pine mortality is higher in the upland areas than on the coastal plain and higher on public land than on forest industry and private nonindustrial land. Slash pine has sustained the highest mortality of all the species measured; however, it is often planted offsite and north of its natural range. Large increases in mortality have occurred in Florida, Georgia, and parts of Virginia. Smaller increases have occurred in North Carolina, South Carolina, and coastal Virginia.

Most of the mortality is due to identifiable causes. Insects are thought to account for 35 to 40 percent of pine mortality. Suppression is the second leading identifiable cause of death. Mortality is highly correlated with initial stand density which suggests that increased

Table 4.2-8. Changes in Annual Mortality of Pine in the Southeast Between 1968-1977 and 1977-1985 Surveys

| Species | Region | Percent Increase In Mortality |
|---|---|---|
| Loblolly Pine | Coastal plain | 32 |
| | Upland* | 142 |
| Slash Pine | Coastal plain | 92 |
| | Upland | 450† |
| Shortleaf Pine | Coastal plain | 20 |
| | Upland | 74 |
| Other Pine Species | Coastal plain | 31 |
| | Upland | 137 |
| All Pine Species | Florida Only | 117 |
| | All states (including Florida): | |
| | Coastal plain | 46 |
| | Upland | 115 |
| All Pine Species | Publically owned land | 107 |
| | Forest industry land | 60 |
| | Private, nonindustrial land | 78 |

*Includes piedmont and mountains.
†Outside normal range of species.

Source: ESE, 1986.

competition is causing death as the stands mature. Disease (e.g. fusiform rust, littleleaf disease, and root rot) is also a major cause of mortality.

Average annual radial increment has decreased between the two most recent surveys for all major pine species growing in natural stands throughout upland areas of the southeast. For most areas, the growth slowdown occurred between the fourth and fifth surveys in the 1970s or early 1980s.

There is little evidence of general growth reductions in natural stands in the coastal plain. Loblolly pine, the most widespread species, showed no change between survey periods in Virginia and North Carolina. In Georgia and South Carolina there was some diameter growth decrease in the smallest diameter classes. Longleaf pine growth showed no decrease in the region except for the smaller diameter classes in Georgia and North Carolina. Natural stands of slash pine in north and south Florida showed no decrease in diameter growth.

Comparisons of diameter growth rates were reported for planted slash pine and loblolly pine only in areas where the sample size was sufficiently large for two or more remeasurement periods. Diameter growth of planted slash pine showed no change in Georgia, an increase in Florida, and a decrease for the smaller trees in South Carolina. According to Sheffield *et al*. (1985), the reduction in South Carolina may be due to the decrease in planting slash pine in that state. Average growth rates in small diameter classes would drop because they represent increasing proportions of suppressed trees as the stands age. Information about loblolly pine in plantations is available only for South Carolina where no change was reported. Data was not sufficient to make statistically significant comparisons between pine diameter growth for plantations in the uplands.

Analyses are in progress to compare measurements recorded in the late 1950s and early 1960s with later measurements. Differences between these and later surveys in the type of data recorded make valid comparisons difficult. Sheffield et al. (1985) conclude that loblolly pine and shortleaf pine in Georgia uplands have been declining since the earlier measurements. The decline for loblolly was greater between 1950-1960 and 1960-1970 than between 1968-1977 and 1977-1985. In South Carolina uplands, radial growth of loblolly and shortleaf pines in 1968-1978 was equal to or higher than growth in 1958-1968. Growth declined in 1978-1983.

Slash pine growth rates declined approximately 40 percent in Georgia coastal plain between 1950-1960 and 1960-1970, but has not declined since then. Similar trends exist for North Carolina and South Carolina.

Over the past 30 years, the average annual radial growth and density of pine stands in the southeast have changed. The average pine stand today is older and more densely stocked than the earlier pine stands. Analyses of upland stands in Georgia show that changes in stand density and differences in stand age do not account for the differences in growth over the last decade. Coastal plain declines of loblolly, slash, and shortleaf pines in Georgia were lower than the declines in the uplands, and most of the decline occurred in the next to the last decade.

The causes of the observed decline have not been identified. According to Sheffield et al. (1985), causes may include the following:

1. Aging of stands--Diameter growth declines as trees mature. A higher proportion of remeasured pines may be in older stands now than in previous inventories. Unfortunately, stand age was not measured in 1957-1966; in subsequent surveys, age was estimated only in broad classes, and many stands were assigned a mixed age. However, even though changes in age structure may explain some of the decline, reductions in average annual radial

increment and stand basal area growth are still apparent after these changes in stand age have been taken into account.

2. Increased stand density--Stand density of forest stands in the southeast has increased in the region's upland areas. As stand density increases, average growth of individual trees normally declines due to greater competition for moisture, nutrients, and light. However, growth rates for trees or stands within any stand density class are lower in more recent surveys than in earlier surveys. This suggests that stand density alone does not account for most of the observed growth reductions.

3. Increased hardwood competition--Improved fire protection and absence of prescribed burning in natural stands have favored the survival and growth of hardwoods and shrubs. The hardwood component of pine stands is increasing in the southeast and may contribute to observed pine growth decline by competing more successfully for moisture, light, and nutrients. Available data are not sufficient to estimate to what extent hardwood competition may account for pine growth reduction.

4. Drought and lower water tables--Moisture stresses were probably higher in the late 1970s and early 1980s than in the previous decade. Drought could explain the recent growth decline in the piedmont, but not declines indicated by data collected in the late 1950s and early 1960s. Moisture stress may have also increased in many coastal plain areas due to lower water tables caused by surface drainage and increased ground water use.

5. Loss of old field sites--Extensive areas of cropland in the southeast were abandoned between 1945 and 1965. Natural pine stands developing on these old fields may have benefitted from residual fertilizer and lack of competing vegetation. In recent

decades, relatively little farmland has been abandoned. New pine stands have been established on cutover forest land where competition is more keen and there is no initial growth advantage.

6. Diseases--Fusiform rust infection of loblolly and slash pines has increased over the past 2 to 3 decades. Littleleaf disease is also common on shortleaf and loblolly pine. However, no one disease can account for the observed growth declines.

7. Atmospheric deposition--There is no evidence to confirm or refute this hypothesis.

8. Combined Effects--Several of the potential causes listed, and possibly others, may have contributed to the decline in pine growth. For example, an increase in disease incidence could result from increased susceptibility to infection caused by drought or air pollutant stress.

The declines are not consistent within the southeastern region. They differ in period of occurrence, species affected, land ownership category, and between coastal plain and upland in the various states. Moreover, there is no correlation between increase in mortality and decrease in average annual radial growth. Florida, for example, shows an increase in pine mortality between the last two survey periods, but no decrease in radial growth. It is difficult at this time to account for the differences in growth rate and mortality between various categories of pine stands with a hypothesis that includes air pollution as a contributing cause. It is also possible that the observed decrease in radial growth is not a decline, but represents natural variation. Regional tree growth rates may be cyclic, particularly in natural stands in which pines are successional species.

Further analyses are being undertaken by the Forest Service to obtain a clearer understanding of the extent and severity of the apparent regional growth decline and to determine the reasons for changes in pine productivity.

No other forest declines have been reported in Florida. Forested wetlands in some areas (e.g., the Green Swamp in Pasco County and Corkscrew Swamp in Collier county) have been studied in detail by the University of Florida Center for Wetlands. No trend of yield reduction has been reported.

Dr. Henry Gholz of the University of Florida School of Forest Resources and Conservation reported that there is no evidence of pine yield declines in managed pine stands in Florida (Gholz, 1985). Harvests from third generation plantations in north Florida show no reduction in yield. There have not been changes in organic matter levels or nutrient budgets (Gholz, 1985). The National Park Service is supporting studies of acid deposition effects on south Florida slash pine (*Pinus elliottii* var *densa*), epiphytic lichens, and vascular epiphytes that occur in the Everglades National Park. Results of these studies are not yet available.

## Causes of Observed Declines

Forest declines are not uncommon. Declines were reported for Norway spruce and for red spruce in the 19th century, but these were attributed to pathogens. Declines of maple, birch, and oak have been observed in this century (Burgess, 1984).

Shaw *et al*. (1985) described a 75-year decline of Alaska cedar (*Chamaecyparis nootkatensis*) affecting 9,700 ha in southeastern Alaska. Diameter growth reduction, crown deterioration, and foliage discoloration culminated in death of the tree. The decline cannot be attributed to pathogens.

Canopy dieback of trees in relatively pollution-free Pacific Island forests have been recognized as a natural phenomenon whose cause has not been identified (Mueller-Dombois, 1983). Jane and Green (1983) described episodic mortality of species in high-elevation cloud forests of New Zealand which they hypothesized was due to periodic drought stress.

Declines of white pine in Tennessee and of ponderosa pine in the San Bernandino Forest in southern California were more clearly related to atmospheric oxidants (McLaughlin, 1985). The causal agent was determined by pollutant monitoring, gradient studies, and replication of field symptoms by controlled exposures. In contrast to the declines in Tennessee and California, no causal relationship has been demonstrated between airborne pollutants and the forest declines in eastern North America and Europe described previously.

Experiments which attempt to determine a causal relationship between acidic deposition and tree growth have been largely restricted to the application of simulated acid rain to seedlings. According to McLaughlin (1985), Abrahamson reviewed many studies of the effects of rain simulants on seedling growth and found no studies in which solutions near ambient acidity caused adverse effects. In many cases, the lower-pH solution stimulated growth. This effect is attributed to the nutrient effects of the added sulfur and nitrogen. Table 4.2-9 shows the results of studies, most of them recent, in which tree seedlings were exposed to rain simulants. Only Percy (1983) reported adverse growth effects at ambient acidities. In general, dry weights were not reduced by pH >2.6. However, a variety of morphological effects were observed in plants treated with pH <5.6. These included reduction of axillary meristems, fewer primary needles, and decreased hypocotyl elongation in red spruce, for example.

The potential direct effect of acid rain on slash pine in Florida was evaluated experimentally as part of the Florida Acid Deposition Study.

Table 4.2-9. Results of Recent Studies on the Effects of Acidic Treatments on Tree Seedlings

| Species | Common Name | Significant Effects and pH Threshholds | Reference |
|---|---|---|---|
| Ectomycorrhizae formation on *Pinus taeda* | Loblolly pine | Maximum at pH 2.4 and 5.6; Lower at intermediate pH | Shafer *et al.*, 1985 |
| *Pinus elliottii* var. elliottii | Slash pine | No difference in height or biomass at pH of 3.5, 4.5, or 5.5 for 90 days | Hart *et al.*, 1986 |
| *Pinus strobus* | White pine | Growth increase at pH 2.3; Increased cation leaching of soil | Wood and Bormann, 1977 |
| *Pinus strobus* | White pine | Increased growth with increased acidity (pH ranged from 5.6 to 3.0); No interaction when ozone added | Reich and Amundson, 1985 |
| *Pinus banksiana* | Jack pine | Height reduced at pH $\leq$ 4.6 | Percy, 1983 |
| *Pinus resinosa* | Norway pine | Cotyledon length and hypocotyl length decreased at pH $\leq$ 4.6 | Percy, 1983 |
| *Pinus ponderosa* | Ponderosa pine | No significant effects on length and dry weight of needles from pH 5.6, 4.0, and 3.0 | McColl and Johnson, 1983 |
| *Quercus rubra* | Red oak | No growth effect (pH ranged from 5.6 to 3.0); no interaction when ozone added. | Reich and Amundson, 1985 |
| *Platanus occidentalis*<br>*Liriodendron tulipifera*<br>*Liquidambar styraciflua*<br>*Robinia pseudo-acacia* | American sycamore<br>Tulip tree<br>Sweet gum<br>Black locust | Growth reduction at pH 2.0 | Neufeld *et al.*, 1985 |
| *Acer saccharum* | Sugar maple | Growth reduction and bacterial infection when nutrient level is high at pH $\leq$ 3.0.<br>Growth increase at pH 3.0 when nutrient level is low | Raynal *et al.*, 1982 |

Table 4.2-9. Results of Recent Studies on the Effects of Acidic Treatments on Tree Seedlings

| Species | Common Name | Significant Effects and pH Threshholds | Reference |
|---|---|---|---|
| *Acer saccharum* | Sugar maple | No growth effect (pH ranged from 5.6 to 3.0); no interaction when ozone added | Reich and Amundson, 1985 |
| *Picea glauca* | White spruce | Axillary meristem number reduced at pH $\leq$ 4.6 | Percy, 1983 |
| *Picea rubens* | Red spruce | Number primary needles reduced at pH 4.6 and below | Percy, 1983 |
| *Pseudotsuga menziesii* | Douglas fir | No significant effect on length and dry weight of needles from pH 5.6, 4.0, and 3.0 | McColl and Johnson, 1983 |

Source: ESE, 1986.

Two-year-old potted trees were exposed for 90 days to acid solutions which resembled Florida convective rain in composition, volume, frequency, rate of application, and intensity. The surface of the growth medium was covered when the solution was supplied so that only foliar effects were tested. Water and nutrients optimum for growth were provided directly to the growth medium. No significant differences in dry mass of needle, stems, or root or in total height increment were observed among the three treatment groups of pH 3.5, 4.5, and 5.5.

Trees can grow to be 200 to 300 years old, and the experiments that have been performed to determine the effect of acidic deposition on tree growth have not simulated the chronic exposure over decades to ambient acidic deposition. Nor have they simulated extreme climatic variations to which trees would be subject over decades of growth. Obviously, the kinds of experiments that could provide conclusive evidence that acidic deposition is either the primary cause or is implicated in observed tree declines are very difficult to perform and would not provide results in a short time. Effects due to chronic cumulative exposure and interaction with biotic and abiotic stresses would have to be demonstrated using controlled levels of pollutants for long time periods. Nonetheless, nearly all of the greenhouse studies of seedlings conducted to date suggest little adverse effect of acidic precipitation on seedling growth and survival.

Several researchers have observed that a severe drought in the eastern United States occurred during the early 1960s and that this drought may be involved in the growth decline of the affected species. However, the drought has ended and the decline has continued. Annual trunk-diameter growth rates have not attained pre-1960s levels, and dieback of red spruce is still observed.

No evidence clearly links acid deposition with the current forest declines in eastern North America and Europe; however, many researchers believe that such a link exists. Researchers refer to the concurrent onset of growth reduction in many different regions, the occurrence of symptoms in all age classes of several species, and the increase in this century in emissions of atmospheric pollutants that are widely transported in regional airsheds to support a hypothesis that such a link may exist. At present, there is little documentation for this hypothesis.

The declines of the forests of northern Europe show several parallels to forest declines in the United States, which indicate that acidic deposition may be a causal factor according to Johnson and Siccama (1983). These parallels include the following:

1. Onset of growth reduction began at about the same time.
2. High-elevation conifers over a wide variety of soils are most severely affected.
3. Drought is associated with the onset of the decline.
4. Foliar chemistry indicates that the foliage of declining trees in New Hampshire and in Germany has 10 percent more sulfur than the foliage of healthy trees.
5. The severity of damage increases with increased elevation.
6. Calcium concentration in the roots of declining spruce and fir indicates the possibility of a calcium deficiency.

The more severe forest decline in Germany is accompanied by concentrations of $SO_4^{-2}$, $NO_x$, and $NH_3$ in the affected areas that are approximately twice as high as in the United States. Heavy-metal deposition is also higher in Germany than in the United States (Burgess, 1984).

Symptoms of forest decline in Germany differ from and are more diverse than the symptoms reported for American forests (Cowling, 1984). In Germany, the oldest needles and branches are affected first. Needles become discolored and die, leading to increased transparency of the

Opposing Evidence--This is a very general hypothesis which does not preclude some of the more detailed explanations that have been presented. It has not been sufficiently described, researched, or analyzed in the literature to develop opposing evidence.

In order to elucidate the causes of the observed forest declines and devise appropriate policies for forest protection, more information is needed about: (1) timing and distribution of recent changes in forest growth; (2) the influence of anthropogenic deposition on soil-rhizosphere-root interactions; (3) concentration, duration, and frequency of ozone, $NO_x$, heavy metal, and acidic deposition in affected areas; (4) reproduction and recruitment in affected areas to evaluate permanence of observed declines; and (5) interactions of acid deposition, gaseous pollutants, and biotic and abiotic stress on plant growth and physiologic processes.

### Summary

Forest declines have been reported in the United States and Europe. The magnitude and extent of these declines are still undefined. Acidic deposition in combination with other stresses is suspected by some scientists to be a causal factor in these declines, but no causal link has been demonstrated. The information currently available is not adequate to accept or reject the hypotheses suggested to explain these declines.

No yield declines that can be attributed to acidic deposition have been reported by agencies or researchers monitoring Florida forests. However, it is not possible to predict the potential effect of acidic deposition on forests in Florida until the reasons for the forest declines in other regions are better understood.

#### 4.2.2.3 Crop Effects

There have been no reports of crop failures or declines similar to observations of forest and fishery declines that lead to a suspicion that acidic deposition is affecting crops. Current knowledge about the potential effects of acidic deposition on crops has been derived from experiments using acid rain simulants on test species either in the field or in a controlled environment such as a growth chamber. It is probable that these are the only ways such effects can be determined. A proposal by Brookhaven National Laboratories to try to correlate existing databases of crop production statistics, pollution statistics, and meteorological data to develop dose-response functions to estimate acidic deposition effects was not recommended for funding by the American Statistical Association Coordinating Committee Crops Review Team (ASACCCRT, 1984). The Committee stated that such an approach was unlikely to lead to a "usable and practically useful" model.

Assessments of the effect of ambient or future acidic deposition on crop production will continue to be based on the results of simulated test situations which attempt to represent real-world conditions. The reliability of such assessments depends on the validity of the tests.

Recent literature reviews of studies on the effects of simulated acid rain on crops have concluded that in general no growth reductions of crops have been shown to occur at ambient pH levels (Irving, 1983 and 1985b; Jacobson and Troiano, 1983).

Irving (1985b) reviewed 27 studies selected because they had been highly replicated, repeated, measured response as marketable yield, were conducted under natural field conditions, and were "supported by data from physiological experiments and other locations." Irving concluded that the only plant that was negatively affected by simulated rain with the highest ambient acidity levels (i.e., pH 3.8 to 4.5) was a soybean cultivar, Amsoy. In an earlier review of 48 studies of crop response to simulated acid rain that were less reliable because of the experimental design and/or because they were conducted under controlled environments most of the cultivars tested showed no effect. Four cultivars were negatively affected and six were positively affected by ambient levels of acidity in precipitation.

Studies have shown increased growth of some plants treated with pH levels of 3.0 and 2.8, bimodal responses where pH levels of 3.0 and 5.0 resulted in increased yield compared with yield of plants treated with pH levels of about 4.0, and yield effects for the same pH that were higher, lower, or no different than yields of plants exposed to higher pH levels, depending upon the cultivar, year of the test, and the experimental environment. Table 4.2-10 demonstrates how the effects of pH can vary between experiments with cultivar tested and experimental variables.

The conflicting results reported in the technical literature have created uncertainty about the potential risk of acidic deposition to crop productivity and have led researchers to focus on the improvement of experimental design and analysis in order to reduce this uncertainty (Jacobson and Troiano, 1983).

The most reliable assessments are those based on field tests using standard agronomic practices, chambers that exclude ambient rainfall, realistic rain simulators, adequate replication and randomization, proper blocking to reduce effects of environmental variability of the site, and ANOVA analysis of all measurable sources of variation. Moreover, as emphasized by Evans and Thompson (1984) and Evans *et al*., (1984a), in agricultural research the unit to be replicated is the plot, not the individual plants or even the rows within the plots. Therefore, several plots must be established for each treatment. A range of treatments, preferably four or five pH levels representing below, above, and ambient VWM values, should be used in order to develop a valid regression of crop yield to pH level.

Table 4.2-10. Results of Some Recent Tests of Acid Rain Simulants on Crops

| Test Species | Exposure | Test Environment |  | Effect | Reference |
|---|---|---|---|---|---|
|  |  | Lab | Field |  |  |
| Radish cultivar Cherry Belle | 1-hr events 10 times during 28 days | X |  | Significant yield reduction at pH 3.8 and 3.4, respectively in 2 experiments | Irving, 1985a |
| Radish cultivar Cherry Belle | pH = 2.6, 3.0, 3.4, 4.2, 4.6, and 5.6; 10 events | X |  | Root mas decreased at pH 4.6, 3.0, 2.6. Shoot mass decreased at pH 2.6 and 3.0 | Evans *et al.*, 1982a |
| Radish cultivar Cherry Belle | Spray-to-wet 3 times weekly until harvest and ambient rain. pH = 2.7, 3.1, 4.0, 5.7 |  | X | No effect | Evans *et al.*, 1982b |
| Beet cultivar Perfected Detroit | Spray-to-wet 3 times weekly until harvest and ambient rain. pH = 2.7, 3.1, 4.0, 5.7 |  | X | Yield reduced at 4.0, 3.1, 2.7 | Evans *et al.*, 1982b |
| Lettuce cultivar Ithaca | pH = 2.7, 3.1, 4.0, and 5.7; 45 events | X |  | Dry mass decreased at pH 2.7 | Evans *et al.*, 1982a |
| Wheat cultivar Waldron | pH = 2.7, 3.1, 4.0 and 5.7; 46 events | X |  | No yield effect | Evans *et al.*, 1982a |
| Wheat cultivars<br>Arthur 71<br>Abe<br>Oasis | 2 times per week for 3 weeks; 1.1 cm for 4.5 minutes. pH = 5.6, 4.3, 4.0, 3.3, 3.0, and 2.3 | X |  | pH 4.3 or 4.0 reduced growth of Abe and Arthur 71. pH 2.3 enhanced growth of all 3 cultivars | Johnston and Shriner, 1985 |
| Snap bean cultivar Provider | pH = 2.6, 3.4, 4.2, and 5.0 with and without ambient rain in 1981 and 1982 |  | X | No ambient rain--Yield increased with increased acidity in 1981; no difference in 1982.<br>Ambient rain--Yield reduced with increased acidity in both years. | Troiano *et al.*, 1984 |

Table 4.2-10. Results of Some Recent Tests of Acid Rain Simulants on Crops
(Continued, Page 2 of 3)

| Test Species | Exposure | Test Environment Lab | Test Environment Field | Effect | Reference |
|---|---|---|---|---|---|
| Soybean cultivar Amsoy | pH = 2.7, 3.3, and 4.1 twice weekly for 15 weeks; 2.08 cm total | | X | Yield reduced with increased acidity at pH 4.1 and higher | Evans et al., 1984b |
| Soybean cultivar Williams | pH = 2.7, 3.3, and 4.1 twice weekly for 15 weeks; 2.08 cm total | | X | No effect | Evans et al., 1984b |
| Soybean cultivar Davis | pH = 2.4, 3.2, 4.1, and 5.4 twice weekly until harvest | | X | No effect on yield, Rhizobium nodulation, or nematode numbers | Heagle et al., 1983 |
| Soybean cultivar Beeson | pH = 2.8, 3.4, and 4.0; 18 1-hour events over 50 days with and without ambient rain | | X | Yield increased with acidity in filtered air; decreased at pH 2.8 with ozone | Troiano et al., 1983 |
| Soybean cultivar Davis with and without mycorrhizal inoculant | pH = 2.8, 3.2, 4.0, and 5.5 twice weekly for 13 weeks | | X (pots) | No yield differences with any treatment. Mycorrhizal sporulation reduced at 2.8 | Brewer and Heagle, 1983 |
| Kidney bean cultivar Redkloud | Spray-to-wet 3 times weekly until harvest and ambient rain. pH = 2.7, 3.1, 4.0, 5.7 | | X | No effect | Evans et al., 1982b |
| Alfalfa cultivar Honeoye | Spray-to-wet 3 times weekly until harvest and ambient rain. pH = 2.7, 3.1, 4.0, 5.7 | | X | No effect | Evans et al., 1982b |
| Alfalfa cultivar Honeoye | pH = 2.7, 3.1, 4.0, and 5.7; 57 events | X | | No yield effect | Evans et al., 1982a |

Table 4.2-10. Results of Some Recent Tests of Acid Rain Simulants on Crops (Continued, Page 3 of 3)

| Test Species | Exposure | Test Environment |  | Effect | Reference |
|---|---|---|---|---|---|
|  |  | Lab | Field |  |  |
| Tomato cultivar Chico seedlings | pH = 2.5, 3.5, 4.5, and 5.5 5 times weekly for 2 weeks, then harvested. Inoculated with bacterial speck (pH = 5.5 applied to soils only. Other treatments applied as rain to soil and foliage | X |  | Dry root mas reduced at $\leq 4.5$; Height reduced at $\leq 3.5$ Bacterial injury reduced by increasing acidity if inoculated before treatment; injury increased if inoculated after treatment | Bisessar et al., 1984 |
| Tomato cultivar Floradade | pH = 3.5, 4.5, and 5.5 3 times weekly for 69 days | X |  | Fruit yield reduced at pH 4.5; no vegetative effect | Hart et al., 1986 |
| Citrus cultivar Valencia | pH = 3.5, 4.5, and 5.5 3 times weekly for 119 days | X |  | Fruit yield higher at pH 3.5; no vegetative effect | Hart et al., 1986 |

Source: ESE, 1986.

Even if these recommended conditions are employed, similar experiments will probably have different results. Real rain events vary in duration, rate of deposition, and pH throughout the growing season. To date, research has not included attempts to simulate variation in rainfall exposure. Moreover, differences exist between the soils and microclimates of experimental sites and between the climatic variables of precipitation, temperature, wind, and humidity each year. Yields, therefore, will vary depending on the year and the site of the study. Studies have shown that acidic deposition can interact with gaseous pollutants, pathogens, and insect predators to influence yield. Since pollutant concentrations and abundance of pathogenic organisms and predators can vary between years and sites, the synergistic and indirect effects due to the interaction of acid deposition with these factors can also affect crop yield differently between years and sites.

According to ASACCCRT (1984), the effect of acidic deposition on a crop's yield should be regarded as a sampling problem in which each experiment samples a population of environments to which the plants will be exposed. On the basis of a relatively small sample of these environments, a behavior (yield effect) will be inferred for the entire population.

The costs of employing the recommended methods to study acidic deposition effects on the yield of a single crop are enormous and effectively exclude the study of most of the nation's crops. Only the most economically valuable crops nationally (e.g., soybeans, wheat, and corn) are likely to receive funding for study. Vegetable, fruit, and pasture crops which are valuable on a local or regional level are unlikely to be funded for full-scale studies. For this reason, screening studies such as those conducted on citrus and tomato as part of the Florida Acid Deposition Study are important for providing some evaluation of risk and for prioritizing research efforts (Table 4.2-10). For the Florida Acid Deposition Study, containerized plants in a controlled environment were exposed to acid solutions which resembled Florida's convective rain in ion composition, total volume, frequency and rate of application, intensity, and sulfate-nitrate ratio. Cultivars tested were those most commonly grown in Florida: Floradade tomato and Valencia orange. The surface of the growth medium was covered with plastic during application of the solution. Water and nutrients optimum for growth were provided directly to the growth medium. Solutions with pH values of 3.5, 4.5, and 5.5 were applied to tomatoes over their entire growth cycle and to citrus during the flowering and fruiting stage.

Fruit yield of tomatoes treated with pH 4.5 was lower than fruit yield of tomatoes treated with pH 5.5; yield of tomatoes exposed to the pH 3.5 treatment showed no difference compared to yield of tomatoes treated with pH 5.5. Magnesium and calcium content of the foliage was lower in plants exposed to lower pH rain compared to foliage of plants exposed to pH 5.5 rain.

Fruit yield of oranges was highest for the plants receiving the pH 3.5 treatment compared with plants exposed to higher pH rain. No difference in foliar element concentrations were observed between treatments.

The citrus study indicated that fruit yield is probably not affected by ambient levels of acidic deposition. The tests on tomatoes, although conducted in the laboratory where plants usually show more sensitivity to acidic deposition than in the field, indicate that a field test of the Floridade tomato would be desirable to better evaluate crop risk.

At present, there is little evidence from controlled studies or field observation that acidic deposition has any significant economic impact on crops. Furthermore, the risk is low that present levels of acidic deposition significantly affect crop yields on a regional level for the following reasons:

1. Most crops are sown and harvested annually; therefore, long-term chronic effects are not likely to occur.

2. Cropland is periodically amended with lime and fertilizers which neutralize soil acidity or replace any leached nutrient cations.
3. The few effects on crops which have been reported are at acidities which represent the high extreme of the range of ambient acidity. This is true even for soybeans which is the crop most extensively studied. When all recommended experimental methods are used, only one soybean cultivar has been shown to be sensitive to acidities that approach ambient levels (Evans _et_ _al_., 1984a).

## 4.3 RESPONSE OF AQUATIC SYSTEMS TO ACIDIC INPUTS

Lake acidification is the integrated effect of a variety of processes, both natural and anthropogenic in origin, contributing to a net increase in lakewater acidity. Recent lake acidification observed in Scandinavia, Canada, and the northeastern United States has been ascribed or conjectured to reflect inputs of strong acids, most notably $H_2SO_4$ and $HNO_3$, present in acidic deposition (Beamish and Harvey, 1972; Schofield, 1976; Thompson *et al*., 1980; Davis *et al*., 1978; Henriksen, 1980; Baker *et al*., 1984). Observed and hypothesized effects of lake acidification have been reviewed extensively by, for example, Dickson (1980), Muniz and Leivestad (1980a), Overrein *et al*. (1980), ESE (1982c), Dillon *et al*. (1984), National Swedish Environment Protection Board (NSEPB, 1983), Baker *et al*. (1984), and Magnuson *et al*. (1984) and include:

1. Loss of alkalinity and associated reductions in pH of as much as 1.5 to 3 pH units within short timeframes (from hours to several years).
2. Changes in major cation watershed export rates and corresponding changes in concentrations of major lakewater ions.
3. Solubilization of trace elements, particularly aluminum, manganese, cadmium, and lead.
4. Direct toxicity to aquatic biota by mobilized trace elements (particularly aluminum).
5. Changes in trophic structure at all trophic levels, including reductions and/or losses of amphibian and fish populations, and changes in phytoplankton and zooplankton and benthic communities.
6. Reductions or alterations in cycling of nutrients critical for algal growth.

Subsection 4.3.1 reviews research relevant for describing or inferring the effects of acidic deposition on the chemistry of lakes within Florida; related effects on aquatic biota are discussed in Subsection 4.3.2.

## 4.3.1 EFFECTS ON AQUATIC CHEMISTRY

### 4.3.1.1 Overview of General Limnological Principles in Relation to Acidification

Acidity in lakewater is typically described in terms of hydrogen ion activity by determining the solution pH (Westcott, 1978):

$$pH = -\log_{10} aH^{+} \qquad (4.3\text{-}1)$$

where H+ is the hydrogen ion or proton activity. Water ($H_2O$) weakly dissociates to form equivalent quantities of acid and base which can be represented by:

$$H_2O + H_2O = H_3O^{+} + OH^{-} \qquad (4.3\text{-}2)$$

At 25°C, pH 7.00 corresponds to an exactly neutral solution of pure water (i.e., $H_3O^{+} = OH^{-}$). In mineral-bearing natural waters, pH levels characteristically lie within the fairly narrow range of 6 to 9 (Stumm and Morgan, 1981).

It is important to note that pH defines only proton activity and provides no information on the amount of base or acid required to shift the solution pH to a new defined level. More specifically, pH is an intensity factor, and capacity factors such as ANC (or alkalinity) and base neutralizing capacity (BNC) (or acidity) can be rigorously defined for a particular reference proton level or equivalence point (Stumm and Morgan, 1981). For natural waters, carbonic acid ($H_2CO_3$) and $H_2O$ constitute a convenient reference level and ANC can be defined (Stumm *et al.*, 1983; Schnoor and Stumm, 1985) as:

$$ANC = [HCO_3^{-}] + 2[CO_3^{-2}] + [OH^{-}] - [H^{+}] \qquad (4.3\text{-}3)$$

Although pH is of more direct ecological significance than ANC, ANC is generally regarded as a better indicator of sensitivity because it is a measure of the instantaneous ability of the water column to neutralize acidic inputs (e.g. Norton *et al.*, 1982; Schindler *et al.*, 1985). ANC is conceptually equivalent to alkalinity but is the preferred usage in this report. "Alkalinity" is often equated with $HCO_3^-$ concentration, and consequently "alkalinity" is a more ambiguous term. Although in most natural waters the carbonate system is the principal contributor to ANC, fulvic and humic acids can contribute and may predominate in highly colored systems. In addition, the hydrolysis of aluminum in dilute surface waters may contribute appreciably to ANC. Under these circumstances, ANC is explicitly expressed (Barnard, 1985) as:

$$
\begin{aligned}
[ANC] = {} & \sum_{i=1}^{N} \sum_{x=0}^{z} (z - x)\,[H_x A_i^{x-z}] \\
& + \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \{nz[(M_j)_m (A_i)_n^{my-nz}]\} \\
& + \sum_{j=1}^{M} \sum_{q=1}^{\infty} q[M_j(OH)_q] + [OH^-] - [H^+] \qquad (4.3\text{-}4)
\end{aligned}
$$

where: $[ANC]$ = acid neutralizing capacity or alkalinity (eq/L);
$A_i$ = any ligand (excluding $OH^-$) that may coordiante with metals or protons of charge $-z$;
$M_j$ = metal cation of charge $+y$;
$N$ = number of ligands in solution;
$M$ = number of metals in solutions;
$m$ = stoichiometric coefficient for metal in complex;
$n$ = stoichiometric coefficient for anion in complex;
$q$ = number of hydroxides coordinated with metal;
$x$ = number of protons coordinated with anion;
$y$ = charge of uncomplexed metal cation;
$z$ = negative charge of fully deprotonated anion;
$[OH^-]$ = hydroxide ion concentration [moles per liter (moles/L)]; and
$[H^+]$ = hydrogen ion concentration (moles/L).

Alkalinity has been used frequently to describe and/or map the sensitivity of natural waters to acidic deposition (e.g. Gmur, 1981; Omernik and Powers, 1982; Twaroski et al., 1983; NAPAP, 1983). Use of alkalinity as an indicator of sensitivity also is implicit in approaches adopted by Henriksen (1980) and Glass (1980). Glass (1980) empirically described the relationship between pH, alkalinity, and sensitivity for 230 northern Minnesota and Wisconsin lakes. Sensitivity was defined by the calcite saturation index (CSI), which incorporates alkalinity, pH, and calcium concentration data to determine the degree of saturation of lakewater with respect to calcium carbonate (Conroy et al., 1974; Kramer, 1976). Henriksen (1980) regarded lake acidification induced by acidic deposition as a "large scale titration" in which acidification proceeds as a titration of a bicarbonate solution with strong mineral acids (notably $H_2SO_4$).

An ANC concentration of 200 µeq/L is often cited as the threshold level delimiting lakes as either sensitive or insensitive to acidification (e.g. Hendrey et al., 1980). Threshold alkalinity values can be defined by first evaluating biological response as a function of pH and then empirically relating pH to ANC. Coupling this approach with a maximum observed increase in lakewater sulfate concentrations of approximately 100 µeq/L (in the northeastern United States), Baker et al. (1984) concluded that lakes whose ANC is less than 200 µeq/L are potentially sensitive to long-term acidification at current levels of acidic deposition.

However, as Baker et al. (1984) observed, there are some problems inherent in using ANC as a univariate descriptor of sensitivity. Titrimetric determinations of lakewater ANC are instantaneous measures buffering ability and neglect watershed and internal contributions of biological and physicochemical processes to ANC production and consumption. These processes, which are summarized in Table 4.3-1, include nutrient uptake during algal photosynthesis (Brewer and Goldman,

Table 4.3-1. Biogeochemical Processes That Consume or Produce Alkalinity in Lakes and Watersheds

---

1. Mineral Weathering

   A. Congruent Dissolution:

   $Al(OH)_3 + 3H^+ \text{ ----> } Al^{+3} + 3H_2O$

   $CaCO_3 + H^+ \text{ ----> } Ca^{+2} + HCO_3^{-2}$

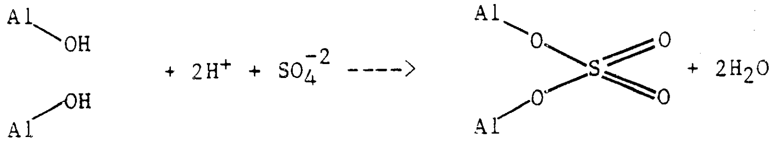
   B. Incongruent Dissolution:

   $2NaAlSi_3O_8 + 2H^+ + 9H_2O \text{ --> } 2Na^+ + Al_2Si_2O_5(OH)_4 + 4Si(OH)_4$

2. Cation Exchange

   $M^{+n} - X + nH^+ \text{ ----> } M^{+n} + X - nH^+$

3. Sulfate Adsorption



4. Sulfate Reduction

   $2H^+ + SO_4^{-2} + Fe(OH)_3 + 9/4\ CH_2O \text{ ----> } FeS_{(s)} + 19/4\ H_2O + 9/4\ CO_2$

5. Reactions of the Nitrogen Cycle

   A. Nitrate Assimilation:

   $106CO_2 + 122H_2O + HPO_4^{-2} + 16NO_3^- + 18H^+ \text{ ----> } (CH_2O)_{106}(NH_3)_{16} + 138O_2$

   B. Ammonium Assimilation:

   $106CO_2 + 106H_2O + 16NH_4^+ + HPO_4^{-2} \text{ ----> } (CH_2O)_{106}(NH_3)_{16} + 14H^+ + 106O_2$

   C. Denitrification:

   $5CH_2O + 4NO_3^- + 4H^+ \text{ ----> } 5CO_2 + 2N_2 + 7H_2O$

   D. Nitrification:

   $NH_4^+ + 2O_2 \text{ ----> } NO_3^- + H_2O + 2H^+$

---

Source: ESE, 1986.

1976), mineral dissolution and cation exchange (Hongve, 1978), and sulfate reduction (Schindler et al., 1980b; Kelly et al., 1982; Baker et al., 1984; Baker et al., 1985; Perry et al., 1986). In addition, specific adsorption (Reaction 3 in Table 4.3-1) with iron and aluminum sesquioxides can contribute to ANC (cf. Rajan, 1978). Another factor which may be quite important in shallow Florida lakes is sediment resuspension which can be induced periodically by wind events (cf. Pollman, 1983; Pollman and Brezonik, 1985). Excess concentrations of $HCO_3^-$ which develop in the interstitial fluid as a product of sulfate reduction and ammonification of organic matter are released to the water column as the sediments are entrained and resuspended. In addition, because of the high CEC of detrital organic matter and clays, resuspended particulate matter can contribute to ANC via ion exchange.

Another fundamental problem with use of ANC as univariate descriptor of sensitivity is related to the operational definition of ANC. Although ANC is a capacity term relating the total amount of acid required to lower lakewater pH to a defined reference point, it does not predict the change in pH upon addition of smaller quantities of acid (cf. Faust, 1983; Kramer, 1984). Morel et al. (1976) define a more appropriate expression, the interaction capacity, which explicitly describes the interaction between, for example, pH and the addition of a constituent, Y:

$$\delta'_{H,Y} = \frac{\partial pH}{\partial TOTY} \qquad (4.3\text{-}5)$$

where: $\delta'$ = interaction capacity, and
TOTY = total analytical concentration of Y.

For the addition of sulfuric acid, the pH change would be approximated by:

$$pH \simeq (2\delta'_{H,H} + \delta'_{H,SO_4}) \times \Delta(H_2SO_4) \qquad (4.3\text{-}6)$$

For softwater systems in which ANC is dominated by bicarbonate, Kramer (1984) has derived the following simplified expression relating sensitivity to acidification as an explicit function of ANC and pH:

$$\delta' = \frac{-1}{2.3([H^+] + \frac{([ANC] + [H^+])\,[H^+]}{([H^+] + K_1)}} \qquad (4.3\text{-}7)$$

where $K_1$ is the first acid dissociation constant of $H_2CO_3$ ($\sim 10^{-6.3}$).

However, as Kramer (1984) observed, the assumption that ANC reflects strictly the carbonate system is not always valid in natural waters, and the influence of organic acids, inorganic species, and solid phases must be considered. As a result, Kramer (1984) concludes that , or buffer intensity, is a suitable indicator of sensitivity only for a particular lake and for a particular point in time for which has been derived.

Organic acids generally constitute the dominant fraction of DOC in natural waters (Thurman, 1985; McKnight et al., 1985). Humic substances (humic and fulvic acids) typically comprise 50 percent of DOC in aquatic systems and an additional 30 percent includes hydrophilic acids (Thurman, 1985). The origin of these acids in lakes and streams is decaying organic material derived from both the watershed soils (i.e., allochthonous inputs) and internally through principally algal productivity (i.e., autochthonous inputs). Streams and rivers tend to be dominated by allocthonous sources (Wetzel, 1975). In lakes, autochthonous inputs become increasingly important as a function of lake hydrology and size. DOC concentrations in oligotrophic lakes typically approximate 1 to 3 mg/L (Thurman, 1985).

Humic substances have received considerable attention because of their role in trace element complexation (see for example Morel, 1983) and the effects of complexation on toxicity and availability for biological uptake [e.g., Allen et al., 1980; Baccini and Suter, 1979; and Baker and Schofield, 1980]. Recently attention has focused on the importance of organic acids in the acid-base balance of dilute softwater systems (e.g., Oliver et al., 1983; Eshleman and Hemond, 1985; Krug et al., 1985). Organic acids can influence the acid-base regime through dissociation of primarily carboxylic acid functional groups:

$$RCOOH + H_2O = RCOO- + H_3O^+$$

where R represents the polymeric humic molecule and COOH is the undissociated or protonated carboxylic acid functional group. The extent of dissociation is represented by the acid dissociation constant, Ka:

$$\frac{[RCOO^-][H^+]}{[RCOOH]} = K_a$$

Values of the number of carboxylic acid groups per unit mass of DOC and reported pKa's (the negative logarithm of Ka) from several studies in North America, Scandinavia, and Scotland are summarized in Table 4.3-2. It is important to note that, because of the extreme complexity of humic substances, the interpretation and application of both parameters in Table 4.3-2 is not very straightforward. Perdue et al. (1980) discuss in detail the operational problems in defining functional group content. Furthermore, both Perdue et al. (1980) and Oliver et al. (1983) observe that the pKa varies with solution pH. For example, Oliver et al. (1983) derived the following empirical model describing pKa as a function of pH:

$$pK = 0.96 + 0.90pH - 0.039(pH)^2$$

The significance of organic acids to the buffering of softwater systems is often inferred on the basis of an apparent excess of cations in the balance of major cations and major anions. Gorham et al. (1985) examined

Table 4.3-2. Carboxylic Acid Content and Acid Dissociation Constants ($K_a$) of Humic Substances

| Study | Location | Carboxylic Acid Content (meq/L) | $pK_a$ |
|---|---|---|---|
| Glover and Webb (1979) | Tovdal River, south Norway | — | 6-6.3 |
| Henriksen and Seip (1980) | South Norway and southwest Scotland | 5.5 | |
| Webb (1982) | South Norway | 2.3 | |
| Perdue *et al*. (1980) | Satilla River, Georgia | 4.4 | Varies with pH |
| Oliver *et al*. (1983) | Various lakes, streams, wetlands, and ground waters in N. America | 10 | Varies with pH |
| Gorham *et al*. (1985) | Various bogs in Canada, Minnesota, and New England | 4.8 | |
| Cronan and Aiken (1985) | Lakes Panther, Woods, and Sagamore watersheds, Adirondacks | 4-5 | 3.85 |
| McKnight *et al*. (1985) | Thoreau's Bog, Massachusetts | 4.9 | |
| Eshleman and Hemond (1985) | Bickford Watershed, Massachusetts | 7.5 | 3.5-3.7 |
| Thurman (1985) | Lakewater fulvic acids | 5.5-6.2 | |

Source: ESE, 1986.

anion deficits in series of bogs across Minnesota, Canada, and New England and found a strong correlation between the anion deficit and DOC. A similar but somewhat weaker correlation was observed between DOC and $H^+$. Through photooxidation studies Gorham et al. (1985) demonstrated that organic acids derived from the incomplete oxidation of organic matter were responsible for low pH levels observed in unpolluted bogwaters (mean pH 4.03). Similar results were obtained by McKnight et al. (1985) who used charge balance calculations and functional group analysis to show that fulvic and hydrophilic acids regulate Thoreau's bog at approximately pH 4.

Oliver et al. (1983) examined the ionic balances of three highly colored rivers in Nova Scotia and demonstrated that organic acids were significant components of the overall ion balance. However, the contribution of organic acids to the buffering of softwaters is a function of the amount of base cations derived from weathering and ion exchange reactions in the watershed soils and sediments as well as the total organic acid content (Gorham et al., 1985; Oliver et al., 1983). This is apparent in the well-known Henderson-Hasselbach equation which describes the relationship between pH and the pKa and extent of dissociation of a weak acid HA:

$$pH = pK_a + \log([A-]/[HA])$$

Data collected on the Tovdal River (southern Norway) serve as useful examples to illustrate this relationship. Glover and Webb (1979) inferred the pH of the Tovdal River due to the presence of organic acids. Based on a measured organic acid concentration of 17 to 46 ueq/L (Gran titration) and an estimated pKa of 6, Glover and Webb calculated a pH of about 5.2 to 5.3 in the absence of excess strong acids. This analysis, however, assumes the absence of ANC due to dissociation of the organic acid and ion exchange of protons with base cations in the soils of the watershed:

$$HA + S\text{-}Me = S\text{-}H + Me + A^-$$

Thus Glover and Webb's analysis represents a lower limit of pH in the Tovdal River. For example, if an additional 46 ueq/L of the organic acid anion accompanied by base cations is present, the inferred pH of the Tovdal River in the absence of strong acids is 6.0.

### 4.3.1.2 Distribution of Lakes with Respect to Buffering Characteristics

Delineation of the spatial distribution of Florida lakes as a function of sensitivity to acidic deposition should consider all the factors that define changes in ANC in response to acid loadings (see Subsection 4.3.1.1). Regional data for many of these variables are non-existent or poorly described, and sensitivity mapping efforts in Florida have focused rather on the geographical distribution of lakes and lake districts with similar buffering characteristics. ANC, pH, and CSI were used as mapping variables for a database of 179 lakes compiled by Pollman and Hendry (1983; ESE, 1983a). The majority of the lakes examined by Pollman and Hendry were acidic and contained low levels of ANC (Figure 4.3-1); 63 percent were characterized by pH levels 7.0 or less, and 11 percent of the lakes surveyed averaged less than pH 5.0. Lakewater pH correlated strongly with ANC, indicating that pH of the Florida lakes is controlled by the carbonate system. Nevertheless, it should be noted that comparison of the observed and the theoretical relationship between ANC and pH (at atmospheric pressure) shows almost uniformly lower pH values than predicted by ANC (Figure 4.3-2) and illustrates the importance of dissolved $CO_2$ dynamics (Norton and Henriksen, 1983; Herczeg and Hesslein, 1984) and organic acids on lakewater pH (Oliver et al., 1983; Thurman, 1985; Eshleman and Hemond, 1985).

Pollman and Hendry (ESE, 1983a) observed a close relationship between the distribution of lakewater and soil buffering characteristics. Although local variations are apparent, lakewater ANC and pH increased generally

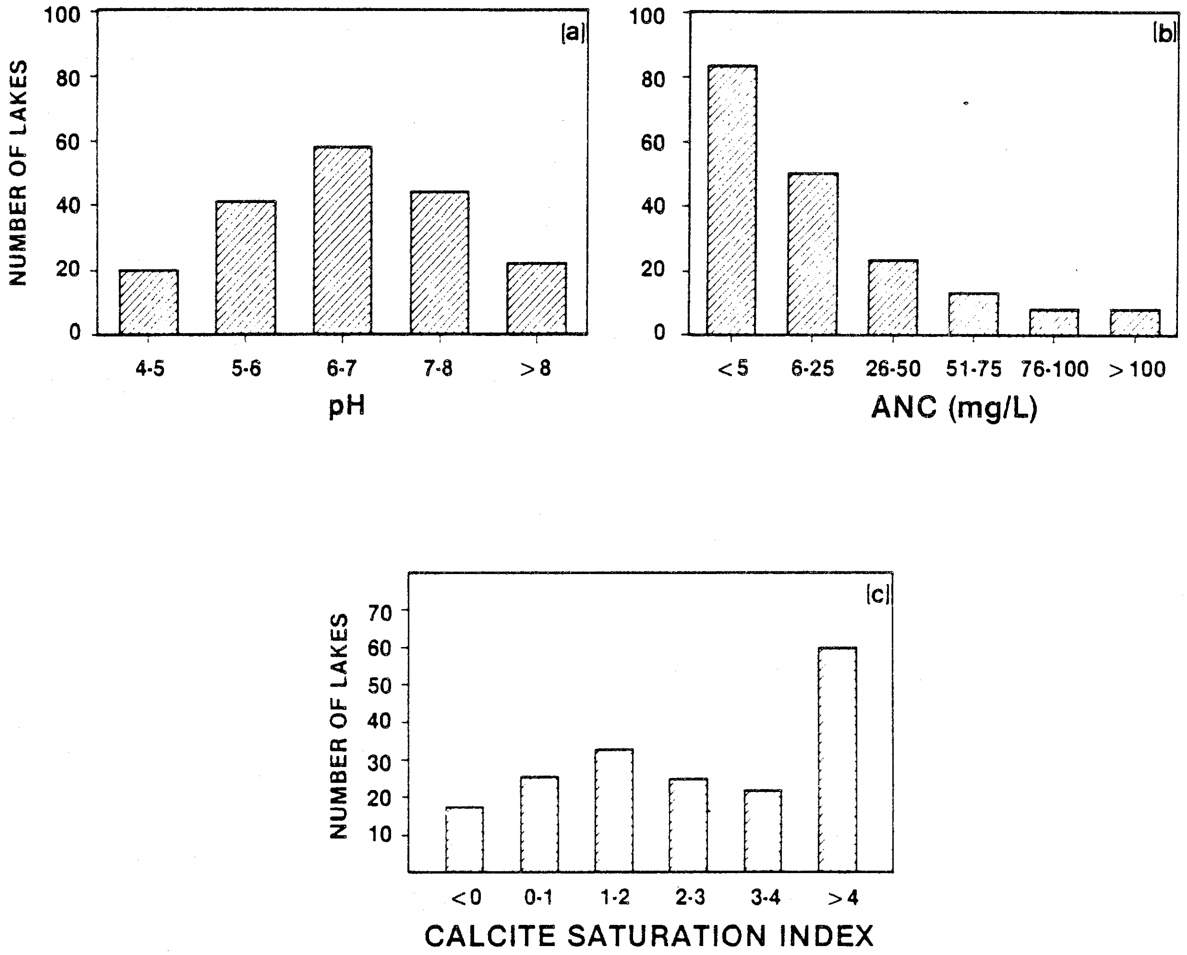


Figure 4.3-1
FREQUENCY DISTRIBUTIONS OF FLORIDA LAKES INCLUDED IN THE STUDY (N = 179) AS A FUNCTION OF (a) pH, (b) ANC, AND (c) CALCITE STATURATION INDEX

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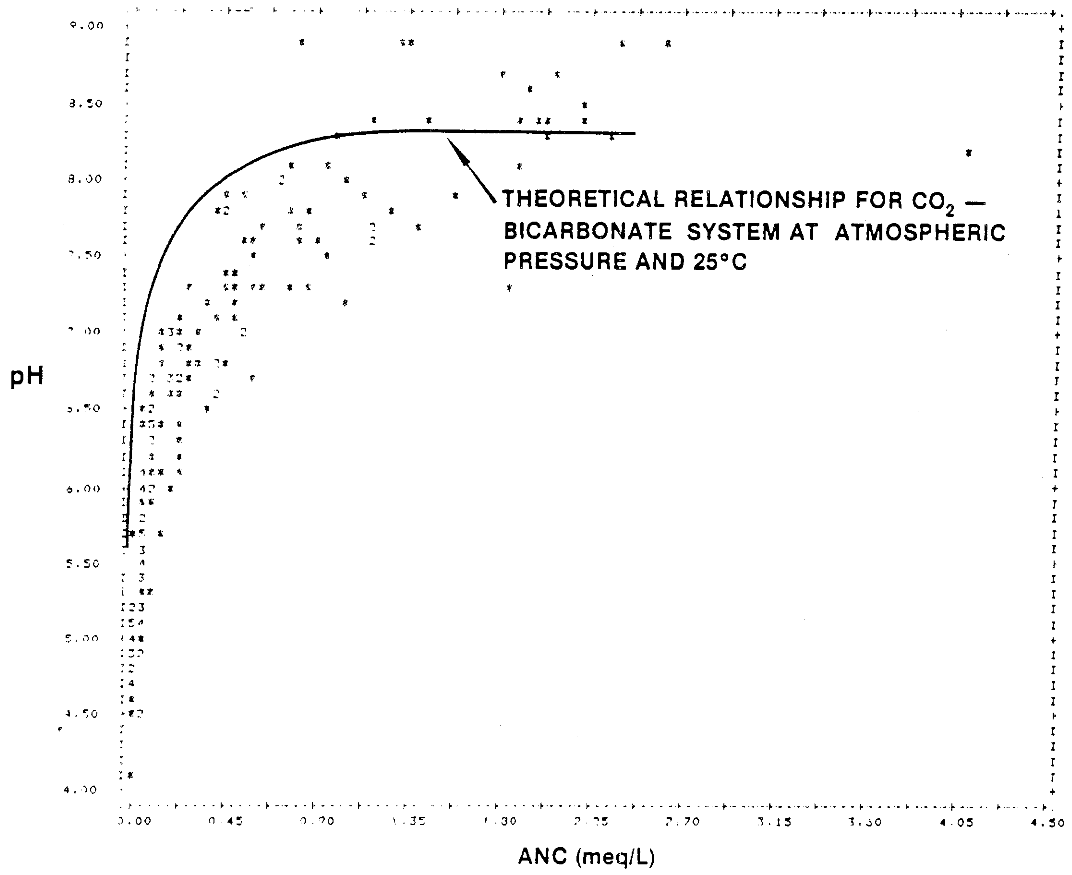

NOTE: Solid curve depicts the theoretical relationship where pH is controlled by the $CO_2$ · biocarbonate system at atmospheric $CO_2$ partial pressure and 25°C.

Figure 4.3-2
ANC OF FLORIDA LAKES INCLUDED IN THE STUDY (N = 179) AS A FUNCTION OF pH

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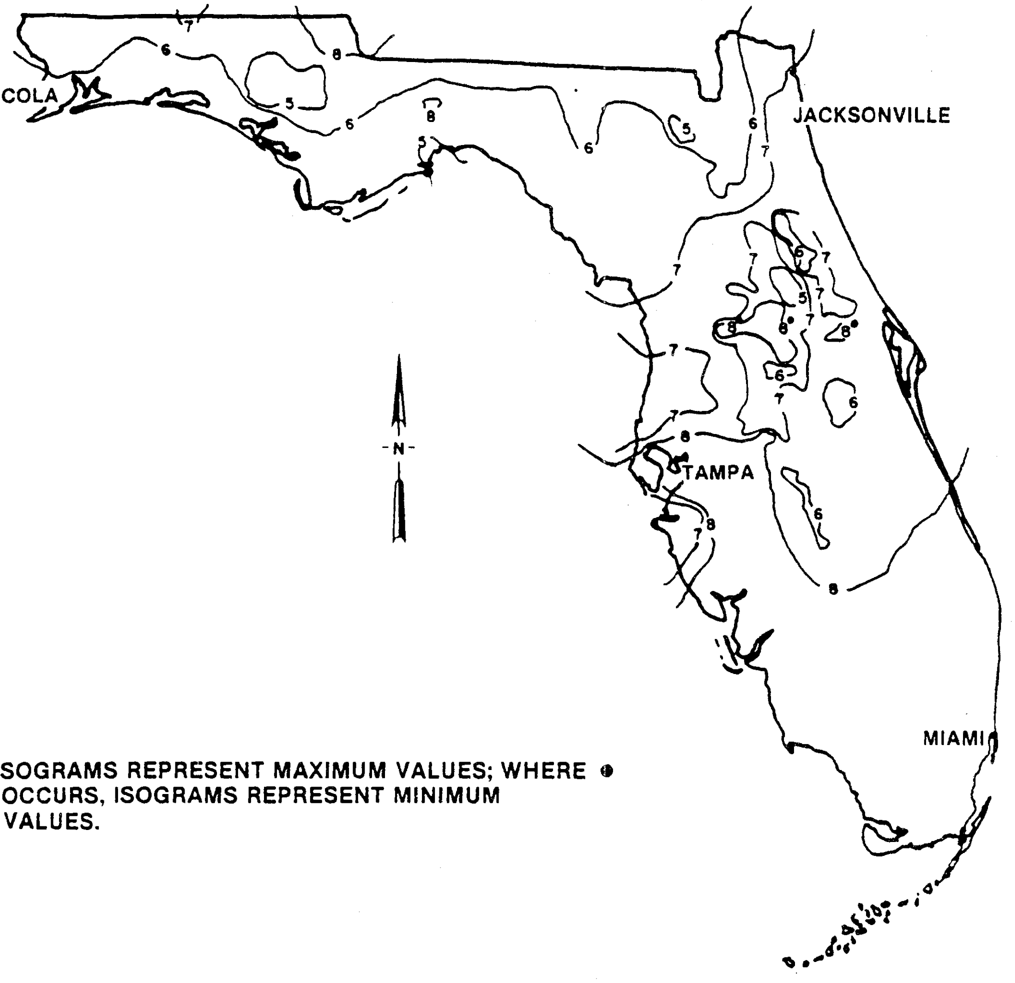
along a north-northwest to south transect of the state. These gradients corresponded to a general change in soil buffering capacity (defined by CEC) mapped by McFee (1980). Poorly buffered, acidic lakes were associated with the highlands and ridge physiographic regions of the state. Most prominent are the Western Highlands of the panhandle and the Central Ridge, which includes the Trail Ridge and the Lake Wales or Highlands Ridge lake districts in north- and south-central Florida, respectively. Exceptions to this general model were observed, apparently as a result of localized cultural activities within the watershed (e.g. seepage from septic tanks) and hydrogeological factors such as artesian supply of ANC fron the calcareous Floridan Aquifer.

A similar geographical analysis was conducted by Canfield _et al_. (1983) using a database of 165 lakes located throughout Florida. These lakes, which were also used by Pollman and Hendry (ESE, 1983a) in their analysis, were sampled by Canfield _et al_. (1983) three times between August 1979 and September 1980. Canfield _et al_. (1983) used their results, which are presented in Figures 4.3-3 and 4.3-4 for pH and ANC respectively, to emphasize the effect of surficial geology on pH and ANC. For example, the greatest diversity in lakewater pH, ANC, and calcium concentrations was observed in central Florida, directly reflecting the discontinuous geological characteristics and physiography of the region. In accordance with the very similar structure of their respective databases, spatial patterns of ANC and pH distribution defined by Canfield _et al_. (1983) corresponded well with similar maps developed by Pollman and Hendry (ESE, 1983a).

Canfield _et al_. (1983) hypothesized that lakes within Florida most likely to be sensitive to acidic deposition are softwater, clear seepage lakes characterized by no surface inlets or outlets. These lakes have small watersheds relative to their surface areas; as a result, precipitation directly to the lake surface constitutes a rather significant or perhaps dominant fraction of the hydrologic inputs, and the chemistry of these



NOTE: ISOGRAMS REPRESENT MAXIMUM VALUES; WHERE ● OCCURS, ISOGRAMS REPRESENT MINIMUM VALUES.

Figure 4.3-3
DISTRIBUTION OF LAKE pH VALUES IN FLORIDA

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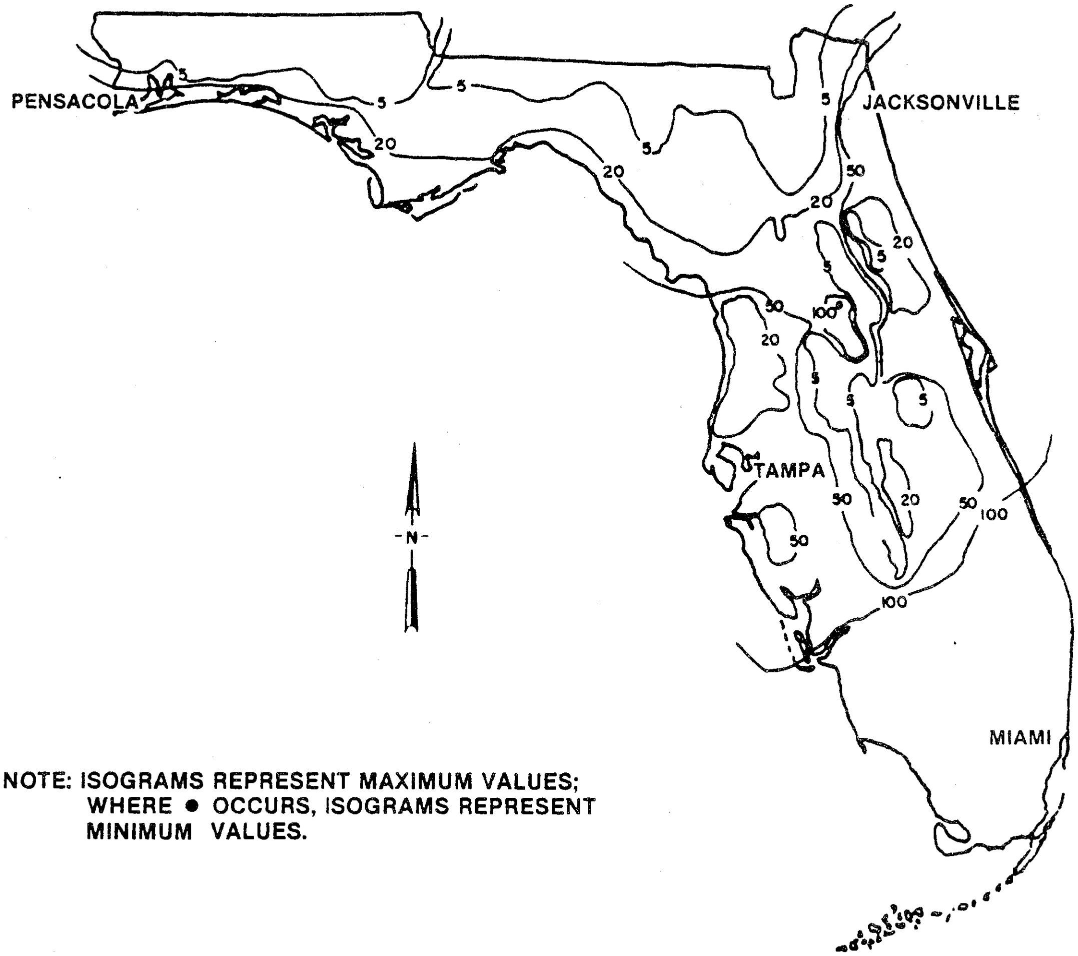

NOTE: ISOGRAMS REPRESENT MAXIMUM VALUES;
WHERE ● OCCURS, ISOGRAMS REPRESENT
MINIMUM VALUES.

Figure 4.3-4
DISTRIBUTION OF LAKE TOTAL ALKALINITY CONCENTRATIONS (mg/L as $CaCO_3$) IN FLORIDA

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lakes is more likely to reflect precipitation inputs than lakes receiving substantial surface runoff. Accordingly, lakes with higher watershed-to-surface-area ratios should have higher ANC and pH values. This hypothesis can be examined by using the relatively large Florida Lakes Data Base (FLADAB) compiled by Huber et al. (1983). This database includes morpometric and chemistry data for nearly 600 lakes in Florida. Regression analysis of ANC and pH as functions of watershed-to-surface area ratios shows essentially no relationship (Pollman, unpublished data); however, the relationship between watershed area as determined by topographic contours and the actual watershed area which contributes hydrologically to seepage lakes via both surface and ground water in particular is unclear and confounds the analysis.

An alternative approach is to examine the distribution of ANC and pH as a function of lake size. Results of this analysis using the FLADAB database are presented in Tables 4.3-3 and 4.3-4. For both ANC and pH no obvious relationship is evident, and the frequency of occurrence of lakes in Florida within a particular range of pH or ANC values appears to be independent of lake size. Using the larger FLADAB database, ANC and pH frequency distribution are rather similar to previously reported values (ESE, 1983a; Canfield et al., 1983); 58 percent of the lakes included in FLADAB are acidic (pH <7.0), and 32 percent have ANC concentrations less than 200 μeq/L.

Use of existing databases such as the FLADAB set can be criticized as not being representative of the true population of Florida lakes. Many of the lakes included in FLADAB originally were studied because of concern about eutrophication; this is apparent by considering the number of lakes included in FLADAB with small surface areas. Of the 3,191 named lakes in Florida, more than 77 percent are less than 50 ha and 23 percent are less than 10 ha in size (Dickinson et al., 1983). The FLADAB database, however, is skewed toward larger, more accesssible lakes, and the number of lakes less than 10 and 50 ha represents less than 23 and 40 percent

Table 4.3-3. Frequency Analysis of Lake Alkalinity of FLADAB Lakes by Lake Surface Area Group

| Surface Area Group* | Alkalinity (meq/L) <50 | 50-100 | 100-200 | 200-500 | >500 | Total Count |
|---|---|---|---|---|---|---|
| SA1 | 11 | 6 | 4 | 11 | 34 | 66 |
| SA2 | 21 | 17 | 17 | 32 | 43 | 130 |
| SA3 | 40 | 37 | 26 | 30 | 72 | 205 |
| SA4 | 14 | 16 | 12 | 17 | 45 | 104 |
| Total Count | 86 | 76 | 59 | 90 | 194 | 505 |
| | Percentage | | | | | |
| SA1 | 0.17 | 0.09 | 0.06 | 0.17 | 0.52 | |
| SA2 | 0.16 | 0.13 | 0.13 | 0.25 | 0.33 | |
| SA3 | 0.20 | 0.18 | 0.13 | 0.15 | 0.35 | |
| SA4 | 0.13 | 0.15 | 0.12 | 0.16 | 0.43 | |

*SA = surface area
SA1 = <10 ha
SA2 = 10 to 50 ha
SA3 = 51 to 500 ha
SA4 = >500 ha

Source: ESE, 1986.

Table 4.3-4. Frequency Analysis of Lake pH of FLADAB Lakes by Lake Surface Area Group

| Surface Area Group* | pH <4.5 | 4.5-5.0 | 5.0-5.5 | 5.5-6.0 | 6.0-7.0 | >7.0 | Total Count |
|---|---|---|---|---|---|---|---|
| SA1 | 0 | 2 | 5 | 6 | 22 | 29 | 64 |
| SA2 | 0 | 1 | 13 | 14 | 44 | 46 | 118 |
| SA3 | 2 | 8 | 16 | 27 | 67 | 75 | 195 |
| SA4 | 0 | 0 | 8 | 11 | 31 | 54 | 104 |
| Total Count | 2 | 11 | 42 | 58 | 164 | 204 | 481 |
| | | | Percentage | | | | |
| SA1 | 0.00 | 0.03 | 0.08 | 0.09 | 0.34 | 0.45 | |
| SA2 | 0.00 | 0.01 | 0.11 | 0.12 | 0.37 | 0.39 | |
| SA3 | 0.01 | 0.04 | 0.08 | 0.14 | 0.34 | 0.38 | |
| SA4 | 0.00 | 0.00 | 0.08 | 0.11 | 0.30 | 0.52 | |

*SA = surface area
SA1 = <10 ha
SA2 = 10 to 50 ha
SA3 = 51 to 500 ha
SA4 = >500 ha

Source: ESE, 1986.

respectively of the database. Furthermore, Florida contains an additional 4,127 unnamed lakes larger than 4 ha in size, most of which have surface areas less than 40 ha. Because the nutrient regimes of the lakes included in FLADAB are largely influenced by cultural development within respective watersheds, it is arguable whether FLADAB and other databases such as Canfield (1981) and Pollman and Hendry (ESE, 1983a) are representative of many of the uninhabited and largely unstudied small seepage lakes located in the highlands of the Florida panhandle and Central Ridge.

Data collected by EPA as part of the National Lake Survey (NLS) avoid the problems inherent in using a selectively biased database to infer the distribution of lakes in Florida with particular buffering characteristics. The NLS involved the random sampling of over 1,600 lakes in the northeast, upper midwest, and southeast regions of the United States and included 141 lakes from Florida. The random approach was adopted to allow statistical inferences regarding the number of acidic and low-ANC lakes present in geographical regions thought to be particularly susceptible to acidic deposition. Determination of causes of low pH or ANC was not addressed by the study. Lake sampling was conducted by helicopter in late fall 1984 and generally was restricted to lakes with surface areas exceeding 4 ha.

Preliminary NLS results for Florida generally confirm the previous findings of Pollman and Hendry (ESE, 1983a), Canfield et al. (1983) and more recently Crisman (1984); viz., lakes with ANC concentrations less than or equal to 200 μeq/L are located principally in the highlands of the panhandle and along the central Florida ridge, including the Ocala National Forest, the Trail Ridge and Highlands Ridge lake districts (Linthurst and Thornton, unpublished data). ANC generally appears to be lowest in the panhandle, which appears to have a preponderance of lakes with ANC levels less than 40 μeq/L, and gradually increases along a southerly gradient. Although spatial trends in ANC and pH distribution in the NLS set of lakes are similar to previously reported patterns, a substantially greater frequency of low-ANC, low-pH lakes was observed. Preliminary population estimates derived from the NLS results indicate approximately 54 percent of the Region 3B lakes (which included Florida and parts of southern Georgia) have ANC less than 200 µeq/L compared to an observed frequency of 44 percent of the FLADAB lakes. A similar comparison for pH gives a population estimate of 12 percent of Region 3B lakes with pH levels less than 5.0; only 3 percent of the FLADAB lakes are as acidic. In part, these differences reflect the statistical design of the NLS program resulting in a more representative sampling of the population of small, undisturbed seepage lakes. In addition, the estimates from databases such as FLADAB to date have strictly examined the frequency distribution of the sample population with no inference regarding the lake population of Florida as a whole. The NLS population estimates in turn are based on extrapolation of the sample population results to all the lakes within a geographically homogeneous area and undoubtedly provide a better estimate of the distribution of Florida lakes as a function of ANC and pH.

### 4.3.1.3 Chemical Response to Acidic Deposition

#### pH

Most of the research in Florida on the effects of acidic deposition on lakewater pH has focused on Lake McCloud, a small (5-ha), softwater seepage lake located in the Trail Ridge lake district of north-central Florida. Hydraulic inputs to the lake are dominated by precipitation directly to the lake surface; only 10 percent of the total inflow is attributed to seepage of ground water (Baker, 1984). Lakewater pH approximates or is somewhat lower than ambient precipitation levels, ranging from 4.11 to 4.64 between October 1980 and August 1982 (Baker, 1984). There is a limited historical database for Lake McCloud extending from 1968-1969 (Brezonik *et al.*, 1969) to 1978-1979 (Hendry, 1983; Brezonik *et al.*, 1983) and including 1980-1982 (Baker, 1984; Ogburn, 1984). These data have been compiled by Baker (1984) who subsequently noted an apparent decline in lakewater pH from 4.85 to generally less than 4.6 between 1968 and 1982--essentially a doubling of $H^+$ concentrations in 15 years. The cause of the apparent decline in pH is uncertain. Ogburn (1984), for example, notes an approximate 50-percent increase in conductivity during this period and suggests that concentration of ions by evaporation may account for some of the observed decline. Ogburn cites as support for this hypothesis decreases in pH observed in Lake McCloud from September 1981 through January 1982 which corresponded with declines in lake stage; subsequent increases in rainfall caused lake levels to begin recovery to normal stage and a pH shift upward. Examination of chloride concentrations between 1968 and 1982, however, shows relatively stable concentrations while calcium, magnesium, and sulfate concentrations all increased. As a result, Baker (1984) indicated that variations in precipitation and evaporation cannot account for the observed differences in $H^+$.

Considering the relatively long hydraulic residence time of seepage lakes in general (>3 years, cf. ESE, 1985), it seems reasonable that lakewater pH in seepage lakes within Florida is slow to respond to antecedent factors such as individual rain events. While it is apparent that seepage lakes will take some time (i.e., years) to essentially equilibrate or achieve a new steady-state regime in response to changes in acid loading rates, recent data collected by Battoe (unpublished manuscript) indicates that short-term fluctuations in pH can be induced by a single rain event. In May 1985 Battoe monitored the short-term effects of a convective storm on surface pH levels in Lake Annie, a 37-ha seepage lake located on the Highlands Ridge in south-central Florida. The storm delivered 2.5 cm of pH 4.00 rain to the lake, resulting in a depression of surface pH (approximately 15 to 20 cm below the surface) of greater than 0.1 unit from 5.26 to 5.13. Although more extensive analyses for major ion concentrations in lakewater were not performed, Battoe's measurements of precipitation pH were consistent with laboratory analyses performed by ESE (pH 3.99, cation/anion = 0.96; unpublished data). Measurements of pH deeper within the water column were not reported by Battoe, but it is highly unlikely that similar depressions in pH occur below the lake surface. Battoe's results are consistent with mass balance calculations which show that in the absence of ANC a pH decline of 0.13 unit below ambient is expected with one important consideration, viz., this projection assumes no immediate mixing of the rainwater with the water column occurs below approximately 13-cm depth. Lake Annie is a warm monomictic lake that typically stratifies around the 1.8- to 2.4-m depth (Layne, 1979); water above the thermocline freely circulates and any immediate depression in pH attributable to rainfall should be diluted accordingly within hours as circulation proceeds. Potential short-term effects consequently should be confined largely to the planktonic community residing at the air-water interface (i.e. the neuston and epineuston). Subsequent measurements made 3 days after the rain event indicate that surficial pH recovered to the pre-event value of 5.26 (Battoe, unpublished manuscript).

Perhaps the most complete database documenting relatively short-term changes in pH for a softwater acidic lake in Florida was the one developed by Baker (1984) for Lake McCloud. Baker monitored pH and major ion chemistry monthly in Lake McCloud from October 1980 to August 1982. With the exception of one observation in February 1981, pH in McCloud Lake varied on the order of 0.03 to 0.07 unit per month and pH generally remained between 4.40 and 4.60 (Figure 4.3-5). The apparently anomalous observation in February 1981 may reflect sample bottle contamination with nitric acid (Brezonik et al., 1982b) and should be regarded as suspect. Between September 1981 and August 1982, precipitation quantity and chemistry as well as lake stage and volume were included as monitored variables. These data can be used to examine the relationship, if any, between lakewater pH and acidic deposition or lake hydrology. Precipitation volume, proton loading due to precipitation, seepage estimates, and lake volume were used as input variables and lakewater proton concentration as the dependent variable for stepwise regression

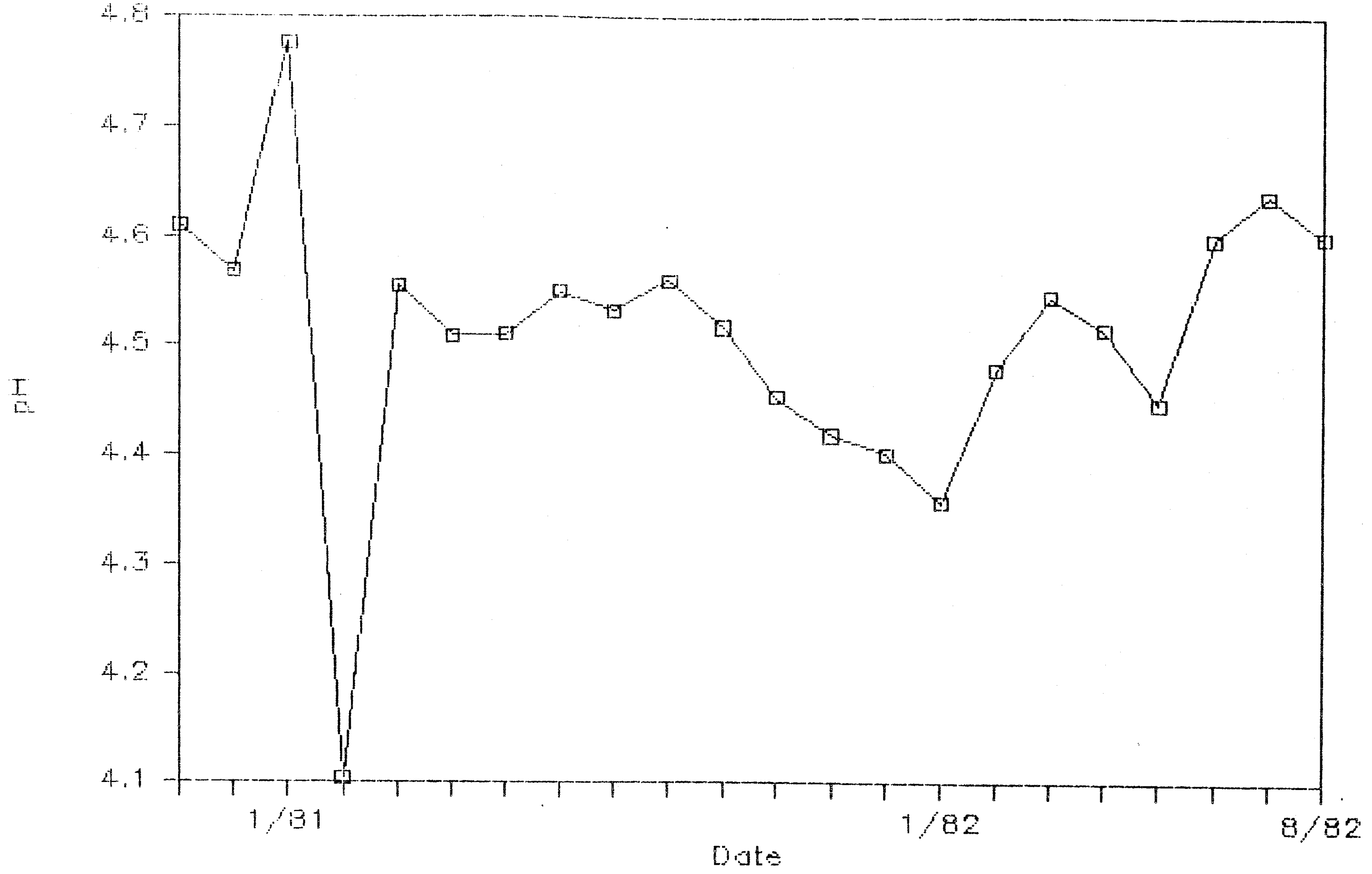

**Figure 4.3-5**
**SHORT-TERM VARIATIONS IN LAKE McCLOUD pH**

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analysis (Crunch Software, 1984). Results of the stepwise analysis suggest that for Lake McCloud short-term variations in pH are driven to a significant degree by changes in lake hydrology as reflected in volumetric changes rather than antecedent rainfall events. In-lake proton concentrations correlated significantly with changes in lake volume (Figure 4.3-6):

$$H^+ = 90.3 - 0.45(VOL) \qquad (R^2 = 0.47;\ p = 0.013)$$

where: $H^+$ = concentration (μeq/L), and
VOL = lake volume [x$10^3$ cubic meters ($m^3$)].

None of the other variables were found to be significantly correlated in the stepwise model. In other words, lake pH decreases during periods of low rainfall when evaporation results in a net reduction in volume. These changes can equate to a nearly twofold change in $H^+$ over the course of a year. Nevertheless, it should be observed that this rather simple model accounts for only 47 percent of the variability in lakewater $H^+$; furthermore, simple mass balance considerations indicate that only a fraction of the decline in pH can be attributed to evapoconcentration.

There is considerable evidence in the literature indicating that internal processes in lakes influence or regulate to some extent the pH regime of softwater Florida lakes such that consideration of lakewater ANC alone does not provide an accurate assessment of a lake's buffering abilities. Initial attempts by Baker (1984) and Ogburn (1984) to change McCloud lakewater pH through acid and base additions in a series of in situ enclosures open to the sediments required greater additions than calculated to reach target pH levels based on ANC determinations. The areal buffering rate of the acidified mesocosm (which was dosed with sulfuric acid) was 1.2 milliequivalents per square meter per year ($meq/m^2/yr$), and the neutralization of added $H^+$ was closely paralleled by losses of sulfate, suggesting that sulfate reduction was probably

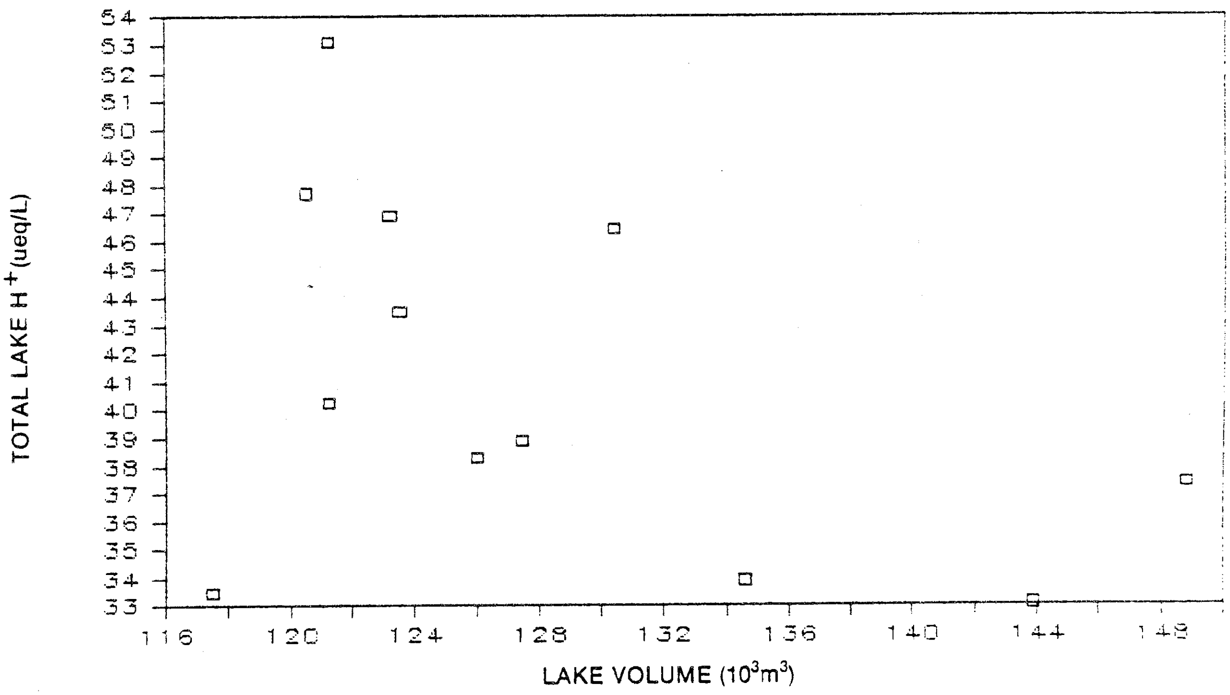

**Figure 4.3-6**
**LAKE VOLUME AND IN-LAKE $H^+$ STORAGE FOR LAKE McCLOUD**

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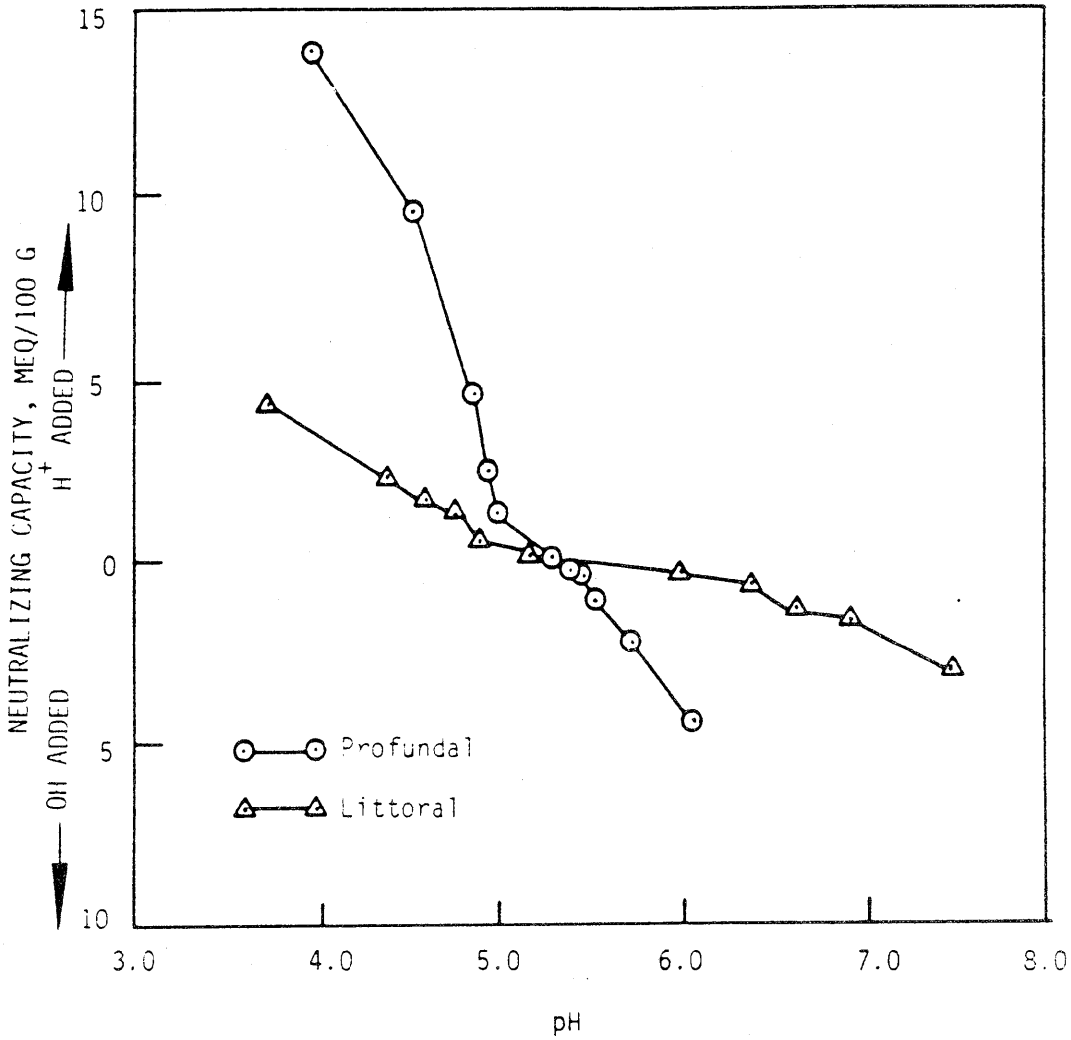
responsible for the generation of ANC (Baker, 1984). In the mesocosm receiving base additions, added $OH^-$ [as sodium hydroxide (NaOH)] was removed rapidly from solution and repeated additions of NaOH failed to sustain the target pH. Baker (1984) observed that $Na^+$ did not behave conservatively, and losses equivalent to 71 percent of the $OH^-$ neutralization occurred over a 14-week period. In view of the traditional perspective that $Na^+$ is relatively conservative in natural waters, the loss of $Na^+$ from the mesocosm was troublesome and was unexplained by the author.

The influence of the sediments on the pH of overlying lakewater was investigated further by Baker (1984) in a series of microcosm and batch experiments conducted in the laboratory. Batch studies were conducted to determine the neutralizing capacity of the sediments by adding $H_2SO_4$ or NaOH to slurries of sediment and distilled water. Bacterial activity was inhibited by adding $CHCl_3$. Microcosm studies consisted of a sediment-water system using littoral sediment from Lake McCloud and simulated McCloud lakewater. Results of the sediment batch studies are shown in Figure 4.3-7 as a set of titration curves for McCloud profundal and littoral sediments. Baker concluded the greater buffering by the profundal sediments was related to the higher concentrations of organic material or possibly clay minerals deposited in deeper water. Typical neutralizing capacities (NC) of profundal sediments ranged from 8 to 10 meq/100 g for the pH range 4.5 to 5.0; by comparison, buffering by the sandy littoral sediments was considerably poorer over the same pH range (NC = 0.6 to 1.2 meq/100 g).

Neutralization in the batch studies was quite rapid, proceeding toward completion within several hours, and, as shown by changes in ion composition, was consistent with a cation-exchange-type mechanism rather than mineral dissolution. Increases in $Ca^{+2}$ and $Mg^{+2}$ concentrations indicate that proton displacement of these two species from cation exchange sites is the major mechanism of buffering (excluding biological



SOURCE: Baker, 1984.

**Figure 4.3-7**
TITRATION CURVES FOR LAKE McCLOUD SEDIMENTS

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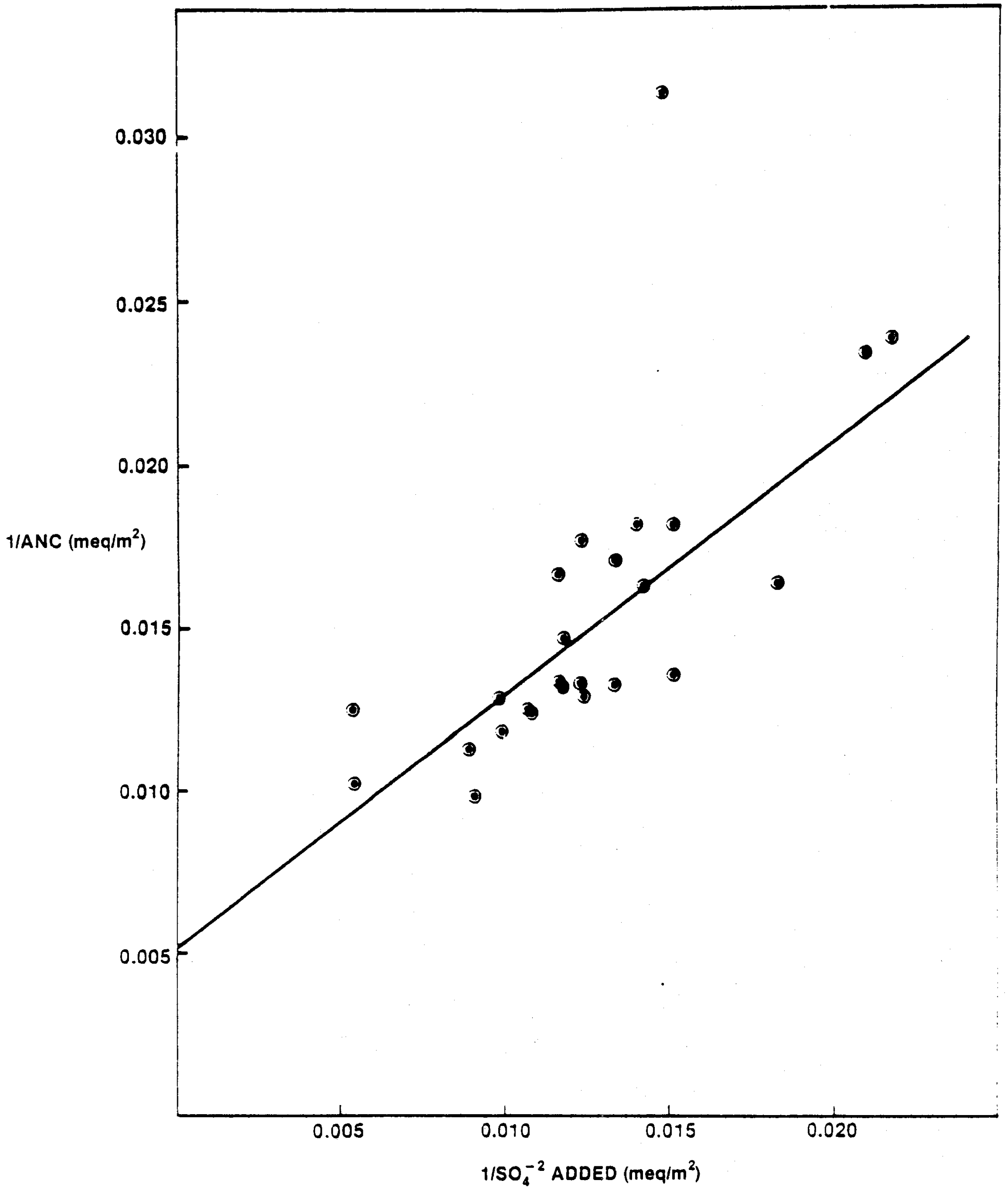
processes) in Lake McCloud. Baker reports similar results for several other Florida and Wisconsin lakes. Aluminum solubilization from the McCloud sediments accounted for less than 10 percent of the total neutralizing capacity throughout the pH range 4.0 to 7.0. Similar results were obtained from the microcosm studies with one important distinction--biologically mediated sulfate reduction was an important contributor to neutralization along with cation exchange. As pH was reduced and sulfate concentrations increased, sulfate reduction became increasingly important as a neutralization mechanism. It also should be noted that at relatively high pH levels (~pH 6 to 6.6), humic acids apparently assume an increasingly significant role in neutralization. In his batch experiments, Baker observed that the sediment-water solutions above pH 6.0 became visibly colored and that the fraction of buffering unaccounted for by mineral dissolution or cation exchange increased to about 30 percent at pH 6.6.

Studies on the role of lake sediments in buffering lakewater against changes in pH was examined further for Florida lakes by Perry _et al_. (1986; ESE, 1984) and Baker and Brezonik (ESE, 1985). Perry _et al_. (1986; ESE, 1984) collected sediment cores from the profundal and littoral areas of 12 softwater lakes (and a series of littoral cores from an additional lake) to evaluate the importance of sulfate reduction and sediment ion exchange in neutralizing acidity. All of the 13 lakes studied were located in the Trail Ridge and Highlands Ridge lake districts of north- and south-central Florida and were originally included in the softwater lake survey conducted by Brezonik _et al_. (1983) in 1978 to 1979. The lakes were selected to provide a continuum of pH levels ranging from pH 4.66 to 6.70. Acidification experiments using sulfuric acid were performed on undisturbed cores (which, along with the overlying lakewater remained intact during the course of the study) to simulate _in situ_ lake sediment-water conditions and on slurries of extruded sediment to quantify ion exchange processes and evaluate the total mineralogical potential for acid neutralization. As in the previous batch studies conducted by Baker (1984), chloroform was added to the batch slurries to inhibit biological contributions to ANC generation. The results confirmed for a broad range of softwater lakes the initial results observed by Baker (1984) for Lake McCloud; viz., chemical and biological processes in the sediments tend to counter inputs of acidity to the water column. Analysis of changes in major ion chemistry in the overlying water of the intact cores indicates that microbially mediated sulfate reduction exceeds ion exchange as the principal ANC-producing mechanism. Neutralization of added acid attributable to the sediments ranged from 32 to 101 milliequivalents per square meter (meq/m$^2$) over the 4-month duration of the study and appeared to follow Monod-type kinetics with sulfate availability limiting ANC generation at low sulfate concentrations (Figure 4.3-8). ANC attributable to ion-exchange mechanisms was strongly related to organic content; consequently, ion-exchange ANC was more pronounced in organic-rich pelagic sediments than in littoral sediments that are more subject to wind-induced scour and characteristically have low organic contents. Calculated areal buffering capacities in a 1-cm section of sediment resulting from ion-exchange ranged from 6 to 150 meq/m$^2$, indicating sufficient buffering is available in 1 to 2 cm of sediment to neutralize annual wet deposition rates of $H^+$ (see Section 2.3 for the range in $H^+$ deposition rates) via ion exchange alone.

Subsequent studies by Baker and Brezonik (ESE, 1985) examined in more detail the rate and mechanisms of ANC generation by sediment processes in softwater Florida lakes. Experimentation on sediment cores from three lakes in the Trail Ridge lake district was conducted in two phases. In the first phase, HCl was added to sediment-water microcosms to determine the magnitude of neutralization with an acid having a non-reactive anion as the counterion. Following equilibration with HCl to establish the pH of the microcosms at target pH levels ranging from 4.0 to 5.0, sulfate was added as a neutral salt and maintained at constant concentrations to determine the rate of sulfate reduction as a function of pH under steady-state conditions. Results from the first phase indicated that diffusion



NOTE: Each datum represents the ANC generated after a 4-month period.

SOURCE: Perry *et al.*, 1986.

Figure 4.3-8
ANC GENERATION BY INTACT CORES AS A FUNCTION OF $SO_4^{-2}$ ADDITION RATES

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of alkaline porewater and/or hydrochloric acid across the sediment-water interface can contribute significantly to neutralization during the initial stages of acidification. Sulfate reduction initially present in the lakewater and some ion exchange of calcium and magnesium contributed to ANC production as well. As microcosm pH was reduced in the initial phase of the study, the relative contributions of sulfate reduction and ion exchange became increasingly smaller. Several factors may account for these results: (1) there was no continuing source of sulfate to support sulfate reduction; (2) as pH in the overlying water was reduced, some aluminum and iron solubilization occurred, resulting in neutralization of equivalent quantities of $H^+$ [previous studies (ESE, 1984) have demonstrated this effect for aluminum alone]; and/or (3) because of a more pronounced $H^+$ or ANC gradient across the sediment-water interface at lower pH levels in the overlying water, diffusional fluxes of ANC from the sediments likely were enhanced.

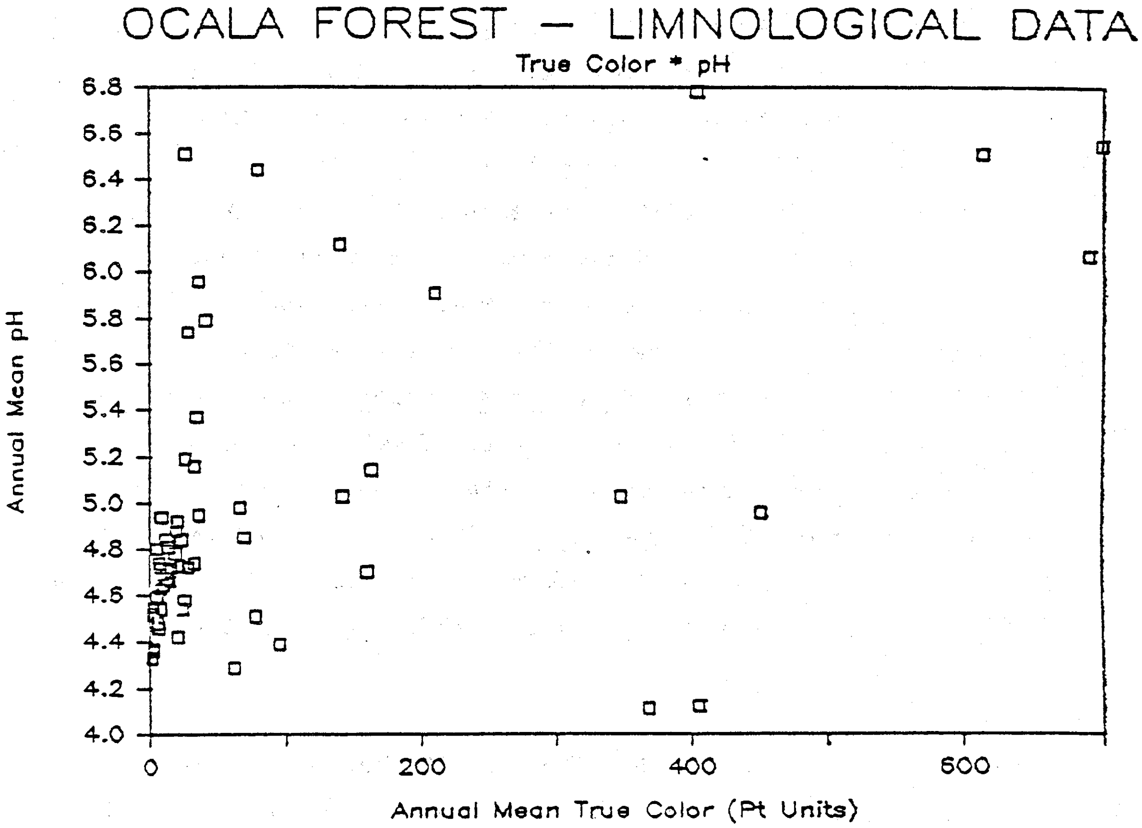
Results of the second phase of the study in which sulfate was added to the microcosms as a neutral salt and maintained at constant concentration suggest that sulfate reduction in fairly organic sediments can be described by first-order kinetics; i.e., appears to increase linearly with increasing lakewater sulfate concentrations. In sandy, organically impoverished sediment, sulfate reduction rates were independent of sulfate concentrations, probably as a consequence of the limited availability of organic matter. The relative contribution of organically depleted littoral sediments and organically enriched profundal sediments is a lake-specific function of morphometry; nevertheless, fairly organic sediments should dominate the bottom coverage in most lakes and application of first order kinetics to model sulfate appears reasonable.

## Organic Acids

The role of organic acids or DOC as a buffering system mediating both pH and metal toxicity response to acidification in Florida softwater lakes is not well understood. The principal studies of colored lakes in Florida are largely limited to the recent NLS conducted by EPA and a survey of 62 lakes in the Ocala National Forest conducted by Garren et al. (1984). Preliminary results from NLS suggest that nearly 50 percent of the (inferred) 1,600 seepage lakes in Florida and southeast Georgia are colored [30 platinum-cobalt units (PCU)]. Seepage lakes located in the panhandle were generally low in DOC and color. In contrast, south-central Florida seepage lakes contain more moderate concentrations of DOC and color. The occurrence of highly colored lakes in relation to soil type was examined by Garren et al. (1984), who observed that colored lakes often have organic muck soils within their immediate watershed which characteristically contain large amounts of humic material. Bald cypress (*Taxodium distichum*) typically is the dominant form of vegetation and contributes further to organic acid inputs to these lakes (Garren et al., 1984). Some exceptions to this general pattern occur, and Garren et al. (1984) concluded that hydrological factors such as flow paths in the shallow aquifer and lake hydraulic residence time are important in defining the DOC budget of seepage lakes.

Preliminary results from NLS indicate that DOC can be an important contributor of ANC to colored softwater lakes. Comparison of clear and colored lakes shows that the median ANC concentration in colored lakes is approximately three times higher (163 versus 45 µeq/L). Nevertheless, median pH levels for the two classes of lakes show that pH levels are nearly identical (pH 6.56 and 6.63 for colored and clear lakes, respectively) and further illustrate the role of organic acids as a buffering mechanism toward acidic pH levels.

Garren et al. (1984) found little correlation between color and pH for their survey lakes in the Ocala National Forest (R = 0.5; Figure 4.3-9). This lack of correlation reflects the dual acid-base nature of DOC and underscores the importance of watershed interactions with humic



SOURCE: Garren *Et Al.* (1984).

**Figure 4.3-9**
ANNUAL MEAN pH AS A FUNCTION OF COLOR FOR LAKES IN THE OCALA NATIONAL FOREST

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substances in defining the role of humic substances on the pH regime of a lake. Ion exchange by soils and sediments for $H^+$ associated with DOC yields a net contribution of ANC and higher lakewater pH levels. If the buffering effects of the carbonate system are disregarded, lakewater pH will be dictated by the $pK_a$ of the organic acid and the relative fraction of the total organic acid concentration (associated and dissociated) that enters the lake dissociated with a base cation as the counterion. The ability of lakewater to buffer against changes in pH is a function of the total organic acid concentration and the pH (see Subsection 4.3.1.1). This is illustrated in Figures 4.3-10 and 4.3-11 which depict buffering intensity for two lakewaters at equilibrium with atmospheric $CO_2$ and containing differing levels of DOC. Both figures also show the buffer intensity as a function of pH due to the carbonate system alone. Assumed DOC concentrations were 2 and 6 mg/L for Figures 4.3-10 and 4.3-11, respectively; 6 mg/L approximates the median DOC concentration indicated by preliminary NLS results for seepage lakes. The variable effects of pH on the $pK_a$ were accounted for using the model of Oliver _et al_. (1983); this model also assumes that each milligram of DOC contributes about 10 microequivalent (μeq) of organic acid.

The results of this model analysis indicate that buffer intensity is augmented by organic acids to the greatest relative degree at approximately pH 4.40 (Figures 4.3-12 and 4.3-13). This is also the region of minimum overall buffer intensity; below this pH, buffering by $H^+$ becomes increasingly more important, whereas above this range, the carbonate system becomes more significant. At pH 4.40, the buffer intensity due to the carbonate system is 157 μeq/L (of which 92 μeq/L is due to the buffering of $H^+$); the presence of 6 mg/L increases the buffer intensity by an additional 20 percent to 189 μeq/L. By comparison, DOC concentrations of 2 mg/L contribute a maximum of only 7 percent to the buffer intensity of lakewaters at equilibrium with atmospheric $CO_2$. Although data from NLS on the distribution of DOC in colored lakes are not available, preliminary data using the Oliver _et al_. (1983) model to

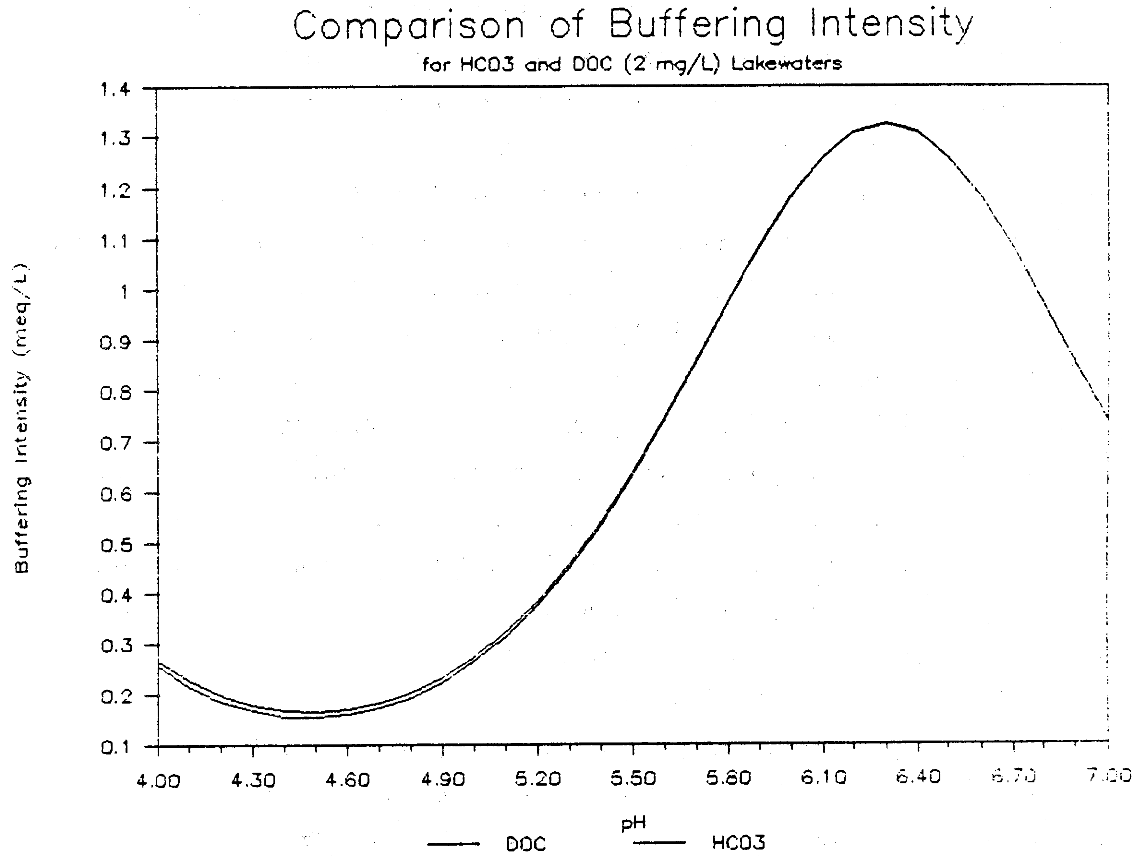

**Figure 4.3-10**
COMPARISON OF BUFFERING INTENSITY FOR LAKEWATERS AT EQUILIBRIUM WITH ATMOSPHERIC $P_{CO_2}$ AND CONTAINING EITHER NO (LOWER CURVE) OR 2 mg/L DOC (UPPER CURVE)

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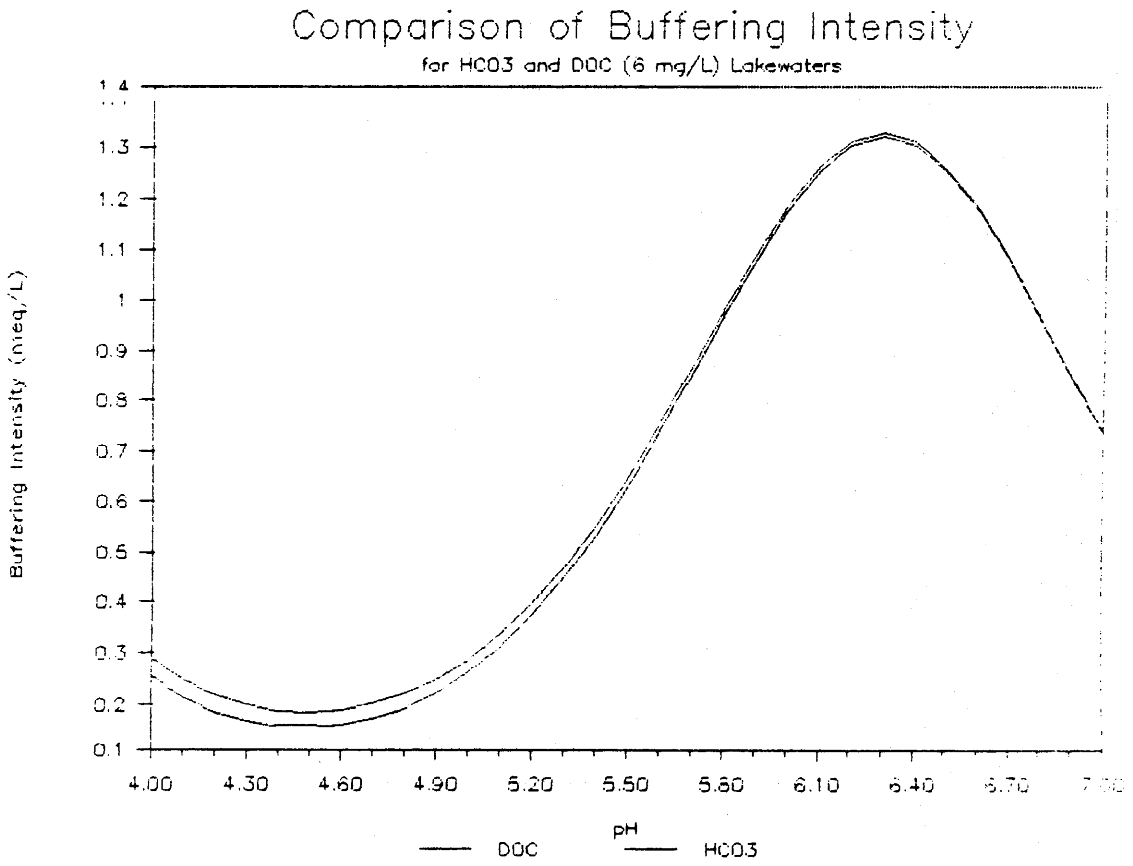

**Figure 4.3-11**
COMPARISON OF BUFFERING INTENSITY FOR LAKEWATERS AT EQUILIBRIUM WITH ATMOSPHERIC $P_{CO_2}$ AND CONTAINING EITHER NO (LOWER CURVE) OR 6 mg/L DOC (UPPER CURVE)

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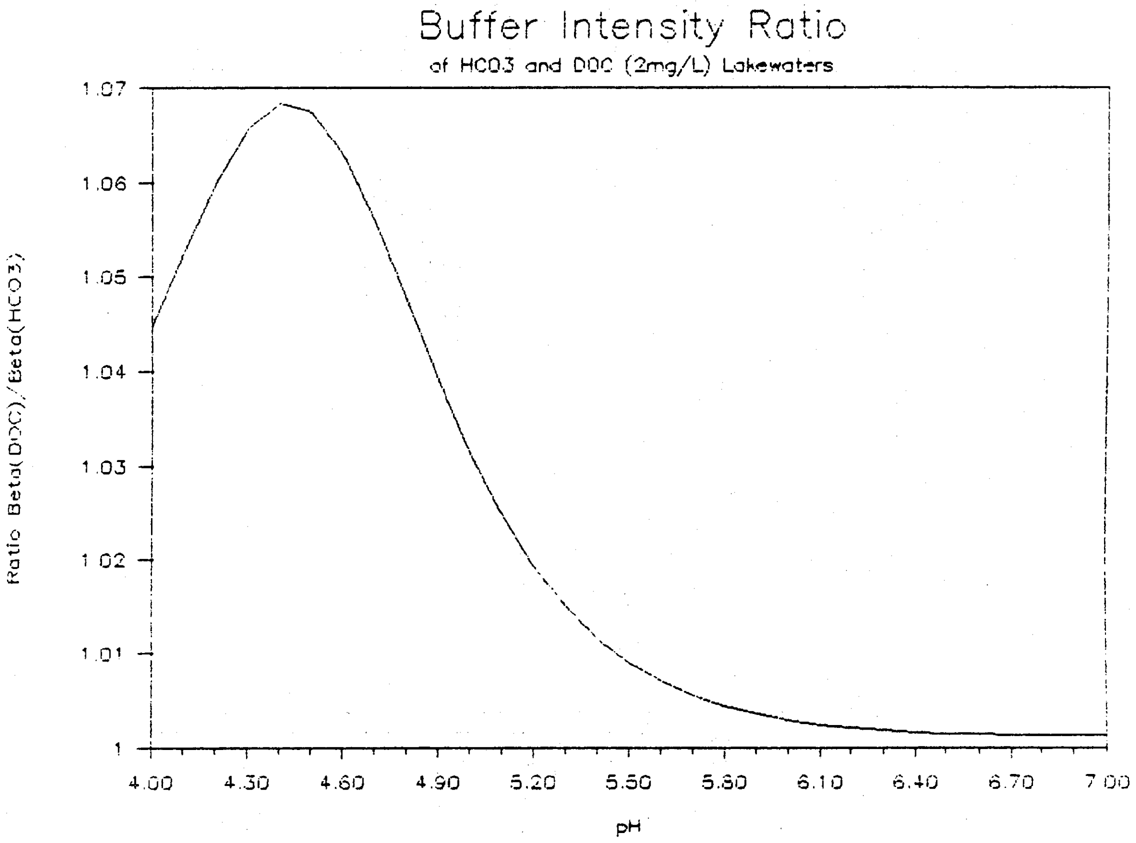

Figure 4.3-12
RATIO OF BUFFER INTENSITY FOR LAKEWATER CONTAINING 2 mg/L DOC AND LAKEWATER IN WHICH DOC IS ABSENT. BOTH LAKEWATERS IN EQUILIBRIUM WITH ATMOSPHERIC $P_{CO_2}$

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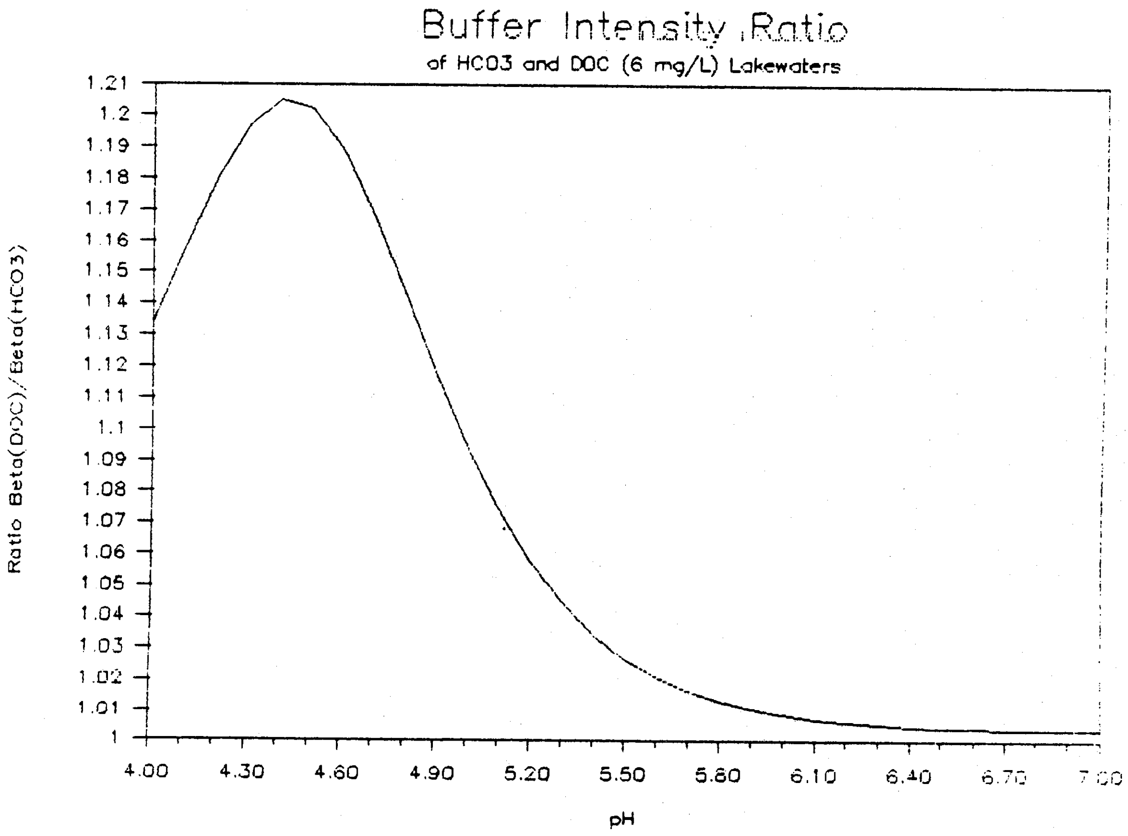

**Figure 4.3-13**
RATIO OF BUFFER INTENSITY FOR LAKEWATER CONTAINING 6 mg/L DOC AND LAKEWATER IN WHICH DOC IS ABSENT. BOTH LAKEWATERS IN EQUILIBRIUM WITH ATMOSPHERIC $P_{CO_2}$

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differentiate between carbonate and weak-acid-buffered lakes indicate median DOC concentrations of 3.9 and 9.0 mg/L, respectively.

It is apparent from this analysis that contributions of DOC to ANC and buffer intensity in colored lakes can be quite important. However, little is known about the distribution of colored lakes and, in particular, the hydrological factors that influence DOC in softwater lakes. Furthermore, little or no data are available characterizing humic substances in Florida lakes, particularly with respect to functional group analysis and $pK_a$. Finally, virtually no data are available describing the complexation of DOC in Florida lakes with aluminum and concomitant effects on aquatic toxicity. Because of its requisite role in the resolution of the issue of acidic deposition and aquatic sensitivity, the uncertainties in organic acid chemistry in Florida lakes dictate the necessity of further research.

### Sulfate

The wide variance in excess sulfate concentrations observed in the NLS data for Florida (Linthurst and Thornton, unpublished data) cannot be explained by the relatively mild gradient in wet (and presumably dry) deposition and may reflect weathering processes in individual watersheds. Kramer (1984), for example, suggests that oxidation of reduced sulfur minerals such as pyrite to form amorphous iron oxide or the mineral jarosite (resulting in the concomitant production of acid) may be a mechanism of widespread importance contributing to acidification and aluminum mobilization. This argument is predicated in part on the work of Carson et al. (1982) who demonstrated the formation of jarosite in acid soils of the mid-Atlantic states and the observations of Ivarson et al. (1982) of pyritic or organic sulfur oxidation in acid sulfate soils throughout Canada.

In Florida, evidence of acid sulfate weathering has been observed in a series of reclaimed phosphatic pit lakes in south-central Florida by

Boody et al. (1985). Adsorption of phosphorus by amorphous iron and aluminum oxy-hydroxides is pH dependent and typically increases with reductions in pH. For example, Hingston et al. (1967 and 1972) have demonstrated that the adsorption maxima of goethite ($FeOOH$) and gibbsite ($Al(OH)3$) increase linearly with decreasing pH. The possibility of sulfate weathering occurring in seepage lakes in the Highlands Ridge lake district in south-central Florida is suggested by sulfate enrichment factors (EF) which relate lakewater ratios of sulfate to chloride to the same ratios for precipitation (ESE, 1985). Comparison of EF values for the Highlands Ridge lakes with seepage lakes in the Trail Ridge district in north-central Florida shows that sulfate is highly depleted in the Trail Ridge lakes with EF values ranging from 0.31 to 0.45; conversely, EF values approached or even exceeded unity for many of the Highlands Ridge lakes. The EF values for the Highlands lakes are inconsistent with microcosm studies which have demonstrated that the sediments of several of these lakes are significant sinks for sulfate, apparently through sulfate reduction (ESE, 1984; Perry et al., 1986). Watershed inputs of sulfate from weathering could explain the anomaly; however, there is no direct geochemical evidence at this time that such a mechanism is operating.

### Nutrients

Among the various effects attributed to lake acidification is a reduction in the rates and efficiency of nutrient cycling, leading to declines in productivity (i.e. oligotrophication). Early studies by Grahn et al. (1974) suggested that acidification results in the buildup of organic matter and reduced rates of nutrient cycling, thus leading to acid-induced oligotrophication. This in turn would result in lower rates of primary production as well as reduced standing crops of phytoplankton and nutrient concentrations. The conclusions of Grahn et al. (1974) were not based on direct measurements of changes in productivity as a lake underwent acidification or on productivity measurements in acidic lakes. Instead, their conclusions were based on survey data on lake transparency, chlorophyll a concentrations, and qualitative observations of macrophyte abundance in lakes of southern Sweden. In particular, the authors noted an increased abundance of sphagnum mats covering the bottom of acidic lakes, and they hypothesized that the presence of these mats interfered with nutrient cycling between the sediments and the overlying water.

Aluminum solubilization in acidified lakes may also contribute to oligotrophication through several mechanisms. Aluminum can undergo precipitation and adsorption reactions with phosphorus as well as forming stable complexes (Stumm and Morgan, 1981), all of which serve to reduce the availability of inorganic phosphorus for algal uptake. In addition, organic phosphate hydrolysis to form inorganic orthophosphorus critical for algal growth may be inhibited by elevated concentrations of aluminum. Jansson (1981) demonstrated that the presence of aluminum inhibited phosphatase hydrolysis of a phosphate ester through complexation or precipitation with the substrate, thus reducing the availability the phosphate ester to enzymatic attack. The inhibitory effect was a function of the relative ratios of three constituents: substrate concentration, enzyme concentration, and aluminum concentration. Correspondingly, incubation studies conducted by Jansson (1981) with lakewater from acidic Lake Gardsjon (pH 4.5) in Sweden showed stimulation of phosphatase activity to counteract increases of aluminum of 500 micrograms per liter (µg/L) above background concentrations (300 µg/L). Jansson thus concluded that acid-induced aluminum mobilization may force phytoplankton to produce large quantities of phosphatase to outcompete aluminum for organic phosphates.

Support in the literature of the acid-induced oligotrophication hypothesis is not conclusive and often contradictory. After 8 years of artificial acidification of Lake 223 in the Experimental Lakes Area (ELA) of western Ontario, phytoplankton biomass and productivity show a possible increase (Schindler et al., 1985). During this study, the entire lake was acidified gradually from pH 6.8 to 5.0 with additions of sulfuric acid. The increase in productivity in Lake 223 appeared to be due to reduced hydraulic flushing rates in the wake of several years of lower-than-normal rainfall; nevertheless, comparison of phytoplankton biomass and productivity with several reference ELA lakes showed similar temporal trends, and the results do not support the acid-induced oligotrophication hypothesis. Concentrations of phosphorus, which is the limiting nutrient in the ELA lakes (Schindler, 1977), were unaffected by acidification. In addition, no decrease in organic matter decomposition rates were observed by Schindler _et_ _al_. (1985) apparently because microflora at the sediment-water interface maintained a microenvironment at a higher pH that precluded effects.

Results of Brezonik _et_ _al_. (1985) from acidification experiments in Little Rock Lake, a precipitation-dominated softwater lake in Wisconsin, tend to confirm the results reported by Schindler _et_ _al_. (1985) for Lake 223. Littoral enclosures open to the sediments were experimentally acidified with sulfuric acid to pH 6.0, 5.5, 5.0, and 4.5. Monitoring of nutrient concentrations, chlorophyll _a_ levels, and primary production rates showed no pH-related effect supportive of acid-induced oligotrophication.

Within Florida, recent studies by Ogburn (1984) generally do not support the acid-induced oligotrophication hypothesis. Ogburn (1984) examined the effect of acidification on phosphorus cycling in Lake McCloud through laboratory and _in_ _situ_ experiments and through an evaluation of the historical database available for the lake. Data collected by Brezonik _et_ _al_. (1969) in 1967 to 1968, Hendry and Brezonik (unpublished data) in 1978 to 1979, and Ogburn (1984) between 1980 and 1982 indicate that an apparent decline in lakewater pH of 0.35 unit over a 15-year period was not accompanied by changes in nutrient concentrations or chlorophyll _a_. _In_ _situ_ mesocosm studies using radio-labeled $^{32}P$ as a tracer essentially supported the apparent decoupling of pH and productivity; comparison of uptake rates in fertilized and unfertilized enclosures exposed to varying degrees of acidification indicated that phosphorus availability exerts a stronger effect on planktonic uptake and turnover of phosphorus than any direct effect of $H^+$. Although acidification of mesocosms established in the littoral zone of Lake McCloud led to reduced concentrations of total phosphorus, trends for the same parameter in pelagic or open-water enclosures were inconsistent and both phytoplankton densities and chlorophyll a concentrations were unaffected by pH. Similarly, community metabolic rates of littoral and pelagic communities originally adapted to the ambient pH (4.6) were not affected by either a reduction in lakewater pH to 3.7 or an elevation in pH to 5.6.

Ogburn (1984) also evaluated the effects of pH on phosphorus adsorption by Lake McCloud sediments. Adsorption isotherms conducted at various pH levels demonstrated that changes in pH between 3.5 and 5.0 influenced the extent of adsorption and the long-term uptake rate (over a 30-day period) only slightly with maximum adsorption occurring at pH 4.7. Above pH 5.0, adsorption maxima calculated using the Langmuir model decreased rapidly with increasing pH. These results are relatively consistent with the adsorption envelope model originally developed by Hingston et al. (1967) which indicates that the extent of adsorption should increase monotonically as a function of phoshorus speciation as pH is lowered below pH 7.2 to approximately pH 2.2. On the basis of these results, Ogburn (1984) concluded that reductions in lakewater pH from 7 to 5 would result in a fairly dramatic increase in phosphorus adsorption but further acidification would have little additional effect. Ogburn's results agree well with isotherm data developed by Edzwald (1977) for phosphate adsorption by kaolinite, which is the principal clay mineral in the Lake McCloud watershed. Maximum adsorption by kaolinite was observed at approximately pH 5 and shifts in pH in either direction resulted in corresponding decreases in adsorption.

It should be noted that iron and aluminum coatings on sediment particles as well as other clay minerals such as montmorillonite may behave in a completely different manner (cf. Edzwald _et al_., 1976); however, it is very unlikely that appreciable quantities of montmorillonite (which has a very high CEC of approximately 80 meq/100 g; Bolt and Bruggenwert, 1976) are found in poorly buffered watersheds characteristic of softwater lakes.

Results suggesting that the acid-induced oligotrophication hypothesis may be applicable to Florida lakes is provided by the survey of 20 softwater lakes in the Trail Ridge and Highlands Ridge lake districts conducted by Brezonik and co-workers (Brezonik _et al_., 1983 and 1984; Hendry, 1983; Hendry and Brezonik, 1984). A good correlation between pH and total phosphorus concentration was observed; similar correlations were observed between pH and both phytoplankton counts and chlorophyll _a_. Separation of the study lakes into two statistically distinct groups based on pH showed significant differences in organic constituents and total nutrients. Productivity appeared to be higher in the non-acidic group (average pH $\geq$5.75) relative to the acidic group (average pH $\leq$5.25). Whether or not the relationship between pH and productivity is causative or merely coincidental correlation reflecting differing hydrologies and therefore differing nutrient loading rates was not determined.

The softwater lake data of Brezonik _et al_. (1983) were analyzed further to estimate nutrient loading rates and the relationship between pH and nutrient concentrations (ESE, 1985). Nutrient loading rates were developed from land-use data and associated nutrient export coefficients derived previously for Florida watersheds by Baker _et al_. (1981) and atmospheric deposition estimates based on bulk precipitation chemistry collected at several sites within Florida by Brezonik _et al_. (1983). Watershed areas used to determine total watershed loading rates were estimated from topographic contours. The results of this study were inconclusive, neither supporting or refuting the acid-induced oligotrophication hypothesis (ESE, 1985). The analysis indicated little relationship between total phosphorus concentrations and pH, and chlorophyll a concentrations were correlated at least as strongly with parameters indicative of watershed influences such as conductivity and relative amounts of residential development, crop, and urban land. Analysis of estimated loading rates, however, inferred much higher nutrient concentrations than observed in the study lakes. Calculated loading rates were poorly correlated with in-lake phosphorus concentrations, probably reflecting the inherent difficulties in defining the portion of a watershed which actually contributes hydraulically to seepage lakes. Alternatively, reduced rates of nutrient cycling, manifested as higher phosphorus retention coefficients (and thus lower phosphorus concentrations than predicted), are due to oligotrophication induced either by aluminum precipitation or reduced decomposition rates. However, aluminum concentrations in the study lakes were quite low, averaging less than 120 µg/L, and do not appear to support oligotrophication. Furthermore, a recent phosphorus budget contructed for acidic and oligotrophic Lake Gardsjon by Broberg and Persson (1984) indicates a low retention coefficient relative to meso- and eutrophic lakes, although its relationship to other, unacidified oligotrophic lakes is uncertain.

A larger survey of 165 Florida lakes conducted by Canfield et al. (1983) showed a positive relationship between chlorophyll a and pH similar to Hendry and Brezonik (1984). Nutrient concentrations were also positively correlated with pH, raising the question whether a low phytoplankton standing crop reflects low pH or low nutrient concentrations. Multiple correlation analysis indicated that the relationship was largely attributable to nutrient availability and Canfield et al. (1983) concluded that low phosphorus and nitrogen concentrations and not pH were responsible for low chlorophyll a concentrations in acidic lakes. Since the correlations are based on 165 lake systems with waters that range from very hard to soft, the database may not be well suited for determining small changes in acidity, nutrients, and productivity.

In summary, evidence either refuting or supporting the acid-induced oligotrophication hypothesis in Florida lakes is not conclusive. Much of the evidence supporting acid-induced oligotrophication is based on positive correlation between lakewater pH and trophic state variables such as chlorophyll a. Cause and effect have not been established for these relationships, and similar analyses show that trophic state variables are correlated at least as strongly with watershed factors, such as land use, as with pH. Laboratory studies indicate that phosphorus adsorption increases with reduction in lakewater pH and suggest that increasing acidification can lead to enhanced phosphorus removal and reduced lakewater concentrations. Nevertheless, in situ mesocosm studies results for total phosphorus are inconsistent and show no effect of pH between 3.7 to 5.6 on algal standing crops. Given these results, it seems unlikely that acidification effects on primary productivity will be profound in Florida lakes.

### Trace Elements

A major consequence of acidic deposition on dilute, softwater systems is the solubilization of trace elements, such as aluminum, as pH is depressed in surface and ground waters (e.g., Dickson, 1978 and 1980; Schindler et al., 1980a; Troutman and Peters, 1980; Driscoll et al., 1984). A related effect is a change in trace element speciation which is intrinsically a function of pH (cf. Stumm and Morgan, 1981; Westall et al., 1976); trace element speciation in turn affects aquatic toxicity (e.g., Muniz and Leivestad, 1980b; Peterson et al., 1984).

Aluminum mobilization in response to lake acidification has been studied in Florida both in the laboratory in microcosm studies (Baker, 1984; ESE, 1984) and through cross-sectional surveys. Brezonik and co-workers (Brezonik et al., 1983; Hendry, 1983; Hendry and Brezonik, 1984) included "labile" aluminum as an analytical parameter in their survey of 20 softwater lakes in north- and south-central Florida. Aluminum samples were unfiltered and analyzed colorimetrically by the Eriochrome Cyanine R method (APHA, 1976). These lakes were separated statistically on the basis of pH into an acidic and nonacidic group and comparison of mean concentrations of the two groups indicated that the highest "labile" aluminum concentrations were found in the acidic group (Hendry, 1983; Hendry and Brezonik, 1984). Concentrations for the acidic group averaged 58 µg/L and were statistically different ($p < 0.0001$) than the nonacidic group which averaged only 23 µg/L. With the exception of Cowpen Lake, "labile" aluminum concentrations in all of the lakes surveyed were below 80 µg/L. "Labile" aluminum in Cowpen Lake averaged 116 µg/L with a maximum observed concentration of 150 µg/L. A subsequent survey of total soluble aluminum in 10 acidic north Florida lakes (pH 4.12 to 5.95) by Brezonik _et al_. (1982b) also demonstrates that ambient aluminum concentrations in these lakes are low (18 to 184 µg/L) [Aluminum samples were filtered immediately after collection and analyzed by flameless atomic absorption (AA) (Baker, personal communication)]. Concentrations reported in these two surveys are apparently less than levels found in acidified lakes such as the Adirondack lakes and lakes in Scandinavia which lie within granitic watersheds. Driscoll (1980), for example, reports labile monomeric aluminum concentrations consistently in excess of 200 µg/L for Big Moose Lake in the Adirondacks and Dickson (1980) found total aluminum concentrations approaching 400 µg/L for Swedish lakes with pH levels similar to the most acid lakes included in the Florida survey (pH 4.7 to 4.9). It should be noted that the analytical approach adopted by Hendry and Brezonik (1984) measures labile aluminum and their results may not reflect total concentrations as reported by Dickson (1980); however, comparison of labile and total aluminum in seven Florida lakes indicates that total and labile aluminum is nearly the same in these lakes (Brezonik _et al_., 1982a and 1982b).

Enclosure studies conducted _in situ_ at Lake McCloud demonstrated that acidification of Florida lakes below pH 4.5 may result in aluminum concentrations sufficiently high to cause toxic effects (Brezonik _et al_., 1982b). After acidification to pH 3.7 of an enclosure open to the sediments, Brezonik et al. (1982b) observed a rapid increase in total soluble aluminum concentrations from ambient levels of approximately 100 µg/L to greater than 300 µg/L. Batch studies conducted by Baker (1984) for sediments collected from several softwater lakes in Florida also showed an increase in total soluble aluminum mobilization from the sediments in response to acidification (Figure 4.3-14). Solubility increased rapidly below pH 5.0 to 5.5 and solubility calculations indicated that the mineral phases gibbsite or kaolinite may control solubility at low pH levels.

A microcosm approach was adopted by Perry (ESE, 1984) to study aluminum solubilization from softwater lake sediments after batch studies demonstrated kinetic problems involving aluminum supersaturation that are not likely to occur in the natural environment. Intact sediment cores including the overlying lakewater were collected from littoral and profundal locations from 13 lakes originally studied by Brezonik and coworkers as part of their softwater lake survey. Intact cores were used to more closely simulate inlake conditions. The cores were subjected to periodic additions of 0.135N $H_2SO_4$; seven additions of acid were made over a 4-month period, each addition being sufficient to lower the lakewater pH to 4.0 in the absence of sediment buffering. Monomeric aluminum was measured on filtered (0.45-µm polycarbonate filters) samples using the ferron-orthophenanthroline method of Rainwater and Thatcher (1960). Aluminum concentrations relative to concentrations expected if the mineral phase gibbsite controls aluminum solubility are presented as a function of pH in Figure 4.3-15. Aluminum was generally solubilized by the reductions in pH, and concentrations in the overlying water typically exceeded 200 µg/L. However, it is difficult to use these results to examine further Baker's (1984) conclusion that gibbsite may control aluminum solubility at low pH levels. No strong relationship was found between pH of the overlying water and aluminum concentrations and the high concentrations measured (between pH 5 to 7) and undoubtedly reflect the inherent problem of organic complexation as a positive interferent

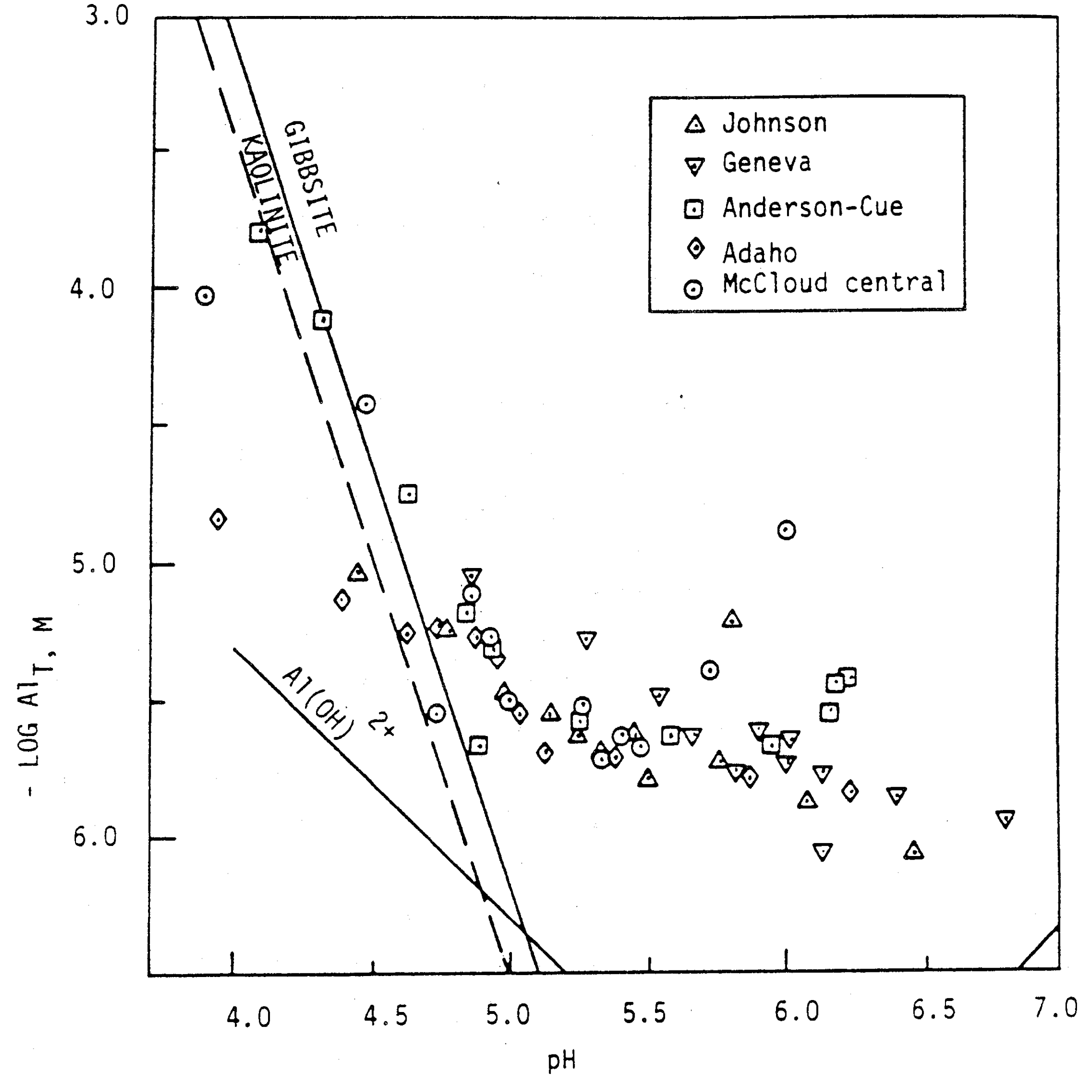

Figure 4.3-14
ALUMINUM CONCENTRATION VERSUS pH IN SEDIMENT NEUTRALIZATION EXPERIMENTS FOR FIVE SOFTWATER FLORIDA LAKES

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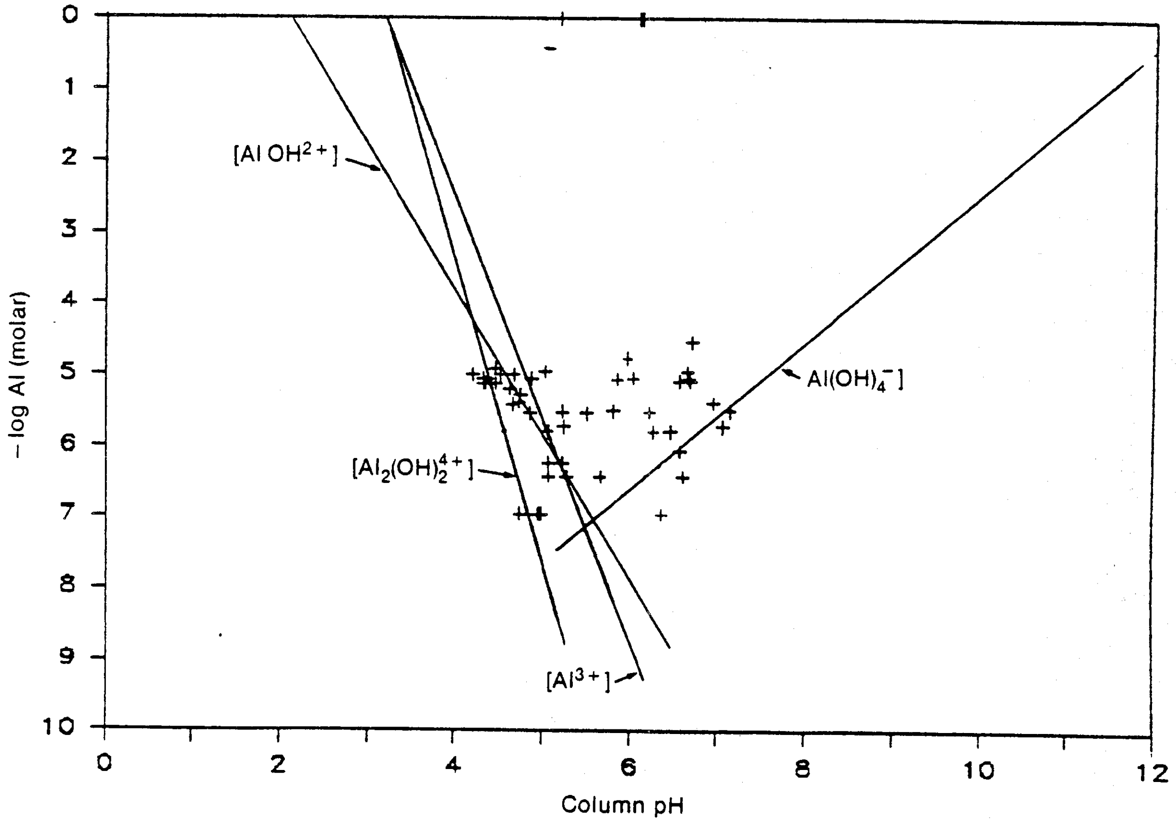

NOTE: EACH LINE REPRESENTS THE pH-DEPENDENT MOLAR SOLUBILITY OF VARIOUS ALUMINUM SPECIES.

Figure 4.3-15
INTACT SEDIMENT COLUMN MONOMERIC ALUMINUM CONCENTRATION DATA AS A FUNCTION OF pH IN RELATION TO GIBBSITE SOLUBILITY

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during the analytical procedure for monomeric aluminum (cf. Driscoll et al., 1984). Initial aluminum concentrations in the majority of the microcosms were similar to lakewater concentrations of Hendry (1983); however, several of the microcosms had initial concentrations greater than 200 µg/L with a maximum concentration of 804 µg/L observed in Lake Letta in the Highlands Ridge. The initial pH of Lake Letta (pH 6.70) was the highest of the lakes studied and Perry (ESE, 1984) concluded that the high concentrations observed prior to acidification may refect complexation of aluminum with organic matter (averge color in Lake Letta is 29 PCU; Hendry, unpublished data).

An additional effect associated with the acidic deposition phenomenon is the mobilization and release of trace elements into the atmosphere during the combustion of fossil fuel which subsequently can result in elevated trace element concentrations in soils, surface waters, and sediments (e.g., Allen and Steinnes, 1980; Forstner and Wittmann, 1979; Galloway and Likens, 1979; Dillon and Evans, 1982; Evans and Dillon, 1982). Dillon and Evans (1982) used sediment cores to define anthropogenic inputs of lead to eight small lakes in southern Ontario. Lead concentration profiles in the sediments of all the lakes showed elevated concentrations in the more recent (i.e., upper layers) sediments. Anthropogenic lead burdens in the sediments of the study lakes were very similar despite large differences in watershed characteristics and Dillon and Evans concluded that watershed inputs of lead were minor and that the only significant source was direct atmospheric deposition to lake surfaces. Similarly, Galloway and Likens (1979) measured increased rates of deposition for silver, gold, cadmium, chromium, copper, lead, antimony, vanadium, and zinc in several relatively remote lakes in the northeastern United States and attributed the increased fluxes to atmospheric deposition.

Possible anthropogenic enrichment of trace elements in Florida lakes was investigated by Thompson (1981), who analyzed the vertical distribution of aluminum, cadmium, chromium, cobalt, iron, lead, manganese, nickel, and zinc in a series of sediment cores collected from seven lakes located throughout peninsular Florida. All of the lakes included in the survey were seepage lakes located along the Central Florida Ridge. Two of the lakes, Annie and Sheelar, are relatively isolated and their watersheds are protected from cultural activities. Lead concentrations were enriched by at least a factor of two above background levels (prior to significant population growth in Florida) in the surficial sediments in all of the lakes studied (Table 4.3-5). Modest enrichment of cadmium and nickel also was observed in all of the study lakes and Thompson attributed the increases in deposition of lead in particular to a combination of factors including the use of leaded gasoline, industrial and municipal incineration of waste materials, and the combustion of fossil fuels. Enrichment ratios of lead (2.3 to 5.6) were lower than values reported by Galloway and Likens (1979) for several lakes in the northeastern United States (4.3 to 150).

### Watershed Effects

The interaction of acidic deposition with a lake occurs both directly via deposition on the lake surface and indirectly through ground water seepage and surface runoff, of which the chemistry reflects biological and weathering transformations. The magnitude of the watershed soils effect on surface water acidification depends both on the chemical changes that occur as precipitation moves through the watershed and the relative contributions of runoff and seepage to the overall hydrology of the receptor lake or stream.

Generally, stream and lakewater chemistry closely reflects the soil or rock conducting the flow to the receptor system; however, if the hydrologic flow paths are restricted or the residence time of water is brief resulting in limited soil contact, surface water chemistry will more closely mimic precipitation (Bache, 1983). Eilers *et al*. (1983) determined through discriminant analysis that hydrologic parameters were

Table 4.3-5. Surface Enrichment Ratios (R) for Metals in Surface Lake Sediments—Florida Lakes

| Lake | Cd | Cr | Co | Cu | Fe | Mn | Ni | Pb | Zn | Subsurface Sample Depth (cm) |
|---|---|---|---|---|---|---|---|---|---|---|
| Conway | 3.1 | 3.4 | 2.0 | 6.2 | 1.4 | 3.1 | 2.5 | 3.1 | 2.5 | 6-7 |
| Geneva | 4.0 | 1.9 | 4.0 | 2.8 | 1.3 | 1.3 | 2.0 | 5.6 | 2.2 | 4-5 |
| Annie A | 4.3 | 1.0 | 1.7 | 4.8 | 1.9 | 2.2 | 2.5 | 2.8 | 24 | 16-18 |
| Annie B | 5.0 | 1.1 | 2.0 | 5.0 | 1.8 | 2.9 | 1.8 | 2.7 | 13 | 16-18 |
| Lowery | 1.6 | 2.0 | 1.1 | 1.5 | 1.9 | 0.6 | 1.2 | 2.4 | 4.8 | 10-12 |
| Brooklyn | 2.5 | 1.1 | 1.1 | 1.0 | 1.5 | 1.1 | 1.2 | 3.2 | 1.0 | 10-12 |
| Sheelar A | 2.8 | 1.4 | 0.9 | 1.1 | 1.7 | 3.1 | 1.2 | 3.6 | 3.2 | 16-18 |
| Sheelar B | 1.6 | 2.5 | 0.7 | 2.4 | 2.1 | 1.6 | 2.6 | 6.7 | 3.3 | 16-18 |
| Weir | 2.2 | 1.3 | 2.3 | 1.2 | 1.1 | 1.2 | 1.3 | 2.3 | 3.2 | 16-18 |

Note: Values in table are defined as:

$$R = \frac{[Me]_s/[Al]_s}{[Me]_{ss}/[Al]_{ss}}$$

where: $[\ ]_s$ = concentration in the surface sediment,
$[\ ]_{ss}$ = concentration in the subsurface sediment,
Me = metal, and
Al = aluminum.

Source: Thompson, 1981.

the most important variables differentiating between a series of low- and high-alkalinity lakes in Wisconsin. The lowest alkalinity lakes were characteristically seepage lakes with water chemistry closely reflecting precipitation inputs.

Further support of the importance of watershed hydrology on the pH and ANC regime of lakes is provided by sensitivity analysis performed by Booty and Kramer (1984) of a coupled, geochemical and hydrological model for a small catchment (1 $km^2$) dominated by podzol-type soils. Booty and Kramer's analysis demonstrated that hydrological parameters such as quantity of saturated flow, field capacity, and surface soil permeability exerted more influence than weathering effects. However, it should be noted that Booty and Kramer's model was restricted to inorganic processes and the additional influence of biological processes on the model results is unknown.

Within Florida, Booty and Kramer's (1984) model analysis appears consistent with results of the softwater lake survey conducted by Hendry and Brezonik (1984; Hendry, 1983) in the Trail Ridge and Highlands Ridge lake districts in north- and south-central Florida, respectively. Using pH as the segregating variable, Hendry and Brezonik defined two statistically distinct groups of lakes: an acidic group comprising 10 lakes with mean pH 5.25 or less and a nonacidic group of 10 lakes with annual mean pH 5.75 or greater. Members of the acidic group were found exclusively in the Trail Ridge district, whereas the nonacidic group included lakes from both lake districts, suggesting that some regional phenomenon is contributing to the observed distribution of lake acidity. Watersheds in both districts are topographically similar and are characterized by highly weathered, acidic entisols. The distinction in acidity between the two groups of lakes thus does not appear to reflect differences in overall watershed soil chemistry and weathering but rather some other factor. One mechanism may reflect an approximately twofold higher rate of proton deposition via wet deposition in north-central

Florida relative to south-central Florida (ESE, 1985). Another mechanism may be differences in relative inputs of ground water between the Trail and Highlands Ridge lake districts (ESE, 1985). The 20 lakes studied by Hendry and Brezonik are seepage lakes; lake hydrology is controlled by precipitation directly to the lake surface, seepage of groundwater both to and from the lake, and evaporation from the lake surface. Surface inflow and discharge are negligible. Examination of differences between annual mean precipitation and pan evaporation infers that ground water inputs to the Highlands Ridge lakes are nearly 50 percent greater than inputs to the Trail Ridge lakes. Given the significant degree of buffering of infiltrating and percolating rainwater demonstrated within the Lake McCloud watershed in the Trail Ridge (Byers, 1984; ESE, 1985), it seems likely that hydrology (specifically inseepage) exerts a profound influence on the pH regime of softwater Florida lakes.

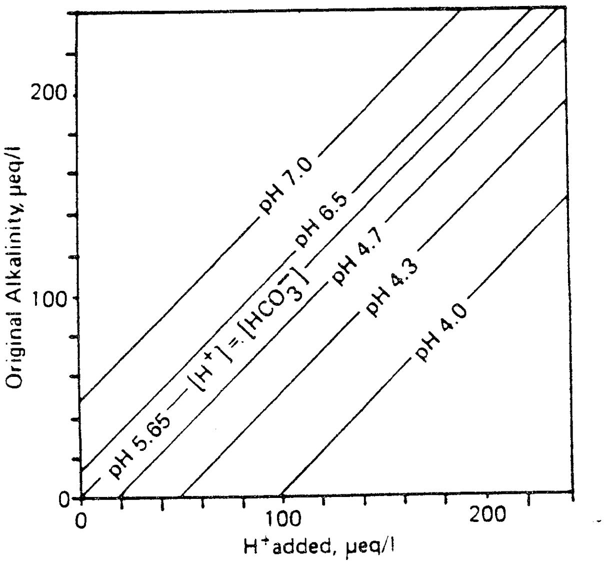
## Predictive Modeling

Modeling the acidification process in lakes has taken a variety of different approaches ranging in complexity from simple empirical formulations such as the Henriksen nomograph (Henriksen, 1980) to complex mechanistic models such as the Integrated Lake-Watershed Acidification Study (ILWAS) model (Chen *et al*., 1984). To date, modeling the potential effects of acidic deposition on the chemistry of Florida lakes has been limited to the application of the Henriksen empirical model by Baker *et al*. (ESE, 1985) to a group of softwater lakes in the sandhills of north- and south-central Florida. As part of their analysis, Baker *et al*. (ESE, 1985) also developed the empirical and theoretical framework of a relatively simple mechanistic model that accounts for the major processes in softwater Florida lakes contributing to internal ANC consumption and production. This section briefly reviews some of the more important models that have been developed and focuses on the model developed by Baker *et al*. (ESE, 1985) and its application to softwater lakes in Florida.

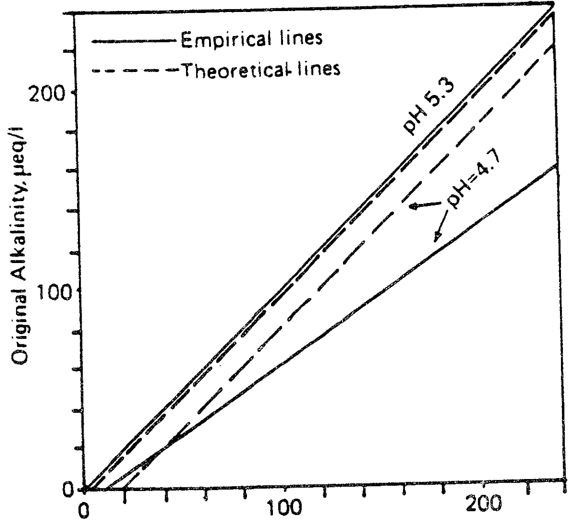
### Henriksen Predictor Nomograph

The Henriksen nomograph (Henriksen, 1979 and 1980) has been used extensively throughout Scandinavia and North America to evaluate the extent of lake acidification. The model is founded on the hypothesis that lake acidification proceeds as a large-scale titration of bicarbonate in lake water by strong acid inputs, $H_2SO_4$ in particular (Figure 4.3-16a). Weathering provides ANC to the lake and acidic deposition delivers the strong acid inputs. The pH at any point in time can be represented as a balance between the ANC originally present and acid inputs, which are represented by excess concentrations of $SO_4^{-2}$ (i.e., the $SO_4^{-2}$ in lakewater not accounted for by sea-salt contributions).

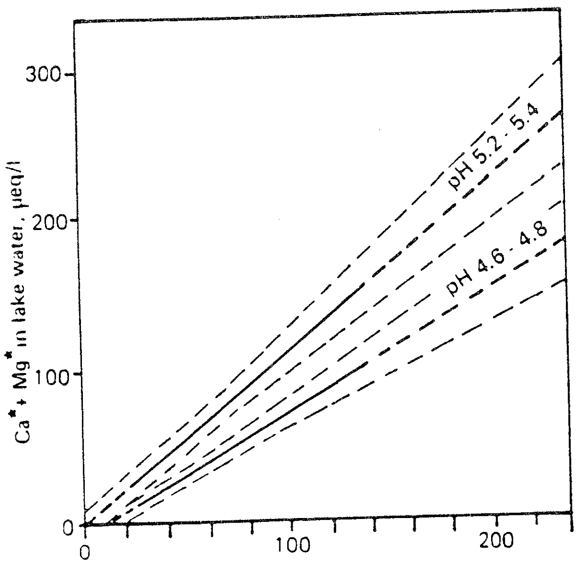
In oligotrophic softwater lakes uninfluenced by acidic deposition, Henriksen (1980) observed that concentrations of non-marine or excess $Ca^{+2}$ and $Mg^{+2}$ are approximately balanced by bicarbonate. As



**A.** *pH-contour nomograph depicting expected pH levels as the result of titration of bicarbonate solutions by strong acid in equilibrium with atmospheric $CO_2$.*

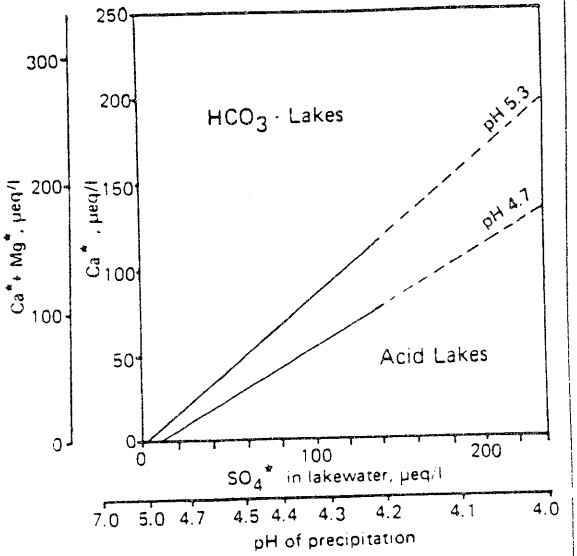


**C.** *The regression lines in Fig. depicted in the pH-contour nomograph (Fig. 5). The non-marine sulphate concentration in the lakes are assumed equal to the amount of acid added and the sum of non-marine calcium and magnesium concentrations are assumed proportional to the original alkalinity. (Alk = 0.91·(Ca* + Mg*)).*



**B.** *Regression lines for the sum of non-marine calcium and magnesium on non-marine sulphate for lakes in southern Norway in the pH-range 5.2 – 5.4 and in the pH-range 4.6 – 4.8. Thin broken lines depict the 95 % confidence limits for the regression lines.*

| *pH-range* | $\overline{pH}$ | *Regression equation* | *r* | *n* |
|---|---|---|---|---|
| 5.2 – 5.4 | 5.28 | $Ca^* + Mg^* = -5 + 1.13\ SO_4^*$ | .96 | 58 |
| 4.6 – 4.8 | 4.69 | $Ca^* + Mg^* = -11 + .75\ SO_4^*$ | .85 | 207 |



**D.** *A nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations or non-marine calcium concentration only and the non-marine sulphate concentration in lake water or the weighted-average hydrogen ion concentration in precipitation. The non-marine sulphate concentrations in lakes are linearly related to weighted-average hydrogen ion concentration of precipitation at each lake. Data for 59 lakes in granitic basins in southern Norway sampled as part of a regional survey in 1974 showed that non-marine sulphate in lakewater ($[SO_4^*]_L$) is highly correlated to non-marine sulphate concentrations (µeq/l) in precipitation ($[SO_4^*]_P$)[14]: $[SO_4^*]_L = -19 + 1.9\ [SO_4^*]_P$, $r = 0.84$. In turn non-marine sulphate and $H^+$ concentrations in precipitation are linearly related as shown by data obtained for precipitation collected July 1974 – June 1975 at 33 stations in southern Norway[4]: $[SO_4^*]_P = -2.7 + 1.37\ [H^+]_P$, $r = 0.89$, where $[H^+]_P$ is the weighted-average $H^+$ concentration (µeq/l) in precipitation. Combining these regression lines gives $[H^+]_P = 9 + 0.38\ SO_4^*$ which provides the pH scale for the abscissa.*

## Figure 4.3-16
## HENRIKSEN NOMOGRAPHS

HENRIKSEN, A. 1980. ACIDIFICATION OF FRESHWATERS—A LARGE SCALE TITRATION. IN: ECOLOGICAL IMPACT OF ACID PRECIPITATION. D. DRABLOS AND A. TOLLMAN, EDITORS. PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON ACID PRECIPITATION, SANDEFJORD, NORWAY.

acidification proceeds, bicarbonate is replaced with $SO_4^{-2}$. Assuming that acidification does not accelerate the release of base cations, the degree of acidification can be estimated theoretically by the relative contribution of excess $SO_4$ to the sum of excess $Ca^{+2}$ and $Mg^{+2}$. This hypothesis was examined by regression analyses of two sets of lakes based on pH (5.2 to 5.4 and 4.6 to 4.8) (Figure 4.3-16b). For the group of higher pH lakes, the regression coincides with the theoretical line indicating that lakes behave as pure bicarbonate solutions when strong acid is added until the pH falls below 5.3 (Figure 4.3-16c). For the group of lower pH lakes, the regression line falls below the theoretical line for pH 4.7 indicating that the pH of lakes within this particular class is higher than predicted. The deviation between observed and theoretical pH values was explained in part by the increasing importance of aluminum in the ionic balance at low pH. By considering $Al^{+3}$, the regression line approximated the theoretically derived line.

These relationships were used by Henriksen to construct his predictor nomograph (Figure 4.3-16d). The nomograph establishes three classes of lakes as a function of excess $SO_4^{-2}$ or rainfall pH and the sum of excess $Ca^{+2}$ and $Mg^{+2}$. Henriksen used regression analysis with data collected from 59 lakes in granitic watersheds in southern Norway to establish the relationship between lakewater excess $SO_4^{-2}$ concentrations and rainfall pH reflected on the abscissa of the nomograph. Henriksen classified lakes above the pH 5.3 line in the nomograph as bicarbonate-dominated; lakes below the pH 4.7 line as strong acid lakes; and lakes with intermediate pH of 4.7 to 5.3 as transition lakes. Henriksen (1980) used the nomograph to predict the pH range of an independent set of 155 Norwegian lakes and reported that 85 percent of the lakes were correctly classified.

Baker _et_ _al_. (1985) evaluated the applicability of the Henriksen model to Florida lakes using the data base of 20 softwater lakes in north- and south-central Florida originally studied by Brezonik _et_ _al_. (1983).

Application of the Henriksen model was not particularly successful (Figure 4.3-17), and attempts to improve the fit of the model to the lakewater data were not helpful. These attempts included reevaluating the pH relationship between excess $SO_4^{-2}$ and the sum of excess $Ca^{+2}$ and $Mg^{+2}$ using the FLADAB database (Huber et al., 1983) and correcting for background $SO_4^{-2}$ according to Wright (1983). The inability of the Henriksen model to predict the pH in softwater Florida lakes was attributed to the assumptions inherent in the model and the failure of those assumptions to be met in Florida. One major limitation is the assumption that sulfate behaves conservatively in aquatic systems. Several studies (both in situ and in laboratory microcosms) of the dynamics of sulfate in Florida lakes have demonstrated significant removal of sulfate from lakewater and the concomitant production of ANC (Baker, 1984; ESE, 1984; ESE, 1985).

The apparent failure of the Henriksen model also reflects the fact that internal ANC generating mechanisms such as sulfate reduction may neutralize a substantial portion of acidic deposition without the production of cations. Because the hydrologic budgets of seepage lakes are apparently dominated by precipitation directly to the lake surface (cf. Baker, 1984), lakewater probably has less contact with the watershed than lakewater in regions where streamflow dominates water input. Consequently, mineral weathering and ion exchange are less likely to be the dominant processes controlling ANC production in Florida seepage lakes. Rather, evaporation appears to have a significant role in determining the ionic character of these systems, both from the perspective that the net balance of precipitation and evaporation controls the magnitude and direction of seepage as well as consideration that net evaporation has a concentrating effect on constituent concentrations.

Model of Acidification of Groundwater in Catchments (MAGIC)

Cosby et al. (1985a) recently developed a model designed to account for

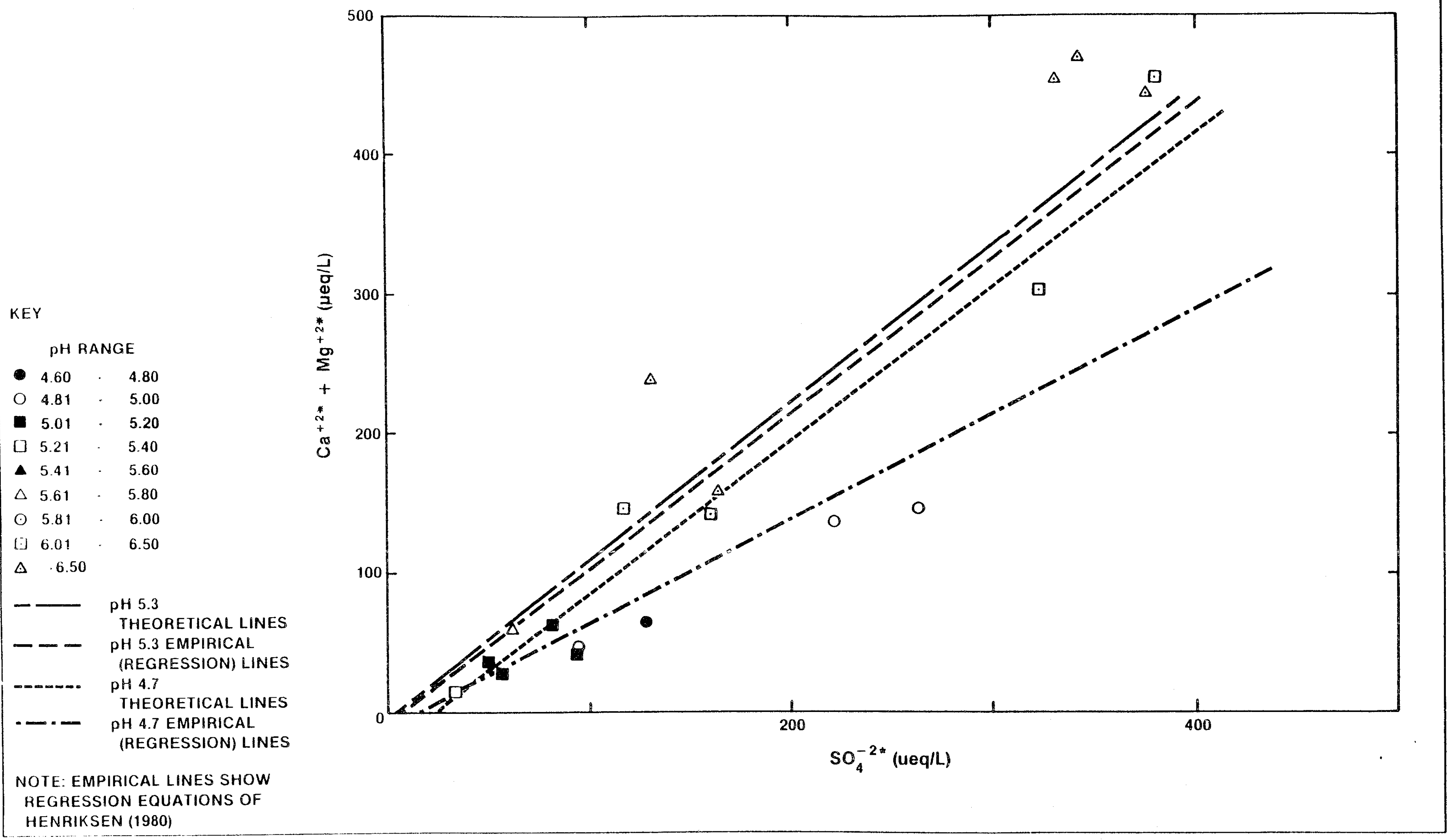


**Figure 4.3-17**
$Ca^{+2*}$ + $Mg^{+2*}$ VERSUS $SO_4^{-2*}$ FOR 20 FLORIDA LAKES

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the most serious effects of acidic deposition on surface water chemistry in catchments, viz., reductions in ANC and pH and increased export of base cations and aluminum. Because the model is based on the premise that reactions in the soils and rocks within a catchment dictate surface water chemistry, Cosby et al. (1985a) entitled their model MAGIC. Cosby et al. (1985a) postulate that the major observed effects of acidification can be represented by a relatively small number of soil processes including:

1. Anion retention (e.g., sulfate adsorption),
2. Cation exchange,
3. ANC generation from the production of carbonic acid and subsequent ion exchange of protons for base cations,
4. Mineral weathering, and
5. Aluminum dissolution.

The conceptual framework of MAGIC is rooted in a relatively simple model of soil-water systems originally developed by Reuss (Reuss, 1980; Reuss, 1983; Reuss and Johnson, 1985) which uses a two-component ($Ca^{+2}$-$Al^{+3}$) system to simulate the acidification of surface waters. MAGIC expands on the Reuss and Johnson conceptual framework to include other cations and anions important in surface water chemistry. For example, Cosby et al (1985a). have expanded the cation exchange reactions considered in the model to include $Mg^{+2}$, $Na^{+}$, and $K^{+}$ and have included the complexation reactions of $F^{-}$ and $SO_4^{-2}$ with $Al^{+3}$ in the suite of reactions describing $Al^{+3}$ equilibria.

The model is not intended to describe the spatial variability of chemical processes in a particular watershed nor is it intended to fully simulate all the chemical reactions that proceed in the soil. One important set of reactions ignored by MAGIC is microbially-mediated redox reactions such as denitrification and sulfate reduction which are important sinks of nitrate and sulfate and may contribute significantly to the production of ANC in soils which periodically become anaerobic. In its simplest form, MAGIC models a catchment as two compartments: one compartment representing the catchment soils, the other the receiving stream. Acidic deposition enters the soil compartment, and the resulting change in soil-water equilibrium chemistry is calculated. Water is then routed to the stream, and the resultant streamwater chemistry is calculated thermodynamically. If necessary, model compartmentalization can be expanded to accommodate catchment-specific characteristics such as extensive profile development.

MAGIC has been applied to the forested catchment of White Oak Run, a small second-order stream in the Shenandoah National Park in Virginia, to estimate the long-term response of the soil, soil water, and surface water to changes in acidic deposition (Cosby _et_ _al_., 1985b). The model was calibrated with data collected for 1984; however, rigorous verification has not been performed because of the lack of long-term water chemistry data (Cosby _et_ _al_., 1985c). Thus the predictive capabilities of the model are not well established. Modeling results for this analysis demonstrated that response is highly influenced by the nonlinearity of the model processes. This is particularly evident for $SO_4^{-2}$ adsorption. As increasing quantities of $SO_4^{-2}$ were loaded to the soil and the adsorption capacity of the soil was approached, an increasingly larger fraction of $SO_4^{-2}$ deposited was exported. A corresponding acceleration in watershed response was observed reflecting the relative loss of $SO_4^{-2}$ adsorption sites, and Cosby _et_ _al_. (1985b) indicate that acidification of surface water in catchments similar to White Oak Run is likely to proceed more rapidly in the future. Should $SO_4^{-2}$ deposition rates decrease, watershed response will be dictated by the reversibility of $SO_4^{-2}$ adsorption. Cosby _et_ _al_. (1985b) indicate that recovery of the water quality of the catchment should be rapid initially and then decelerate as $SO_4^{-2}$ is desorbed. If $SO_4^{-2}$ adsorption is partially reversible, the recovery response correspondingly becomes more rapid.

Subsequent modeling of hypothetical catchments using MAGIC by Cosby et al. (1985c) indicates that catchments with low $SO_4^{-2}$ adsorption capacity and low base saturation (which is characteristic of watersheds in the sandhills of the Central Florida ridge) respond quite rapidly to changes in acidic deposition (on the order of a few years to a decade).

### Trickle-Down Model

Schnoor et al. (1983 and 1984) have developed an alkalinity or ANC mass-balance model that uses a compartmentalized approach to trace the flux of ANC through a watershed in response to acidic deposition. The ANC mass-balance model consists of an open system of $CO_2$ and water which undergoes titration with strong acids and bases derived from external inputs (i.e., atmospheric deposition) as well as internal processes. In the present formulation of the model, these processes are aggregated or lumped together into a single kinetic formulation for individual compartments. The watershed is segregated into a series of discrete compartments including the soils participating in surface runoff, the unsaturated zone, the water-table aquifer, and surface waters. The rate constant for weathering reactions is assumed to be proportional to some fractional power of the $H^+$ concentration. By summing and averaging the ANC contributions over an entire watershed, ANC in a lake can be modeled by the following expression:

$$V \frac{dA}{dt} = -IL_{acy}(1 - f) - QA + kV$$

where: $L_{acy}$ = acidity of precipitation (μeq/L),
I = precipitation volume (L/y),
Q = outflow rate (L/y),
k = zero-order neutralization rate by sediments (μeq/L/y), and
f = fraction of acid neutralized in the watershed.

The solution at any given point in time is:

$$A = \left(A_o e^{-Qt/V}\right) + \left[\frac{kV}{Q} - \frac{I}{Q} \quad L_{acy}(1 - f)\right] (1 - e^{-Qt/V}),$$

with the steady-state solution:

$$A = \frac{kV}{Q} - \frac{I}{Q} L_{acy}(1 - f).$$

The steady-state alkalinity concentration of a lake thus represents the net balance of ANC inputs from neutralization reactions in the sediments and the fraction of acid inputs which are not neutralized by watershed processes. Stumm *et al*. (1983) and Schnoor *et al*. (1983) have used the steady state solution to the trickle-down model to develop a nomograph predicting lakewater pH as a function of acid loading rates and the fraction of the acid load neutralized by the watershed (Figure 4.3-18). Stumm *et al*. (1983) indicate that neutralization by the sediments can be neglected in lakes with watershed drainage areas larger than the surface area of the lake and excluded internal processes from the nomograph. For Florida seepage lakes, the assumption that internal neutralization processes are negligible is tenuous and probably not valid. Application of the model to predict steady state pH and ANC concentrations as a result of changes in acidic deposition rates requires knowledge of the change in the fractional neutralization of acidity by the watershed. It is this variable which represents the greatest amount of uncertainty in the model. Sensitivity analysis of the trickle-down model for a small watershed in northern Minnesota demonstrated that the predicted surface water pH was particularly sensitive to hydrologic flow rates and chemical weathering rates (Schnoor *et al*., 1984).

### ILWAS

The ILWAS model (Chen *et al*., 1979, 1983, and 1984) is conceptually the most ambitious model developed to date for the evaluation of acidic

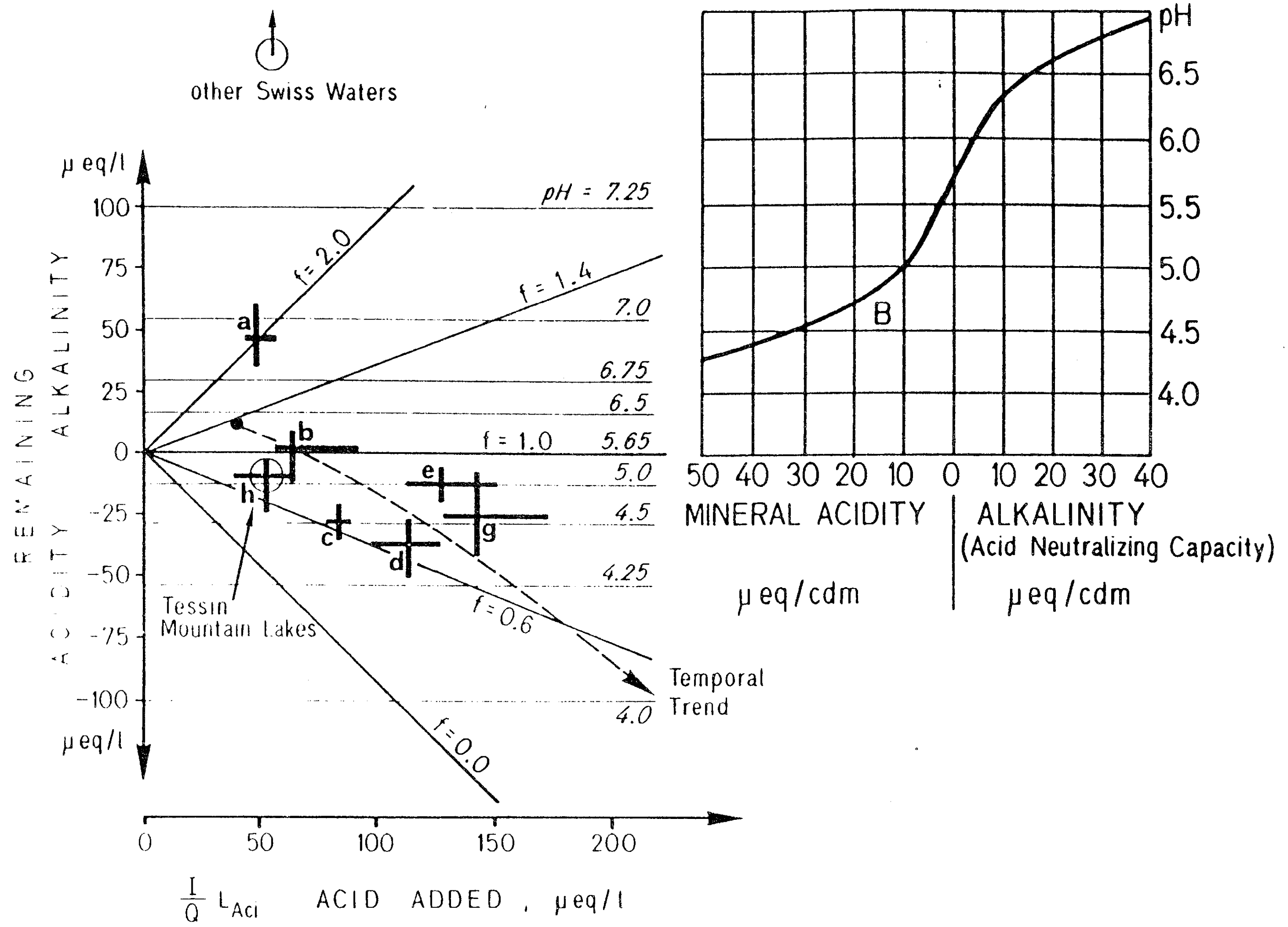

Figure 4.3-18
ALKALINITY OF NATURAL WATERS AS A
FUNCTION OF ACID LOADING

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deposition effects on watersheds. The ILWAS model is designed to calculate surface and ground water chemistry for a particular watershed as a function of time varying inputs such as precipitation chemistry and quantity, temperature, and ambient air quality. ILWAS was developed from an extensive database developed for three lakes in the Adirondack Mountains in close proximity to one another (~30 km) but with differing chemical responses to similar inputs of acidic deposition (cf. Galloway et al., 1983). Despite the differing natures of the three lakes, the conceptual framework for the model is consistent in its application to each of these lakes and should be applicable to systems beyond the Adirondacks.

To account for spatial heterogeneity within a watershed, the ILWAS model represents the watershed as a series of compartments, each of which is considered to be homogeneous. Compartmentalization occurs both horizontally in the watershed (Figure 4.3-19) and vertically (Figure 4.3-20). Major compartments include the forest canopy, snowpack, the surface litter layer, soil organic layer, soil inorganic layers, stream segments, and the lake which also can be subdivided vertically to account for thermal stratification. Each compartment is considered well-mixed and is modeled as a continuous stirred reactor. Chemical transformations and fluxes for each compartment are described by a set of hydrologic and biogeochemical processes specific for the compartment. For example, stream segments include advection, dilution, evaporation, $CO_2$ exchange, thermal transfer, and chemical equilibria (using pH, total aluminum concentrations, ANC, and organic acids as variables) as model processes. In order to simulate a lake compartment, the list of key processes is expanded to include diffusion, algal uptake of nutrients, nitrification, aluminum precipitation, and decomposition. ILWAS also simulates dry deposition as a function of air chemistry and includes oxidation of gaseous $SO_2$ and $NO_x$ in the lake. The full suite of biogeochemical processes considered in ILWAS have been summarized by Chen et al. (1983).

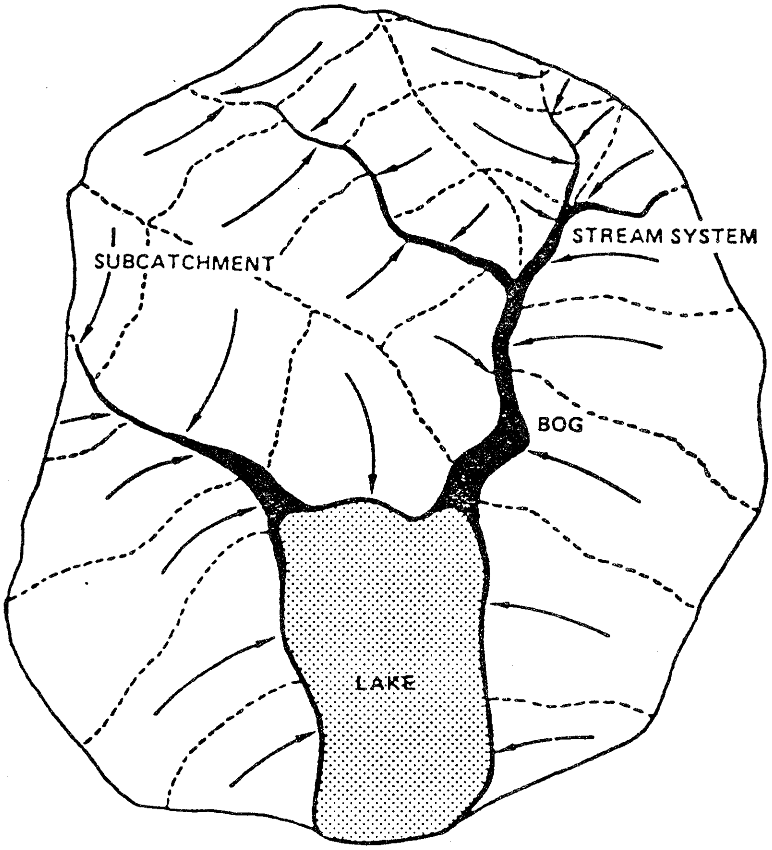

Figure 4.3-19
HORIZONTAL SEGMENTATION OF THE ILWAS MODEL SYSTEM INTO LAND SUBCATCHMENTS, STREAM SEGMENTS, AND A LAKE

SOURCE: CHEN *et al*., 1983.

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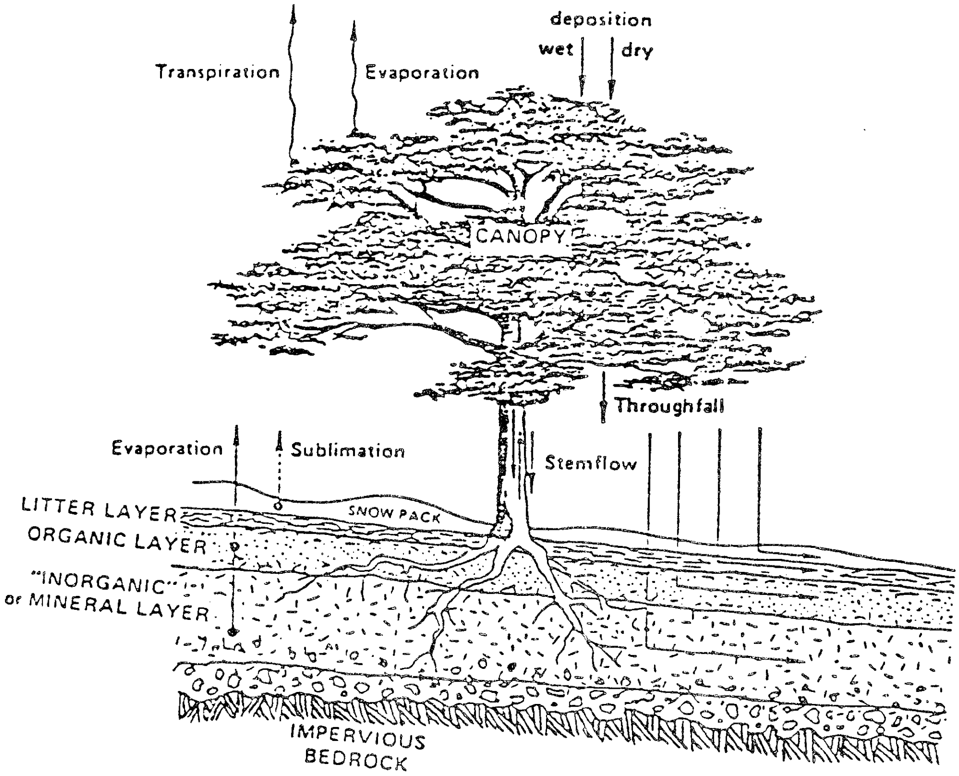

Figure 4.3-20
SUBCATCHMENT VERTICAL SEGMENTATION OF THE ILWAS MODEL

SOURCE: CHEN et al., 1983.

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The conceptual completeness of process description and formulation of the ILWAS model makes the model very attractive as a tool for hypothesis testing. ILWAS has been used to test some 40 hypotheses including an evaluation of the hypothesis that the differences in chemistry between Woods Lake (pH 45 to 5.5) and Panther Lake (pH 7) reflects differences in the depth of till in the lakes' tributary watersheds (Chen et al., 1983). This particular analysis confirmed that lakewater pH for the Adirondack lakes critically depends on the flowpaths taken by water before reaching the lake itself.

## Model Of Internal ANC Generation And Consumption

As part of the Florida Acid Deposition Study, Pollman et al. (ESE, 1985) developed a relatively simple acidification model for Florida seepage lakes that focuses on internal (i.e., within the lake) processes that produce or consume ANC. Development of the model proceeded from an evaluation of long-term changes of major constituents and ANC in the water column of 20 softwater lakes in north- and south-central Florida (ESE, 1985). This analysis was performed through the application of ion enrichment ratios to determine if lakewater concentrations of a particular constituent were enriched relative to atmospheric inputs. The effects of evapoconcentration on lakewater concentrations were removed by normalizing precipitation and lakewater concentrations to respective concentrations of chloride. From their analysis Pollman et al. (ESE, 1985) concluded that ANC dynamics of these lakes reflects to a significant degree internal biogeochemical processes resulting in depletion of sulfate, nitrate, and ammonium. Weathering contributions are also quite important, as evidenced by differences in cation enrichment between lakes in the Highlands Ridge (south-central Florida) and the Trail Ridge lakes (north-central Florida) and significant differences in proton neutralization observed between these two sets of lakes (ESE, 1985). These differences are apparently driven by differing hydrologic regimes; evaporation is relatively greater for lakes in the

Highlands Ridge resulting in relatively more inseepage from the watershed over long periods of time.

Internal ANC dynamics were incorporated in the model by considering $SO_4^{-2}$ reduction and $NO_3^-$ immobilization as the principal ANC-generating processes and ammonium uptake as a major ANC-consuming process. Using a mass-balance approach to describe the dynamics of ANC, the model of Pollman et al. (ESE, 1985) is written as a series of coupled differential equations:

$$\frac{d[ANC]}{dt} = 1/V\{L_{alk} + k_{SO_4}A[SO_4^{-2}] - [ANC]S_o\} - k_{NH_4}[NH_4^+] + k_{NO_3}[NO_3^-]$$

$$\frac{d[SO_4^{-2}]}{dt} = 1/V\{L_{SO_4} - [SO_4^{-2}](S_o + k_{SO_4}A)\}$$

$$\frac{d[NH_4^+]}{dt} = 1/V\{L_{NH_4} - [NH_4^+](S_o + k_{NH_4}V)\}$$

$$\frac{d[NO_3^-]}{dt} = 1/V\{L_{NO_3} - [NO_3^-](S_o + k_{NO_3}V)\}$$

where: [i] = concentration of i [milliequivalents per cubic meter ($meq/m^3$)],
A = area ($m^2$),
V = lake volume ($m^3$),
$S_o$ = seepage outflow [cubic meters per year ($m^3/yr$)],
$L_i$ = loading of constituent i (meq/yr),
$k_{SO_4}$ = apparent settling velocity for $SO_4^{-2}$ [meters per year (m/yr),]

$k_{NO_3}$ = first-order uptake constant for $NO_3^-$ ($yr^{-1}$), and
$k_{NH_4}$ = first-order uptake constant for $NH_4^+$ ($yr^{-1}$).

The loading term of the model is a lumped parameter representing total loading from all sources (wet and dry atmospheric inputs plus inseepage). Sedimentary contributions to ANC generation are modeled as an output of sulfate across the sediment-water interface; i.e. sulfate losses due to sulfate reduction are described by an apparent settling velocity. This representation of sulfate dynamics is functionally equivalent to the first-order kinetics Baker and Brezonik (ESE, 1985) used to describe sulfate losses in microcosm studies conducted as part of a series of experiments for the Florida Acid Deposition Study designed to evaluate the role of sulfate reduction as an internal source of ANC. However, the concept of modelling sulfate reduction and the coupled production of ANC in terms of an apparent settling velocity for sulfate is more consistent with the fact that sediment-water dynamics are properly considered as an areal process rather than a first-order reaction occurring in the water column (cf. Berner, 1971 and 1980; Lerman, 1979; Perry et al., 1986). ANC contributions from weathering reactions are poorly understood for seepage lakes in Florida, and in the absence of an appropriate formulation Pollman et al. (ESE, 1985) assumed weathering is constant (i.e., a zero-order process). A variety of empirical and simulation studies indicates that weathering increases as acid loading rates increase (cf. Stumm et al., 1983; Talbot and Elzerman, 1985; Cosby et al., 1985c; Afifi et al., 1985), and this simplification may represent a major limitation to the model. However, it is important to note that not all weathering reactions are enhanced by acid inputs or reductions in pH. Consider, for example, silicate mineral weathering. Because quartz dissolution is promoted by the presence of strong base, silicate minerals rich in silica-oxygen linkages are resistant to acid weathering (Johnson, 1984).

Insufficient hydrologic and chemical data are available to properly calibrate and verify the model developed by Pollman et al. (ESE, 1985) for softwater seepage lakes. However, some insight regarding the sensitivity of the model and the relative importance of various processes included in the model can be obtained by evaluating model performance through the use of ion budgets. Baker, Brezonik, and Pollman (unpublished data) have constructed ion budgets for two relatively pristine seepage lakes, Lowry and Magnolia, located in the Trail Ridge region. These lakes were selected in favor of lakes in other regions considered sensitive (i.e., the highlands of the panhandle and south-central Florida) principally because of the lack of data for lakes in these other regions. These budgets are based on comparison of lakewater chemistry observed between two points in time separated by approximately 10 years.

Chemical data for Lowry and Magnolia Lakes were collected in 1968 and 1969 by Brezonik and Shannon (1971) and again in 1978 and 1979 by Brezonik et al. (1983). Sampling was conducted every 4 months ($n = 3$) in the early study by Brezonik and Shannon (1971) and quarterly ($n = 4$) by Brezonik et al. (1983). In both studies, vertically composited samples were collected. Changes in mass storage for $H^+$, ANC, $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ in each lake were based on changes in water chemistry and volume (inferred from lake stage measurements and hypsographic curves for both lakes). Atmospheric loading rates for each of these ions were based on wet-deposition fluxes measured between September 1982 and September 1983 by ESE (1984) and dry-deposition estimates derived from dry-bucket determinations of ANC and $NH_4^+$ and ambient air concentrations of gaseous $SO_2$, $NO_2$, and $HNO_3$, and particulate $SO_4^{-2}$ (ESE, 1985). These fluxes were assumed representative of total deposition observed annually between 1969 and 1979. Insufficient monitoring data are available to support this assumption, and errors inherent in this assumption will be reflected in the model performance of predicting ANC concentrations. Seepage hydrologic contributions were estimated monthly by comparing precipitation and pan evaporation measurements from the Gainesville NWS station with changes in lake stage measured at each lake. Changes in stage (and hence lake volume) were compared to precipitation inputs and estimated evaporative losses on a monthly basis between October 1969 and September 1979. Seepage hydrologic contributions were determined by difference for each month, and average annual gross seepage inflow and outflow rates were used as input parameters to the model. Since chemical quality of inseepage was not measured for these two lakes, Baker, Brezonik, and Pollman assumed that the chemistry was similar to inseepage chemistry measured by Baker (1984) at Lake McCloud, also located in the Trail Ridge district. Despite the more exhaustive chemical database available for Lake McCloud, ion budgets for this lake were not constructed because the absence of long-term lake stage data precluded the development of monthly seepage estimates.

Ion budgets constructed for Lowry and Magnolia Lakes are presented in Tables 4.3-6 and 4.3-7 for the period 1969 to 1979. These budgets are sensitive to errors in dry-deposition estimates, evaporation losses, and seepage inputs. Errors in seepage contributions can arise principally from two sources: (1) seepage is determined by difference and will reflect estimation errors of evaporation losses; and (2) the assumptions that seepage chemistry is invariant over this relatively short period of time and is similar to Lake McCloud seepage chemistry have not been substantiated. Pan evaporation was used to estimate evaporative losses, and errors inherent in this approach (cf. Eagleson, 1970) can lead directly to errors in seepage estimates. Because seepage flows are determined by difference, errors in precipitation estimates and changes in lake volume will also result in errors in seepage; however, in the long term, the greatest uncertainty lies with the determination of evaporative losses. Despite these limitations, comparison of calculated model results for the conservative (i.e., assumed to be nonreactive with no internal sources) constituent chloride shows relatively good agreement between concentrations measured in 1979 and concentrations predicted from

Table 4.3-6. Ion Chemistry and Loading Rates for Lowry Lake

| | Change in Storage in Water Column | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1969 | | 1979 | | Change in | | | | | Seepage Inputs | |
| Constituent | Conc. (µeq/L) | Storage (keq) | Conc. (µeq/L) | Storage (keq) | Storage (keq) | Wet Deposition (eq/ha-yr) | Wet Deposition (keq/yr) | Dry Deposition (eq/ha-yr) | Dry Deposition (keq/yr) | Conc. (µeq/L) | Loading (keq/yr) |
| $H^+$ | 4.2 | 107 | 7.0 | 178 | 71 | 510 | 266 | 167 | 87 | 1.1 | 1 |
| $NH_4^+$ | 1.4 | 36 | 3.6 | 91 | 56 | 126 | 66 | 45 | 23 | 3.1 | 2 |
| $SO_4^{-2}$ | 79.1 | 2,009 | 68.0 | 1.727 | -282 | 408 | 209 | 150 | 78 | 38.0 | 26 |
| $Cl^-$ | 135.2 | 3,434 | 132.0 | 3,353 | -81 | 191 | 100 | 105 | 55 | 33.0 | 23 |
| $NO_3^-$ | 7.1 | 180 | 1.4 | 36 | -145 | 174 | 91 | 54 | 28 | 4.0 | 3 |
| $HCO_3$ | 6.0 | 152 | 5.0 | 127 | -25 | 0 | 0 | 45 | 23 | 124.8 | 86 |

keq = kiloequivalents.
keq/yr = kiloequivalents per year.
Seepage volume = 7.01 x $10^5$ $m^3$ input.
14.68 x $10^5$ $m^3$ output.

Source: Baker, Brezonik, and Pollman (unpublished data).

Table 4.3-7. Ion Chemistry and Loading Rates for Magnolia Lake

| | Change in Storage in Water Column | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1969 | | 1979 | | Change in | | | | | Seepage Inputs | |
| Constituent | Conc. (µeq/L) | Storage (keq) | Conc. (µeq/L) | Storage (keq) | Storage (keq) | Wet Deposition (eq/ha-yr) | Wet Deposition (keq/yr) | Dry Deposition (eq/ha-yr) | Dry Deposition (keq/yr) | Conc. (µeq/L) | Loading (keq/yr) |
| $H^+$ | 2.8 | 18 | 12.7 | 81 | 63 | 510 | 41.8 | 167 | 13.7 | 1.1 | 0.1 |
| $NH_4^+$ | 2.9 | 19 | 2.9 | 19 | 0 | 126 | 10.3 | 45 | 3.7 | 3.1 | 0.3 |
| $SO_4^{-2}$ | 68.7 | 439 | 60.4 | 386 | -53 | 401 | 32.9 | 150 | 12.3 | 38.0 | 4.0 |
| $Cl^-$ | 128.7 | 823 | 125.6 | 803 | -20 | 191 | 15.7 | 105 | 8.6 | 33.0 | 3.4 |
| $NO_3^-$ | 7.0 | 45 | 1.9 | 12 | -33 | 174 | 14.2 | 54 | 4.4 | 4.0 | 0.4 |
| $HCO_3$ | 8.0 | 51 | 5.0 | 32 | -19 | 0 | 0.0 | 45 | 3.7 | 124.8 | 13.0 |

Seepage volume = 1.07 x $10^5$ $m^3$ input.
2.28 x $10^5$ $m^3$ output.

Source: Baker, Brezonik, and Pollman (unpublished data).

estimated loadings (within 4 and 11 percent for Magnolia and Lowry Lakes, respectively) and suggests that the budgets are fairly reasonable, at least from a hydraulic perspective.

The estimated ion loadings and measured changes in lakewater chemistry can be used to derive first-order rate constants for $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ as input parameters for the ANC model developed by Baker et al. (1985). More specifically, values for first-order rate constants were derived iteratively from the analytical solution to the following differential equation describing the time dependent concentration of constituents whose behavior (unlike ANC) is not coupled with the other variables of interest (i.e., $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$):

$$\frac{d[C]}{dt} = \frac{1}{V}\left\{ L_c - [C](S_o + K_c V)\right\}$$

which has the following analytical solution:

$$C_t = \frac{L_c}{S_o + K_c V} + \left( C_o - \frac{L_c}{S_o + K_c V} \right) e^{-\left(\frac{S_o + K_c V}{V}\right) t}$$

where: $C_o$ = the concentration at time zero, and
$C_t$ = the concentration at a designated point in time, t.

With these parameters defined, model performance can be evaluated by comparing measured changes in ANC with simulated results. The model was used to simulate the change in concentration in ANC between 1969 and 1970 using a fourth-order Runge-Kutta numerical solution. Table 4.3-8 (Case 1) presents the results of this analysis. The model was initially evaluated using the estimated loadings for $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ as well as the respective rate constants calibrated from the ion budgets to predict changes in ANC concentrations. Loadings of various constituents were assumed constant over the period of simulation. Comparison of predicted

Table 4.3-8. Sensitivity Analysis of Baker et al. (1985) Model of Internal ANC Production and Consumption in Seepage Lakes

| Lake | Observed ANC Concentrations Initial (1969) | Observed ANC Concentrations Final (1979) | Predicted Final ANC Concentrations* Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
|---|---|---|---|---|---|---|---|
| Lowry | 1.8 | -2.0 | 23 | -3.6 | -30 | -21 | 87 |
| Magnolia | 5.2 | -7.7 | 23 | 8.0 | -6.4 | 4.9 | 56 |

*Case 1: No adjustments to loadings developed from ion budgets (Tables 4.3-5 and 4.3-6).
Case 2: Additional $NH_4$-N flux of 0.35 $mg/m^2$-day of nitrogen.
Case 3: Additional $NH_4$-N flux of 0.7 $mg/m^2$-day of nitrogen.
Case 4: Seepage fluxes reduced by 50 percent.
Case 5: Seepage fluxes increased by 100 percent.

Note: All concentrations in $meq/m^3$.

Source: ESE, 1986.

and observed ANC concentrations indicates that for both lakes the model is overpredicting ANC because of overestimation of internal and external contributions to ANC and/or the incomplete accounting of all major sources of acidity.

A potential source of acidity not explicitly accounted for in the ion budgets is the release of $NH_4^+$ from the bottom sediments to the overlying water. As decaying phytoplankton remains and other organic material are deposited in the sediments, $NH_4^+$ concentrations in the interstitial fluid can build up to levels several orders of magnitude in excess of concentrations in the overlying lakewater. [Note: ANC is released as well; however, this component (ANC) is included implicitly in the ANC estimates for inseepage used in the model.] Because of this large concentration gradient across the sediment-water interface the flux of $NH_4^+$ from the sediments to the water column can be appreciable and through algal uptake can contribute to consumption of ANC. On the basis of porewater vertical concentration profiles, Adams et al. (1982) estimated diffusive fluxes of $NH_4^+$ from Lake Erie sediments ranging from 0.7 to 17.2 mg/m$^2$-day of nitrogen. Baker (1984) reports net release rates of $NH_4^+$ from Lake McCloud sediments as high as 13.5 mg/m$^2$-day. The effect of this internal flux on model response was evaluated by initially assuming that the rate of $NH_4^+$ release from the sediments was rather low, 0.35 mg/m$^2$-day of nitrogen (Table 4.3-7, Case 2). A second analysis was performed to further test the model sensitivity to this flux by doubling the internal flux to 0.7 mg/m$^2$-day of nitrogen (Table 4.3-7, Case 3). In both cases, the $NH_4^+$ decay constant was recalibrated; all other parameters remained unchanged.

Including the release of $NH_4^+$ from the sediments greatly improved the model response. At a sediment release rate of 0.35 mg/m$^2$-day of nitrogen, the predicted ANC of -3.6 meq/m$^3$ for Lowry Lake agrees rather well with the observed concentration of -2.0 meq/m$^3$. For Magnolia Lake, the best agreement between predicted and observed ANC concentrations was obtained using the higher $NH_4^+$ release rate (0.7 mg/m$^2$-day of nitrogen). These results illustrate an important point relative to $NO_3^-$ deposition and the rapid uptake of $NO_3^-$ by phytoplankton: although $NO_3^-$ may be almost completely removed from the water column resulting in an equivalent amount of ANC production, a significant fraction of that uptake and ANC generation is subsequently offset by ammonification of organic matter in the sediments.

The sensitivity of the model to changes in seepage chemistry was also examined (Table 4.3-7, Cases 4 and 5). Constituent fluxes in seepage for all model parameters were reduced by 50 percent as one analysis (Case 4). Seepage hydrology was not manipulated, and, as with the previous model runs, the rate constants for $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ were recalibrated to the adjusted fluxes in order to isolate the effects on ANC. A variation of this analysis was also performed using constituent fluxes twice the fluxes estimated in the ion budgets (Case 5). The results of these two analyses demonstrate that the model is quite sensitive to seepage inputs and ANC estimates for seepage chemistry in particular. Relatively small changes in seepage chemistry are predicted by the model to exert significant effects on the ANC regime of seepage lakes--a finding that underscores the need to understand and adequately characterize the hydrologic and chemical interaction of watersheds with seepage lakes. In view of these findings, one possible modification to the model would be to dispense with the black-box approach to watershed processes and couple the in-lake (and sediment interaction) portion of the model with a watershed model such as Cosby <u>et al</u>.'s (1985a, 1985b, and 1985c) ground water acidification model, MAGIC. MAGIC is particularly attractive because initial simulation studies of a small forested catchment performed by Cosby <u>et al</u>. suggest that the model appears to account for all the major processes [with the possible exceptions of biologically mediated redox processes and organic (DOC) interactions] controlling the interaction of acidic deposition with ground water within a relatively simple framework; the Pollman <u>et al</u>. (ESE, 1985) model in turn focuses on the principal internal processes regulating ANC consumption and production in seepage lakes. It should be observed, however, that the applicability of MAGIC to seepage lake watersheds in Florida is untested.

Summary of Predictive Modeling

Model development and application to describe processes such as lake acidification can be viewed as an evolutionary or iterative process: each stage of model development draws upon the results and uncertainty apparent in the modeler's perception of the system in the previous developmental stage. Through application of models, the fundamental processes controlling the variable of interest (e.g., lakewater ANC) are identified, and areas of uncertainty requiring further analysis to improve both the understanding of the system and the model's ability to describe the system response to perturbations are highlighted.

The simplest model approach toward describing lakewater acidification is the titration model developed by Henriksen (1980). Application of the Henriksen model to softwater seepage lakes in Florida has not been successful principally because the inherent assumption that sulfate behaves conservatively in aquatic systems is not valid for Florida. Other limitations of the Henriksen model include: (1) its failure to account for internal processes such as sulfate reduction contributing to the generation of ANC without the concomitant production of base cations, and (2) its lack of consideration of the significance of organic acids and bases in colored lakes.

The influence of in-lake process on lakewater ANC dynamics is the framework of the relatively simple mass-balance ANC model developed by Pollman <u>et al</u>. (ESE, 1985). Internal ANC consumption and generation in Florida seepage lakes is assumed in the model to be principally the result of biogeochemical processes resulting in the depletion of $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$. From application of the internal ANC model developed by Pollman <u>et al</u>. to two small lakes in north-central Florida, it is apparent that ammonium release from the sediments and biotic uptake can be an important source of acidity to seepage lakes. The model also illustrates the importance of watershed processes (as reflected in inseepage chemistry) on lakewater ANC concentrations. The magnitude or the extent of seepage lake response to acidic deposition is thus dependent on the relative contributions of: (1) watershed processes such as anion retention and weathering; and (2) in-lake or internal biogeochemical processes, principally $SO_4^{-2}$ reduction and $NO_3^-$ and $NH_4^+$ uptake. The rapidity of response to long-term changes in acidic deposition in turn is directly a function of lake hydraulic residence time, $\tau_w$. For seepage lakes, $\tau_w$ is simply the ratio of lake volume to seepage outflow rates and consequently is governed by the relative difference between precipitation inputs and evaporative losses. Ultimately, the extent and timeframe of response or equilibration of seepage lakes is coupled to lake hydrology.

The residence time $\tau_w$ reflects not only the rapidity of response but the relative hydrologic importance of inseepage as well. In lakes with short residence times, the magnitude of inseepage is comparatively less than lakes characterized by longer residence times; as a result, inseepage contributions of ANC to seepage lakes with short residence times are relatively smaller and these lakes are less capable of neutralizing acidic deposition than similar seepage lakes with longer residence times.

The likelihood of observing responses to acidic deposition is thus greatest for seepage lakes with low $\tau_w$; furthermore, responses will be elicited more rapidly for this class of lakes compared to softwater seepage lakes with similar ANC concentrations but longer residence times.

### 4.3.1.4 Long-Term Trends in Acidification

Several different approaches have been used to document or infer long-term acidification of surface waters. These approaches, which have been reviewed extensively by Galloway *et al*. (1983), include:

1. Analysis of temporal changes in ANC or pH,
2. Analysis of changes in lakewater sulfate concentrations, and
3. Paleolimnological analysis of changes in diatom assemblages.

All three approaches have been or are currently being applied to lakes within Florida. This section reviews the results and conclusions of studies involving the first two approaches. Paleolimnological analyses for several Florida lakes are currently being conducted by Crisman and co-workers; results, however, have not been completed and are unavailable for discussion.

Hendry (1983; Hendry and Brezonik, 1984) compiled chemistry data for several lakes in the Trail Ridge lake district of north-central Florida to examine historical trends in ANC, pH, and excess (nonmarine) $SO_4^{-2}$. The database used by Hendry included data collected by Clark *et al*. (1964) from 1957 to 1960 and by Shannon (1970) from 1968 to 1969 as well as data collected on a quarterly basis by Hendry from 1978 to 1979. ANC was determined by titration to a fixed endpoint (pH 4.5, determined electrometrically) by Clark *et al*., (1964) whereas Shannon and Hendry both used bromcresol green-methyl red as an indicator of the titration endpoint. Hendry used a pH meter to determine that the endpoint of this indicator was pH 4.5 to 5.1. Hendry subsequently corrected for the difference in analytical techniques by subtracting out 20 μeq/L (i.e., the difference between pH 4.5 and 4.9) from the ANC data reported by Clark *et al*. (1964). Correcting to pH 5.1 would extend the ANC correction applied to Clark *et al*.'s data from 20 to 25 μeq/L.

Hendry's comparison of historical and more recent data may indicate that changes in water chemistry have occurred in at least some of the Trail Ridge lakes in the 20-year period between 1957 and 1978 (Table 4.3-4). Lakes Brooklyn, Lowry, and Magnolia all show apparent decreases in ANC of approximately 20 to 25 µeq/L to levels of essentially 0 ANC. Excess sulfate in these three lakes showed apparent increases in concentration roughly equivalent to the calculated losses in ANC. Two types of systems may be defined to describe the interaction between sulfate and lakewater pH and ANC (Galloway _et_ _al_., 1983). In watersheds with sufficient ANC (Alternative 1), $SO_4^{-2}$ deposition and transport to receptor lakes results in increases in lakewater base cation concentrations (Figure 4.3-21); conversely, in systems characterized by low ANC (Alternative 2), $SO_4^{-2}$ deposited and transported through the watershed to a receptor lake is accompanied by $H^+$ as the counterion and equivalent reductions in lakewater pH may be observed. The results for Lakes Brooklyn, Lowry, and Magnolia appear to be consistent with Alternative 2 systems.

Whether or not these reported changes in $SO_4^{-2}$ and ANC are significant cannot be demonstrated conclusively for several reasons. Statistical analysis of any apparent historical trend between 1957 and 1978 cannot be performed because neither the raw data or standard deviation were reported by Clark _et_ _al_. (1964). Moreover, the magnitude of the apparent reduction in ANC (20 to 25 µeq/L) is quite small and approximates the limits of precision of color-indicator-endpoint titrations [cf. American Public Health Association (APHA), 1976; Kramer and Tessier, 1982]. $SO_4^{-2}$ measurements performed by Clark _et_ _al_. (1964) and Shannon (1970) may be low and thus overestimate any historical differences in lakewater $SO_4^{-2}$ concentrations. These $SO_4^{-2}$ analyses were performed turbidimetrically; at concentrations as low as those measured in the Trail Ridge lakes, the turbidimetric method characteristically underestimates $SO_4^{-2}$. Furthermore, the methylthymol blue (MTB) method used by Hendry may overestimate $SO_4^{-2}$ because of organic interferences (Kramer, personal

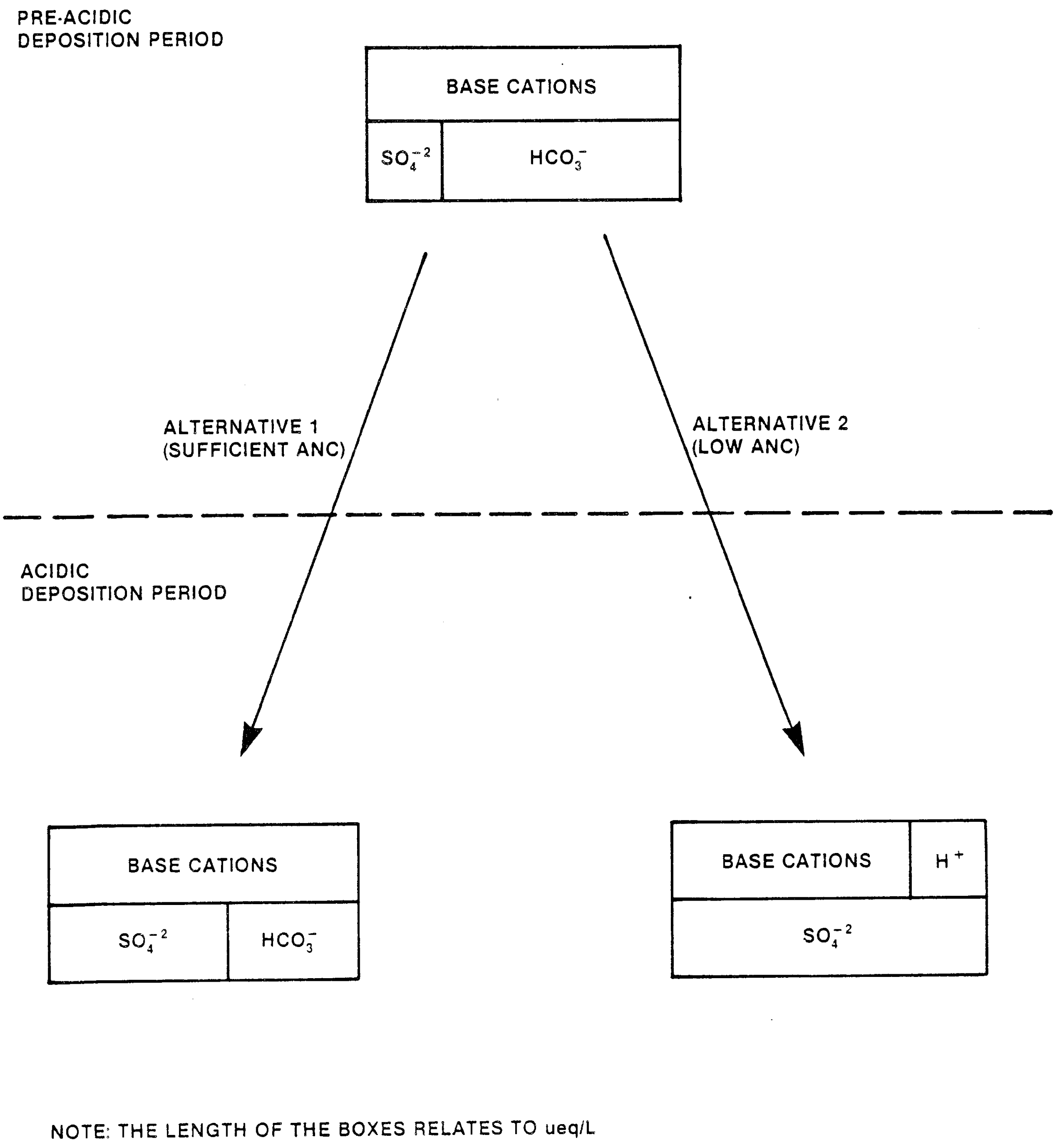

Figure 4.3-21
TWO EXTREMES FOR THE RESPONSE OF AQUATIC SYSTEMS TO A FIVEFOLD INCREASE IN $SO_4^{-2}$

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communication). Both of these analytical biases serve to overestimate any apparent historical differences.

Temporal variability in lake hydrology also confounds the analysis and interpretation of historical trends in lakewater chemistry for the Trail Ridge lakes. Hendry and Brezonik (1984) in the interpretation of their results stressed that the influence of hydrological variables on the chemical composition of seepage lakes is largely unknown. Record droughts occurred in Florida in the mid-1950s, and lake levels were extremely low. The drought ended in 1958/1959, and some lakes such as Brooklyn exhibited large increases in stage. Similar hydrologic variations were observed during the sampling conducted from 1978 to 1979. Some sense of the significance of these extreme variations in hydrology is provided by consideration of the hydrology of Lake McCloud. Stepwise regression analysis of data collected by Baker (1984) detailing temporal variations of pH in Lake McCloud indicate that changes in lake stage significantly influenced pH and that acidic deposition rates were uncorrelated with monthly variations in pH (Subsection 4.3.1.3).

Hendry (1983) also observed increases in excess sulfate in Lakes Geneva and Kingsley over the same 20-year time span; however, unlike Lakes Brooklyn, Magnolia, and Lowry, ANC and pH both increased. Geneva and Kingsley are the two largest lakes in the Trail Ridge district and are among the most developed. Residential developments in the watersheds of these two lakes include septic tanks and Hendry concluded that increases in ANC and pH were probably due to increased nutrient inputs; furthermore, increases in excess $SO_4^{-2}$ could be attributed to septic tank leachate as well as increased atmospheric deposition.

Historical data compiled by Hendry and Brezonik (1984) for Lakes June, Francis, and Letta in the Highlands Ridge between 1967 through 1972 show essentially no change in pH and ANC when compared with data collected by Hendry and Brezonik from 1978 to 1979. Hendry and Brezonik suggested three possible factors to account for the apparent difference in historical trends between the northern and southern Florida groups of lakes: (1) excess $SO_4^{-2}$ loadings are lower and rainfall pH is higher in south Florida relative to north Florida, (2) the Highlands Ridge lakes are characterized by higher ANC concentrations and are thus better able to assimilate acid loadings, and (3) the historical record for the Highlands Ridge lakes extends over only an 11-year period compared to a 20-year record for some Trail Ridge lakes.

Baker (1984) has analyzed in detail historical trends in major ion chemistry over a 14-year period extending from 1968 to 1982 for Lake McCloud (Table 4.3-9). In addition to monthly measurements conducted between 1980 and 1982, Baker's data base included data collected monthly by Brezonik and Shannon (1971) from 1968 to 1969 and quarterly by Brezonik et al. (1983) from 1978 to 1979. Baker noted several problems in using these data to evaluate historical trends, the most serious being changes in analytical techniques between studies. In particular, methods for collecting pH samples and for analyzing for sulfate and chloride changed. In the Brezonik and Shannon (1971) study, pH samples were collected in glass Winkler bottles to prevent $CO_2$ transfer with the atmosphere. A problem with use of soft glass bottles pointed out by Kramer and Tessier (1982) is the contribution of 20 to 100 µeq/L ANC from fresh glass surfaces when samples are stored for less than 12 days. This effect is reduced by cleansing of bottles and rapid analysis; nevertheless, Kramer and Tessier observe that the possible increase of 20 to 60 µeq/L is comparable to some estimates of historical declines in ANC. Baker (1984) inferred from Brezonik and Shannon's (1971) stated concern for $CO_2$ reequilibration effects on pH that sample analyses for pH were conducted on the same day and that comparison with more recent data (in which linear polyethylene bottles were used for sample collection) was probably valid.

Table 4.3-9. Chemical Composition of Lake McCloud, 1968 to 1982

| | 1968-1969* | | 1978-1979† | | 1981-1982 | |
|---|---|---|---|---|---|---|
| | Conc. (μeq/L) | Ci/Cl** | Conc. (μeq/L) | Ci/Cl** | Conc. (μeq/L) | Ci/Cl** |
| $H^+$ | 14 | 0.08 | 19 | 0.13 | 32 | 0.19 |
| $Ca^{+2}$ | 30 | 0.18 | 47 | 0.32 | 66 | 0.39 |
| $Mg^{+2}$ | 47 | 0.28 | 51 | 0.35 | 63 | 0.37 |
| $K^+$ | 6 | 0.04 | 15 | 0.10 | 6 | 0.04 |
| $Na^+$ | 122 | 0.73 | 121 | 0.83 | 153 | 0.90 |
| $SO_4^{-2}$ | 104 | 0.62 | 142 | 0.98 | 173 | 1.02 |
| $Cl^-$ | 167 | 1.00 | 145 | 1.00 | 170 | 1.00 |
| ΣCations | 219 | - | 253 | - | 320 | - |
| ΣAnions | 271 | - | 287 | - | 343 | - |
| Ratio of ΣCations to ΣAnions | 0.81 | - | 0.88 | - | 0.93 | - |

*Brezonik and Shannon, 1971.
†Brezonik *et al*., 1983.
**Ratio of ion i to chloride.

Source: Baker *et al*., 1984.

Sulfate analyses conducted by Brezonik and Shannon (1971) were conducted turbidimetrically (APHA, 1971), which has a detection limit of only 1 mg/L compared to the much more sensitive methylthymol blue technique (0.1 mg/L detection limit) used in the subsequent studies. As a result, Baker (1984) indicates that the mean $SO_4^{-2}$ concentration of 104 μeq/L (5.0 mg/L) may be unreliable. As mentioned previously, the turbidimetric technique is biased toward underestimation of $SO_4^{-2}$ at low concentrations. Indeed, ion balances of the Brezonik and Shannon (1971) data show a large anion excess (cation/anion ratio = 0.81) and that analytical errors were a problem (Table 4.3-8); comparison of ion balances in the more recent studies shows that analyses were more exact (Baker, 1984).

Apart from analytical differences, Baker (1984) indicates that substantial changes in volume for Lake McCloud as a result of long-term variations in precipitation may confound an evaluation of historical trends in the lake. Baker (1984) accounted for these effects by normalizing the concentrations of dissolved ions to the concentration of chloride, which is assumed to behave conservatively (Table 4.3-8).

Baker's analysis suggests that Lake McCloud has become more acidic during the 14-year period from 1968 to 1982. $H^+$ concentrations nearly doubled from 14 μeq/L (pH 4.9) to 32 μeq/L (pH 4.5) with concomitant increases in sulfate from 104 to 173 μeq/L. As evidenced by this large anion excess, sulfate concentrations reported for 1968 to 1969 may be too high and the increase in $SO_4^{-2}$ concentrations may be higher than these data indicate (Baker, 1984). Apparent increases in calcium and magnesium were observed, reflecting enhanced leaching from the watershed. However, Baker cautions that problems may exist with calcium data collected by Brezonik and Shannon (1971) based on the poor ion balance and a large deviation in the ratio of calcium to magnesium subsequently observed by both Brezonik et al. (1983) and Baker (1984). Chloride concentrations were relatively stable, varying by less than 2 percent over the entire period of study, and Baker concluded that dilution or concentration resulting from variations in precipitation and rainfall cannot account for the observed apparent differences in $H^+$, $SO_4^{-2}$, and base cations.

The significance of the change in $H^+$ indicated by Baker (1984) is highly uncertain. Monthly measurements of pH between October and August 1982 show differences in $H^+$ of at least 19 μeq/L (Figure 4.3-5). In addition, measuring pH with an electrode in dilute solutions is difficult because of the high electrical resistance and unbuffered nature of the solution and the liquid junction potential that is developed (Westcott, 1978). Stirring the solution, a common practice in measuring pH during the period Shannon (1970) conducted his study, results in noisy measurements because of changes in the ionic gradient at the liquid junction. Finally, the relative purity of these lakewaters makes them susceptible to pH changes resulting from the introduction of trace contaminants (e.g., the transferral of residual buffer on the electrode).

## Summary

The primary data available to examine historical trends in acidification of softwater lakes in Florida are the rather limited studies of Brezonik and co-workers (Shannon, 1970; Hendry and Brezonik, 1984; Baker, 1984) and Clark et al. (1964) in the Trail Ridge lake district. In several clear (color less than 20 PCU) and relatively pristine Trail Ridge lakes, apparent declines in pH and ANC accompanied by concomitant increases in nonmarine $SO_4^{-2}$ have been noted. The significance of these apparent trends is not clear and is obscured for several reasons. For each parameter, the magnitude of these changes is quite small (approximately 30 μeq/L or less) and may be insignificant when compared to the analytical precision of the various methods used in each study. In addition, analytical techniques for $SO_4^{-2}$, ANC, and pH have changed with time; for $SO_4^{-2}$, and ANC particularly, these changes are biased toward overestimating any apparent differences. The influence of changes in lake stage on lakewater chemistry is also unclear. Because of these uncertainties, additional long-term monitoring is required to definitively establish chemical (and biological) changes in these and other softwater Florida lakes attributable to acidic deposition.

### 4.3.2 EFFECTS ON AQUATIC BIOLOGY

Acidification of fresh waters may be accompanied by changes in the structure of the entire biological community. These effects may range from reductions in diversity without parallel changes in standing crop to virtual elimination of particular groups of organisms. The mechanisms accounting for observed effects may be quite complex and are often unknown. In some cases, effects are undoubtedly due simply to a reduction in pH or the concomitant mobilization of trace elements. Other effects also arise indirectly, since the loss of species can lead to shifts in community structure. Indirect effects may also extend to physical factors which may in turn affect the biological community. For example, lake acidification often results in increased water clarity through precipitation of humic acids, dissolution of inorganic colloids, or through reductions in algal biomass (cf. Schindler *et al*., 1980b). These various effects which have been attributed to acidic deposition for aquatic systems in Scandinavia and North America have been reviewed extensively (e.g., Overrein *et al*., 1980; Muniz and Leivestad, 1980a; Harvey, 1980; Haines, 1981; Dillon *et al*., 1984; Muniz, 1983; Crisman, 1984; Rahel *et al*., 1983). The following chapter is a general review of these effects and reviews in detail the findings of studies specific to Florida.

#### 4.3.2.1 *Macrophytes*

There is some evidence from Scandinavia that acidification of aquatic systems may result in a large reduction of diversity and complete dominance by sphagnum. Grahn (1977) observed species replacement by sphagnum in five out of six acidic (pH 4.4 to 5.4) softwater Swedish lakes compared to comparable non-acidic systems. Grahn *et al*. (1974) have hypothesized that the development of dense sphagnum mats can reduce the exchange of dissolved materials from the sediments to the overlying water and ultimately result in a decline in trophic state, i.e. self-accelerating or acid-induced oligotrophication. Hendrey and Vertucci (1980) subsequently observed dense beds of sphagnum in acidic Lake Colden (pH 4.9) in the Adirondack Mountains and inferred on the basis of tissue analyses that once it is established, sphagnum can promote further lake acidification through ion exchange. However, Hendrey and Vertucci could not discern whether the occurrence of sphagnum was a recent consequence of lake acidification or the result of natural processes. Rahel *et al.* (1983) have reviewed the literature on the relationship between lakewater pH and macrophyte community structure and concluded that trends of dominance by Sphagnum with reductions in pH are not apparent in oligotrophic softwater systems within North America. The trend observed by Grahn (1977) in six Swedish lakes does not appear to be a general property of lake acidification.

Cairns (1985) studied the littoral zone community structure in 21 lakes of varying acidity located in the Ocala National Forest which lies within the Central Highlands in north-central Florida. The lakes studied by Cairns were all softwater oligotrophic systems and ranged in pH from 4.2 to 6.4. A total of 27 macrophyte species was identified with the number of species in a particular lake generally low. Cairns noted a weak relationship between species numbers of macrophytes and pH; a similar weak relationship for submergent macrophytes has been observed by Garren (1982) for north Florida lakes. Macrophyte abundance was quite high in all the lakes studied and appeared independent of pH. With a few exceptions, the distribution of most of the macrophytes identified by Clarkson was ubiquitous with respect to pH. *Utricularia foliosa*, *Hydrilla verticulata*, and *Cabomba caroliniana* (all submergent macrophytes) were found preferentially in higher-pH waters. In addition, a floating leaved species, *Brasenia schreberi*, tended toward waters with higher pH. Only twc species, *Utricularia inflata* (a submergent) and *Eriocaulon compressum* (an emergent), seemed to prefer lower-pH waters.

Clarkson (1985) also analyzed tissue samples in various macrophytes to examine the relationship between pH and trace element uptake. Accumulation of trace elements was species-specific and was inversely related to pH for copper, cadmium, lead, and zinc. These results support the concept that alterations in macrophyte community structure along a gradient in pH may be more related to pH-dependent trace element toxicity rather than a direct response to pH (Gorham and Gordon, 1963).

Crisman (1984) defines two general trends in macrophyte community structure exhibited by Florida lakes in response to gradients in pH. In many acidic lakes, submergent macrophytes are totally absent, and only a narrow fringe of emergent grasses defines the littoral zone. Epiphytic algae are abundant in the grass zone and although algal mats do not develop in deeper areas benthic algae are numerous in the interstices of sandy sediments. The second pattern noted by Crisman is the failure of some comparably acidic lakes to show reductions in either species richness or abundance of submergent macrophytes relative other less acidic softwater systems (cf. Clarkson, 1985). Crisman also observes that acidic lakes in Florida differ from analogous temperate systems in that Sphagnum is generally absent in peninsular Florida.

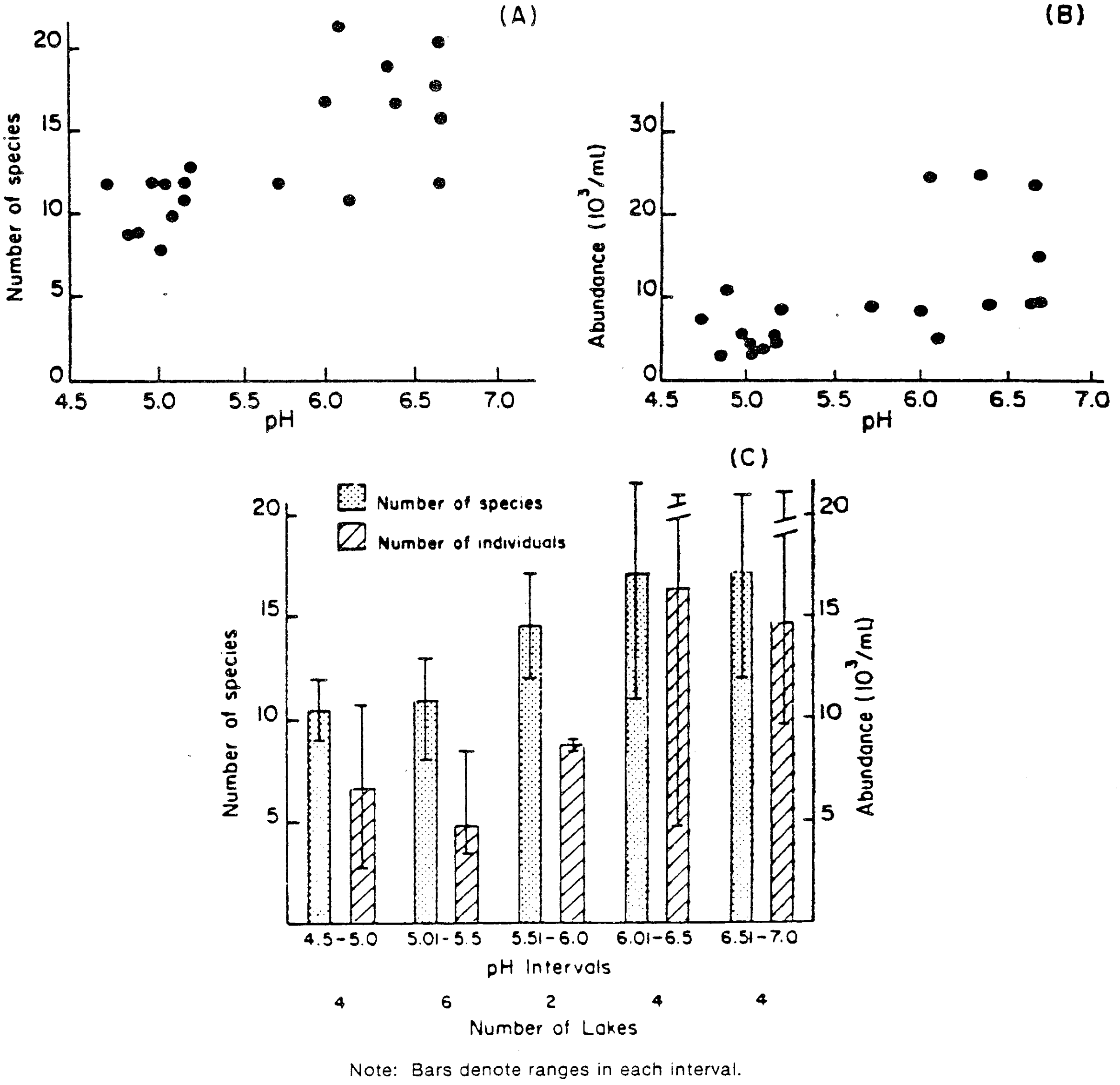
#### 4.3.2.2 Phytoplankton

Lake acidification is usually accompanied by major changes in phytoplankton community structure. Rahel et al. (1983) cite evidence from surveys of acidic lakes in Norway, Sweden, eastern Canada, and the United States demonstrating alterations in the phytoplankton community and reduced species richness with declines in pH. There is, however, no clear relationship between reduction in pH and productivity. After 8 years of artificially acidifying Lake 223 in the Experimental Lakes Area in northwestern Ontario, Schindler et al. (1985) observed no decline in phytoplankton productivity. These results are supported by synoptic surveys which show essentially no correlation between algal standing crop and pH (Raddum et al., 1980; Almer et al., 1978). However, it should be noted that Schindler et al. (1985) observed a reduction in the proportion of phytoplankton of the size edible to zooplankton. As pH declined in Lake 223, small edible species were gradually replaced with larger phytoplankton characterized by tests or mucilaginous sheaths.

Within Florida, Brezonik et al. (1984) examined the abundance and species composition of phytoplankton in a survey of 20 softwater lakes of differing pH. Twelve lakes were located in the Trail Ridge of north-central Florida and the remaining seven lakes were located in the Highlands Ridge of south-central Florida. Samples were collected quarterly for 1 year beginning in April 1978 and ending in February 1979. Phytoplankton species numbers were significantly correlated with pH ($p < 0.01$) although Brezonik et al. (1984) noticed considerable scatter in the relationship, particularly above pH 6.0 (Figure 4.3-22A). Three of the relatively nonacidic lakes had numbers of species similar to the more acidic lakes, and Brezonik et al. (1984) suggested that this trend may reflect lower total phosphorus concentrations relative to the other nonacidic lakes in the survey. Analysis of variance and Duncan's analysis indicate that significant differences exist between different groups segregated by pH; mean numbers of algal taxa for the lowest pH intervals (4.5 to 5.5) were significantly lower than the means for the highest intervals (6.0 to 7.0).

Analysis of changes in species composition across the gradient in pH of the survey lakes shows a replacement in bluegreen algae as the dominant group at high pH with green algae as the dominant group below pH 5.5 to 6.0 (Brezonik et al., 1984). With the exception of an increase in pyrrophytes below pH 5.0, subdominant groups showed little relationship with pH. Unlike temperate lakes of comparable pH and ionic character, diatoms were rare in all the lakes. Brezonik et al. (1984) speculated that the differences in phytoplankton community structure between the subtropical Florida lakes and similar temperate systems may be related to the fact that zooplankton communities in Florida lakes are not as seriously influenced by pH as those in temperate lakes.

The relationship between algal abundance and pH for the lakes surveyed by Brezonik et al. (1984) suggests that phytoplankton abundance may decline with reductions in lakewater pH. Abundance was nearly three times higher



Note: Bars denote ranges in each interval.

SOURCE: BREZONIK et al, 1984.

Figure 4.3-22
MEAN ANNUAL SPECIES RICHNESS (A) AND ABUNDANCE (B) OF PHYTOPLANKTON VS pH AND MEAN VALUES OF THE PARAMETERS OVER 5 pH INTERVALS (C)

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in the nonacidic group of lakes (pH >5.7) relative to the acidic group (pH <5.3). Similar to species richness, phytoplankton abundance was positively correlated with pH, although the relationship appears less well-defined (Figure 4.3-22B). Hendry (1983) notes that at least part of the relationship is explained by the wide range in total phosphorus concentrations found in the lakes. Total phosphorus was correlated with pH but whether or not the relationship is causative or coincidental is uncertain (Brezonik and Hendry, 1984). Subsequent analysis of the watershed characteristics of the survey lakes indicates that chlorophyll a concentrations are correlated at least as strongly with watershed factors such as land use as they are with pH (ESE, 1985).

Manipulation experiments conducted by Ogburn (1984) in acidic Lake McCloud suggest that nutrient availability is a stronger determinant of algal abundance than pH. Ogburn acidified a series of enclosures in Lake McCloud and examined the relationship between chlorophyll a concentrations and pH. No trend with pH was observed for as low as pH 3.7; however, nutrient additions to the enclosures did result in increases in chlorophyll a.

### 4.3.2.3 Zooplankton

Similar to observed effects on phytoplankton, declines in lakewater pH lead to a simplification in the community structure of zooplankton. A survey by Confer et al. (1983) of 20 lakes in the White Mountains (New Hampshire) and the Adirondack Mountains shows a close correlation between zooplankton species richness and pH over the range 4.5 to 7.2. Similarly, Overrein et al. (1980) document a reduction of zooplankton species in low-pH clearwater lakes (<pH 5.0) compared to less acidic lakes in Norway.

In general, the species dominant in acidic lakes are also present in non-acidic lakes in the same region (Rahel et al., 1983). Invasion of new species does not occur; rather, species originally present become more important as more sensitive species are eliminated. During the whole-lake experimental acidification of Lake 223, Schindler *et al.* (1985) observed the near extinction of the opossum shrimp, *Mysis relicta*, when the average lakewater pH reached 5.9. Further reduction in pH to 5.6 resulted in the complete loss of the copepod *Epischura lacustris* as well as the decline of the cladoceran *Daphnia galeata mendotae*. These declines were marked by increases in other species, notably the cladocerans *Bosmina longirostris* and *D. catawba*. As acidification of Lake 223 proceeded, Schindler *et al.* (1985) observed that rotifers and particularly cladocerans increased, coupled with a large relative decline in calanoid copepods and, to a lesser extent, cyclopoid copepods. Mean body size of the zooplankton decreased as a result of the increase in rotifer and small bodied cladocerans abundance, and Schindler *et al.* (1985) hypothesized that this shift in heterotroph structure could account for the survival of larger phytoplankton.

Zooplankton community structure in Florida was studied as part of the softwater lake survey conducted by Brezonik *et al.* (1984). Zooplankton diversity was lower in the more acidic lakes included in the survey and species richness was positively correlated with pH ($p < 0.001$). The trend for zooplankton was less consistent than the relationship defined between phytoplankton and pH. Analysis of variance failed to show any differences in mean species richness of zooplankton when the survey lakes were separated into different classes defined by pH intervals. These results are inconsistent with progressive declines in zooplankton species numbers observed in temperate lakes as a function of pH (e.g., Raddum *et al.*, 1980; Confer *et al.*, 1983) and Brezonik *et al.* (1984) hypothesized that surficial geological differences (i.e., apparently lower lakewater concentrations of heavy metals because of the highly weathered soils characteristic of Florida) may account for the higher diversity. Brezonik *et al.* (1984) also cite other factors such as climatic differences and the possibility of natural selection for a regime that has been predisposed to low pH under natural circumstances.

Brezonik *et al*. (1984) found several species of zooplankton that were dominant in all of the survey lakes regardless of pH. These species included the cladocerans *Eubosmina tubicen* and *Daphnia ambigua*, the copepods *Diaptomus floridanus*, *Cyclops varicans*, and *Mesocyclops edax*, and the rotifer *Keratella cochlearis*. The zooplankton assemblages in the Florida survey lakes were smaller bodied than assemblages in comparable temperate lakes. Rotifers were the most diverse group in all the lakes although their relative importance diminished with pH; conversely, copepod species numbers increased with lower pH and Brezonik *et al*. (1984) observed no elimination of cyclopoid copepods associated with declines in pH. Brezonik *et al*. (1984) inferred from their results that the rather insensitive response of zooplankton to pH in acidic Florida lakes may explain the dominance of the phytoplankton assemblages by chlorophytes rather than the relatively inedible pyrrophytes.

Crisman (1984) indicates that the most significant response by members of the zooplankton community to decreasing lakewater pH in Florida is exhibited by ciliated protozoans. Beaver and Crisman (1981) studied the distribution of ciliated protozoans along a gradient in pH (4.7 to 7.0) represented by 21 lakes in Florida. Declines in both total abundance and biomass in response to decreasing pH were observed with the most pronounced response occurring below pH 5.0. Beaver and Crisman (1981) attributed their results to an inferred reduction of bacterial and algal populations with decreasing pH. Reductions in pH also were accompanied by a compositional shift from a small-bodied to a large-bodied assemblage.

*In situ* enclosure studies in Lake McCloud in the Trail Ridge of north-central Florida indicate that majcr changes in the zooplankton community structure will occur if the lake undergoes a decline in pH. Comparison of community structure in a littoral zone enclosure acidified to pH 3.6 with sulfuric acid with the structure of a control enclosure (pH 4.6) and one which received base additions (>pH 5.1) showed the decline and replacement of copepods with rotifers (Crisman *et al.*, 1982). Total zooplankton abundance in the acidified enclosure was greatly reduced. Subsequent acidification of pelagic enclosures confirmed the almost complete elimination of copepods at pH 3.7 (Ogburn, 1984).

The effects of lowered pH on zooplankton response were tested directly by Gourlie (1981) for the calanoid copepod *Diaptomus floridanus*. Gourlie collected Diaptomus individuals from two lakes located in the Trail Ridge, Lake McCloud (pH 4.6) and Lake Geneva (pH 6.2), to examine acute toxicity within a 96-hour period as a function of pH. Eight pH intervals were evaluated for Lake Geneva (pH 3.8 to 6.2), and six intervals (pH 3.7 to 5.0) were tested for Lake McCloud. Diaptomus individuals showed essentially no toxic response between ambient pH levels and 4.25; at pH 4.0 mortality increased, and reduction of pH to 3.8 resulted in complete mortality within 24 hours. Similar results were obtained for Diaptomus specimens collected from Lake McCloud with one distinction: complete mortality (also within 24 hours) was shifted lower by 0.1 pH unit to 3.7. In both tests, a reduction of pH by only 0.1 unit below the LC50 resulted in total mortality. These results are consistent with previous *in situ* enclosure studies conducted at Lake McCloud in which *D. floridanus* was eliminated upon reduction of the enclosure pH below 4.0 (Gourlie, 1981).

Gourlie (1981) also examined the effects of decreasing pH on grazing rates by Diaptomus. Grazing-rate experiments were conducted at various pH levels using Diaptomus collected from Lake Geneva and Lake McCloud. Filtering or grazing rates from both lakes declined linearly with decreasing pH. Comparison of overall rates between the two lakes showed no significant difference, although filtering rates were somewhat higher for Lake McCloud organisms and may reflect adaptation to a lower-pH regime (Gourlie, 1981).

### 4.3.2.4 Fish

The effects of acidification on aquatic biota are most widely documented for fish. Effects include the disappearance of fish populations from lakes in Scandinavia (Wright and Snekvik, 1978; Muniz and Leivestad, 1980a; Almer et al., 1978), Ontario (Harvey, 1975 and 1980), and the Adirondack Mountains (Rahel et al., 1983). Abundance of fish in acidified waters may be reduced with a shift in age-class composition to older animals because of spawning failure, death of larval fishes, or failed egg maturation (Ryan and Harvey, 1977 and 1980). Other effects may include behavioral responses (Johnson and Webster, 1977; Muniz and Leivestad, 1980a) and growth effects (Nelson, 1982). In addition, solubilization of trace elements with reductions in pH can lead to elevated tissue concentrations (Overrein et al., 1980; Dillon et al., 1984) and aluminum solubilization has been widely implicated as a direct toxic effect (Schofield and Trojnar, 1980; Muniz and Leivestad, 1980b).

The potential effects of acidification on fish in Florida lakes have been evaluated largely through surveys. Schulze (1980) conducted a qualitative survey of fish populations in three acidic lakes (pH 4.6 to 5.1) and found breeding populations of largemouth bass and bluegills at pH levels considered lethal to the same or congeneric species in temperate lakes. This apparent discrepancy may be explained in part by the fact that aluminum concentrations in acidic Florida lakes are characteristically below 100 µg/L (Brezonik et al., 1982b).

Crisman et al. (1982) conducted a series of bioassays to test the interaction of aluminum and pH on Florida gamefish. Redear sunfish (*Lepomis micropholus*) obtained from a hatchery was used as the test organism to examine acute toxicity across gradients in pH (3.5 to 5.0) and aluminum concentrations (50 to 400 µg/L). The pH at which the animals were reared was not reported nor is there any indication of acclimation to a lower pH prior to the assay. Crisman et al. (1982) observed that acute toxicity of redear sunfish was apparently more related to pH than to aluminum (Table 4.3-10) and that longer term studies may be necessary to properly evaluate the effects of aluminum solubilization. Reduction in pH to 3.5 resulted in complete mortality within 24 hours, whereas only 20 percent mortality was observed at the highest aluminum concentration (400 ug/L) at pH 4.5, and no mortality was observed at pH 4.0 at any aluminum level. These results suggested to Crisman *et al*. (1982) that the elimination of centrarchids (sunfishes), which are the dominant fish in Lake McCloud, may result should further acidification of Lake McCloud to pH 4.0 to 3.5 occur.

Newman and Matter (ESE, 1984) compiled fish distributional data from a variety of sources (notably the collection maintained at the Florida State Museum by G. Burgess and unpublished files of the Florida Game and Fresh Water Fish Commission) in order to relate the geographic distribution of fish in Florida to pH. The Newman and Matter analysis (ESE, 1984) analysis was hindered by a paucity of water chemistry data; nevertheless, sufficient data were available to identify pH-distributional groupings. Their results indicate that Florida fish exhibit a broad range of tolerance to low pH. A large group of species appears to tolerate naturally low-pH regimes with 66 Florida species found below pH 5.0 and 37 species found at pH values as low as pH 4.0 or less. Newman and Matter identified a small group of five species apparently intolerant of low pH: the redear sunfish; the flagfish, *Jordanella floridae*; the Seminole killifish, *Fundulus seminolis*; the redeye chub, *Notropis harperi*; and the threadfin shad, *Dorosoma petenense*. The causal relationships defining intolerance of low pH were not well established and, besides direct effects, could reflect indirect effects such as loss of food base for the redear sunfish with declining pH or some correlate with pH as well.

A general pattern of occurrence at lower pH levels relative to temperate systems was observed by Newman and Matter (ESE, 1984) for Florida fish species. A comparison of the pH range for species of fish common to both Florida and Wisconsin demonstrates that the Florida populations of these

Table 4.3-10. Percent Survival of Redear Sunfish after a 96-Hour Bioassay

| Aluminum (µg/L) | pH 3.5 | | pH 4.0 | | pH 4.5 | | pH 5.0 | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| 50 | 0 | 0 | 100 | 100 | 100 | 100 | 100 | 100 |
| 150 | 0 | 0 | 100 | 100 | 100 | 100 | 100 | 100 |
| 250 | 0 | 0 | 100 | 100 | 100 | 90 | 100 | 100 |
| 400 | 0 | 0 | 100 | 100 | 100 | 60 | 100 | 100 |

Note: A and B denote separate trials for a given treatment.

Source: Crisman *et al.*, 1982.

species may be more resistant to low pH than their northern counterparts (Figure 4.3-23). Newman and Matter suggest that many of the fishes of Florida may be physiologically different races of the same representative species found in temperate systems and possibly reflect a genetic resistance to lower pH developed over many more generations of exposure.

The qualitative assessment of Newman and Matter (ESE, 1984) is supported by Keller (1984), who compared the relationship between lake pH and fish species richness for Florida lakes with similar relationships derived for lakes in Wisconsin and Canada (Figure 4.3-24). Keller's database, which includes fisheries, water chemistry, and morphometric data for 38 lakes in the panhandle and north-central Florida, shows that at a given pH (below approximately pH 7.5) Florida lakes are more likely to have more fish species than comparable temperate lakes. The derived regression relationships for Florida and a merged data set for Canadian and Wisconsin lakes were significantly different ($p < 0.001$) and suggest that a greater change in pH should be required to alter the species number in Florida lakes. Several factors can contribute to the relatively higher species abundance in Florida lakes: differing teperature regimes, timing of acid inputs (i.e., no short-term pulses of the magnitude delivered in spring snowmelt), higher primary productivity, lower aluminum concentrations, and the constancy of environmental conditions (Keller, 1984).

Keller (1984) used a smaller set of eight softwater oligotrophic lakes located in south- and north-central Florida to examine changes in age-specific condition factors for largemouth bass (*Micropterus salmoides*) across a gradient in pH (4.5 to 7.0). Chlorophyll *a* concentrations correlated very well with condition factors for first-year largemouth bass; however, condition factors for second-year bass showed virtually no relationship with algal standing crop but correlated significantly with total nitrogen. For both age classes of fish, the

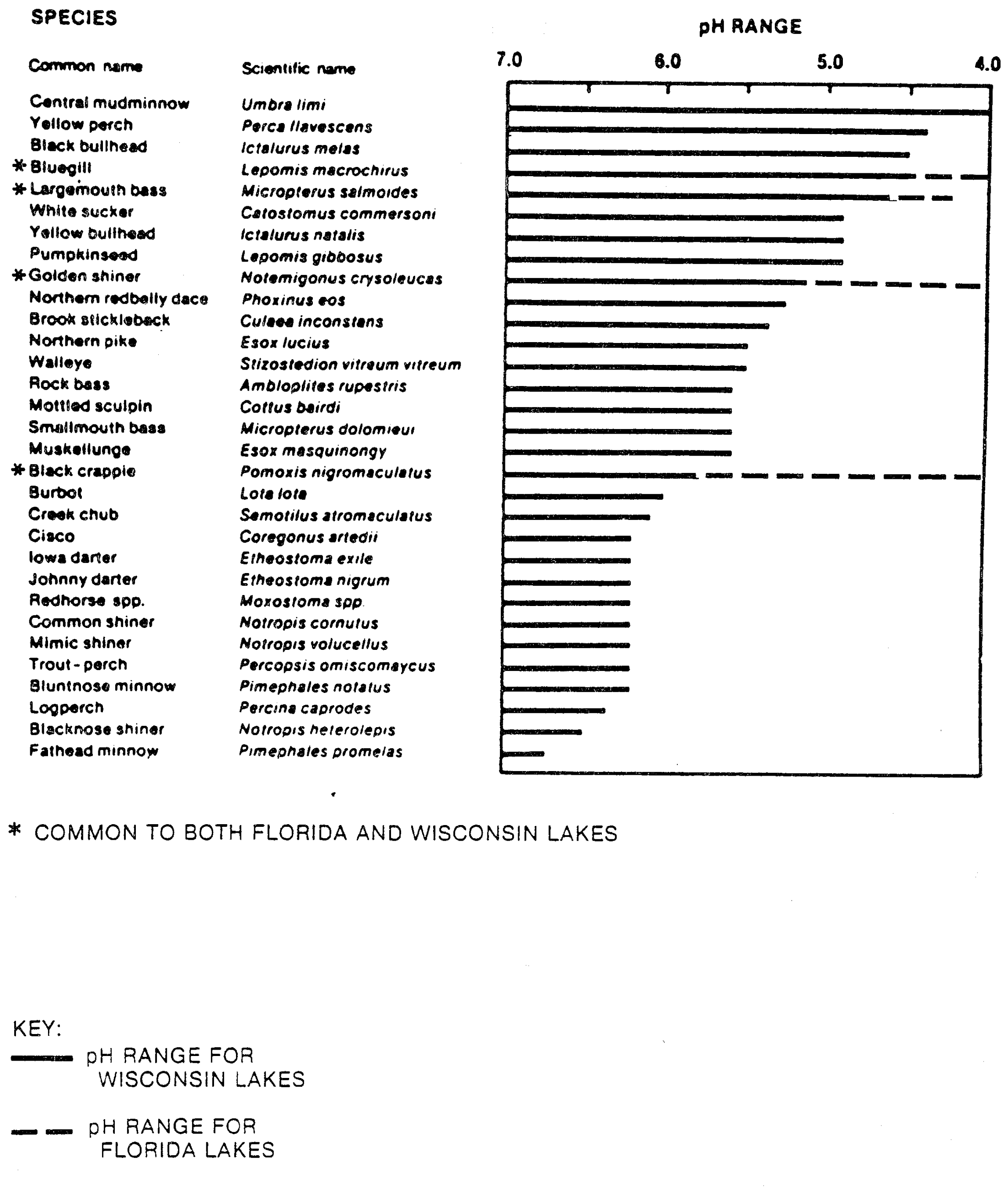

Figure 4.3-23
COMPARISON OF THE REPORTED pH DISTRIBUTION RELATIONSHIPS OF FOUR FISH SPECIES FOUND IN BOTH WISCONSIN AND FLORIDA LAKES

SOURCES: RAHEL AND MAGNESON, 1983; ESE, 1984.

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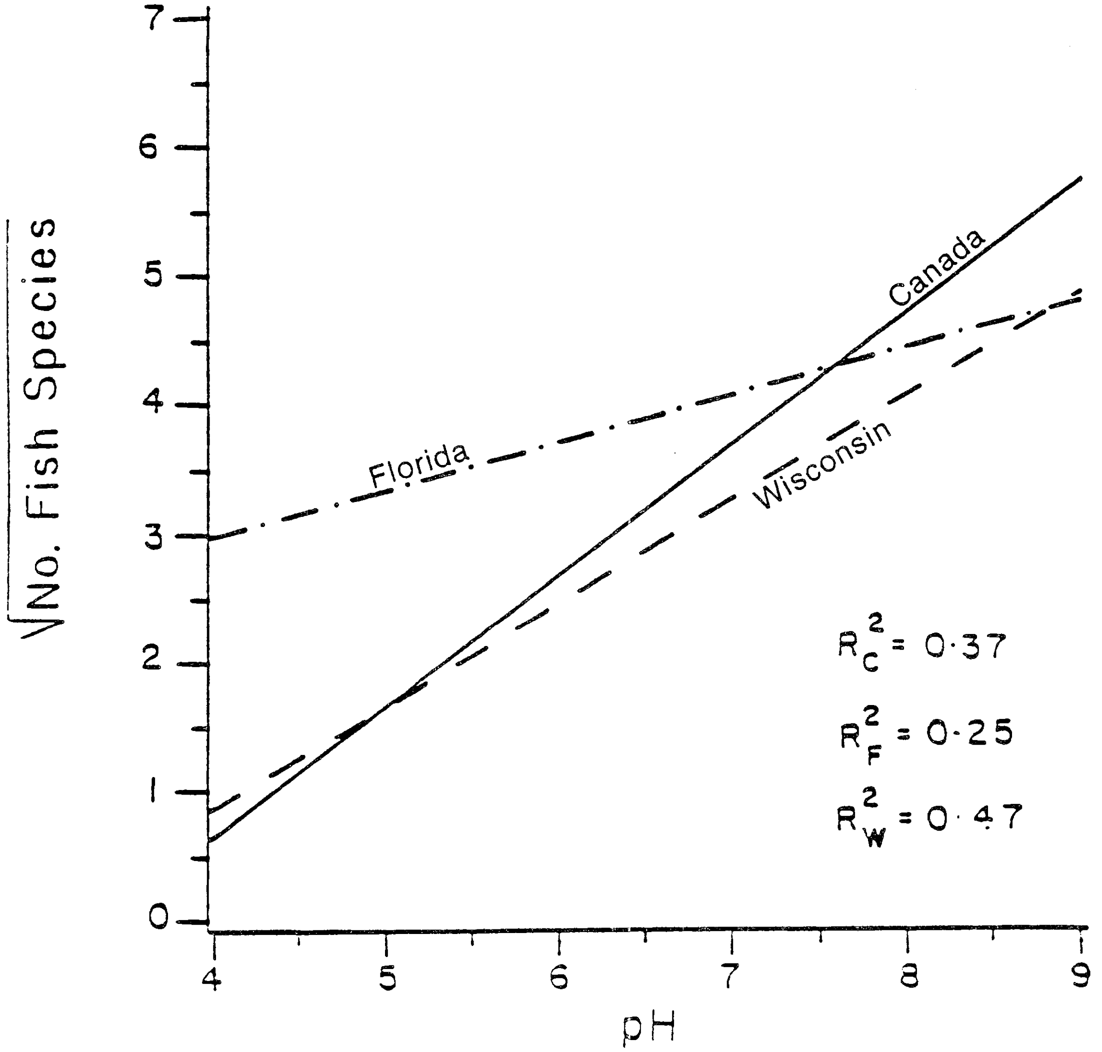

SOURCE: KELLER, 1984.

Figure 4.3-24
RELATIONSHIP BETWEEN LAKE pH AND NUMBER OF FISH SPECIES FOR LAKES IN FLORIDA, WISCONSIN, AND CANADA

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relationship between condition factors and pH was weak and statistically insignificant, and Keller concluded that chlorophyll-a concentrations and total lake primary production are the best predictors of largemouth bass growth rates and conditions in oligotrophic Florida lakes.

## 4.4 EFFECTS ON MATERIALS

Since the Florida Acid Deposition Study did not include any original studies of material effects, this section is based on a summary of the literature. A variety of environmental factors including sunlight, moisture, oxidizing gases, and acidic deposition, can affect the deterioration of architectural and cultural structures and other manmade materials. The direct effects on materials exposed to the atmosphere and indirect effects on potable water piping systems due to acidification of raw water supplies are discussed in this section.

### 4.4.1 DIRECT EFFECTS ON MATERIALS

Effects on materials directly exposed to acidic deposition are analyzed by studying the mechanism of exposure and evaluating the damage to the materials using laboratory and field experimentation.

#### 4.4.1.1 Mechanisms of Exposure

Generally, the modes of acidic deposition are classified as dry deposition of pollutants and their oxidized forms and wet deposition of acidic species in the form of acidic precipitation (i.e., rain, snow, and fog). Both pathways potentially can damage exposed materials; however, in some instances, rainfall may lessen the damage as a result of dilution and washout effects. Specific mechanisms of exposure and deposition have been proposed based on the presence of acidic precursor gases (e.g., $SO_2$ and $NO_2$), their transformation products, and moisture. Yocom and Baer (1983) developed the following list of simplified mechanisms:

1. Adsorption of dry, acidic precursor gases on a relatively dry material surface followed by formation of acids upon exposure to moisture which attack the material (dry gas, dry surface);
2. Absorption of dry, acidic precursor gases by moisture on surfaces resulting in acid attack (dry gas, wet surface);
3. Deposition of large, dry particles containing acidic components on the dry material surface leading to direct damage (large, dry particles, and dry surface);

4. Deposition of small particles containing acidic compounds such as sulfuric or nitric acid salts which can react with moisture to form aqueous acids or directly impact a wet or dry surface (small particles, dry or wet surface); and
5. Acidic precipitation in which rain or snow containing acidic components falls on material surfaces and leads to direct damage.

This list is not exhaustive but describes a wide range of processes whereby acidic deposition could damage materials. Near local sources where levels of primary gaseous pollutants are relatively high, Mechanisms 1, 2, and 3 may dominate; although under appropriate conditions, Mechanisms 4 and 5 may be important. Mechanisms 4 and 5 may dominate in remote and rural areas where concentrations of acidic precursor gases and large acidic particles are not appreciable.

To date, few studies have been conducted to isolate the specific influence of any of the proposed mechanisms. Chamber studies are currently in progress as part of NAPAP to evaluate some of these mechanisms under laboratory-controlled conditions (Yocom, 1985).

### 4.4.1.2 Laboratory and Field Study Approaches--Advantages and Limitations

Damage to materials by acidic deposition has been evaluated in laboratory and field studies. Quantitative changes in some physical or chemical features of the material (weight loss, reflectivity or appearance degradation, and corrosion damage) are measured and used in developing damage functions. In laboratory studies, such as those conducted by Spence and Haynie (1976), Haynie *et al*. (1978), and Harker *et al*. (1982), representative materials are exposed in chambers to known combinations of pollutant concentrations and environmental variables. The conditions of exposure are controlled, and the specific effects of a single pollutant or environmental parameter are isolated. Typically, accelerated tests are conducted in which the material is exposed continuously to high pollutant concentrations or high humidity to produce measurable damage. For instance, several exterior paints have been exposed to 2,620 $\mu g/m^3$ of $SO_2$ in an environmental chamber for up to 1,000 hr (Campbell et al., 1972). Important advantages of the laboratory approach are:

1. Tests can be completed in a timely manner,
2. Specific exposure scenarios can be carried out to identify and quantify the effect of a specific acidic pollutant and environmental factor, and
3. Laboratory results can help in interpreting field data.

There are inherent limitations to the laboratory approach because the experimental conditions often do not represent the actual field conditions involving complex interactions of environmental factors in the ambient atmosphere.

Field studies are normally conducted by exposing materials to ambient atmospheres with different environmental characteristics. Resulting damages to materials are evaluated by determining weight loss or using electronic sensors such as recently developed instantaneous atmospheric corrosion rate monitor (ACRM) for metals in outdoor exposures (Mansfeld et al. 1985). Statistical models are developed in which the extent of damage is expressed as a function of important parameters [e.g., pollutant concentration, humidity, and time-of-wetness (Haynie and Upham, 1974)]. An advantage of this approach is that effects of acidic deposition are evaluated under actual atmospheric conditions. Although field studies may yield more useful and meaningful data on damage than laboratory studies, the field approach is also subject to the following limitations (Yocom and Baer, 1983):

1. The requisite duration of the experiments in order to observe damage is typically longer.
2. Materials exposed may not represent materials in actual use.

3. Interactions of other materials in contact with the test materials are not considered. In normal use, materials are found in combination. Some of these conditions have been described as incompatibility factors caused by deleterious interactions between adjoining materials (Brown and Masters, 1982) and not strictly by acidic deposition. One important interaction phenomenon referred to as galvanic contact or corrosion in metals (Fontana and Green, 1978).
4. Effect of one environmental factor is difficult to isolate because the damage measured is a complex function of many environmental parameters (e.g., temperature, relative humidity, sunlight, wind).
5. Some measured variables (e.g., pH and $SO_2$ levels) may be interrelated in rainwater.

#### 4.4.1.3 Damage to Materials by Acidic Deposition

Along with other environmental factors, acidic deposition can potentially damage several classes of materials, including metals, masonry, painted surfaces, other important manmade materials, and cultural structures. Although other materials may be damaged, this discussion is limited to the more economically and historically important materials.

Metals--Atmospheric corrosion is the primary process by which exposed metals are damaged in the environment. Metal corrosion is generally regarded as an electrochemical process governed by diffusion of corrosive agents, particles, moisture, oxygen, and other substances to the surface.

Primary pollutant gases ($SO_2$ and $NO_x$) can be transformed into acidic corrosion stimulators ($H_2SO_4$ and $HNO_3$) which can enhance the corrosion damage to metals. Several mechanisms of metal corrosion involving the key roles played by $SO_2$ and $H_2O$ have been proposed, particularly for damage to iron and steel by acidic deposition (Barton, 1976).

Several studies have been conducted to relate the metal corrosion damage with atmospheric pollutants and environmental parameters. In most of these studies, particular attention was focused on isolating the effect of $SO_2$ under the influence of moisture as relative humidity, although it is tacitly recognized that the magnitude and variability of other meteorological factors also play important roles. Consequently, the literature is replete with damage functions expressing metal corrosion rates as a function of only $SO_2$ or in combination with either relative humidity or time-of-wetness (the time a certain critical, relative humidity is exceeded). Haynie *et al*. (1976) found a strong relationship between steel corrosion and $SO_2$ concentration from laboratory experiments designed to simulate field conditions by controlling pollutant concentration, sunlight, and dew formation. Using field data from steel samples, Haynie and Upham (1971) developed an empirical function relating the depth of corrosion penetration to $SO_2$ concentration and relative humidity. Other damage functions relating steel corrosion to $SO_2$ concentration and relative humidity or time-of-wetness have been derived by other researchers and summarized by Haagenrud *et al*. (1982) and EPA (1982). For other nonferrous metals, regression coefficients for $SO_2$ concentration and time-of-wetness have been determined by several researchers for estimating zinc and galvanized steel corrosion rates (Cavender *et al*., 1971; Guttman, 1968; Guttman and Sereda, 1968; Haynie and Upham, 1970; Haynie *et al*., 1976). Recently, Haynie (1982) derived a damage function for galvanized steel corrosion penetration in terms of $SO_2$ concentration and time-of-wetness. It was based on an average relative humidity of 70.6 percent and time-of-wetness equivalent to 25 percent of the exposure time and expressed as:

$$\text{corr} = (3.9 + 0.0383\ SO_2)\ tw \qquad (4.4\text{-}1)$$

where: corr = loss of thickness due to corrosion (μm),
$SO_2$ = $SO_2$ concentration ($\mu g/m^3$), and
tw = time-of-wetness [years (yr)].

Differentiating Equation 4.4-1 with respect to $SO_2$ or time-of-wetness while holding the other variables constant yields:

$$\left(\frac{\partial \, corr}{\partial \, tw}\right)_{SO_2} = 3.9 + 0.0383 \, SO_2 \qquad (4.4\text{-}2)$$

$$\left(\frac{\partial corr}{\partial SO_2}\right)_{tw} = 0.0383 \, tw \qquad (4.4\text{-}3)$$

which indicates that the extent of corrosion damage due to tw changes predominates over that induced by $SO_2$ concentration changes. Under natural or background conditions where $SO_2$ is negligible or absent, the function gives a corrosion penetration of 0.97 µm/yr for a 1-year exposure period (tw = 0.25 yr). Increasing the $SO_2$ concentration to 10 and 30 $\mu g/m^3$ yields corrosion loss of 1.07 and 1.26 µm/yr, respectively. On the other hand, at constant $SO_2$ concentration of 10 $\mu g/m^3$, increase in tw from 0.25 yr to 0.40 and 0.50 yr results in thickness loss of 1.71 and 2.14 µm/yr, respectively, and thus demonstrates the stronger influence of time-of-wetness. In other studies, $SO_2$ has not been found to be a very critical factor for corrosion damage to other metals. Mansfeld (1980) could not establish any significant correlation between corrosion and $SO_2$ levels from his exposure tests using weathering steel samples. Haagenrud (1978) exposed samples of carbon steel and measured the monthly corrosion rates for almost 2 years in Sweden. He concluded that infrequently encountered episodes of pH <4 and high $SO_2$ concentrations do not seem to influence the corrosion rates.

Additional studies have been conducted to increase our understanding of the atmospheric corrosion of metals in relation to acidic deposition. EPA did field research to partition the effects of dry and wet deposition on galvanized steel. After 2 years of exposure at Research Triangle Park, North Carolina, the weight loss of uncovered metal specimens was found to be twice that of the covered samples (Spence et al., 1985). Wet deposition (rainfall) has been considered to be removing the protective film on the uncovered galvanized steel thus exposing the metal surface to further corrosive attacks. In another related study, corrosion of galvanized chain-link fence was evaluated in four cities with different atmospheric and meteorological conditions (Philadelphia, Hartford, Denver, and Houston). No statistically significant differences in corrosion rates of zinc-coated fences among the cities were found (Cunningham et al., 1985) despite difference in $SO_2$ levels and various environmental factors.

Haynie (1985) analyzed the 30-month exposure data for weathering steel in the St. Louis, MO, area and evaluted the corrosion rate with respect to pollutant fluxes during both wet and dry periods, temperature, and exposure history. He pointed out that the corrosion process involves competing mechanisms of formation and dissolution of a protective oxide layer during times of wetness, and found that $SO_2$ increases the solubility of the film while $NO_2$ and rain favor the film dissolution.

Very recently, corrosion damage functions for several metals were developed by Lipfert et al. (1985) from a database of environmental variables which included $SO_2$ concentration, $Cl^-$ particle deposition, precipitation amounts and acidity, densefall loading, and times of surface wetness. The different damage functional forms for each metal suggested that time-of-wetness is most important for steel, while $SO_2$ seems to be the only important pollutant for copper, aluminum, zinc, and galvanized steel. Damage functions for copper, aluminum, and steel are not reliably accurate but appear to be adequate for the purpose of materials damage approximation.

In assessing the extent of metals damage in relation to air pollutant levels, care must be exercised in applying the corrosion rate functions. There is considerable uncertainty in the reliability of these functions even though they may be the only tools available for damage evaluations.

Some of the functions were developed from inadequate databases in which other environmental parameters were not measured. It must be stressed that atmospheric corrosion of metals is a complex process affected in the broadest sense by five broad categories of environmental factors--weathering, biological, mechanical, incompatibility, and use factors (Brown and Masters, 1982). Therefore, it seems unlikely that a reliable metal damage function can be explained simply in terms only of one air pollutant and one meteorological variable.

Masonry--Construction and decorative materials (stone, marble, and some mortar, etc.) known collectively as masonry, are susceptible to damage potentially caused by weathering agents, acidic deposition, and other atmospheric factors. These materials contain basic $CaCO_3$ which can be chemically attacked by acidic pollutants. Generally, the reaction of $CaCO_3$ with acidic pollutants during wet and dry deposition form products which exert mechanical stress to destroy the stone structure. These reaction products together with some stone particles, can be leached out by rainfall and removed by other weathering agents (Livingstone and Baer, 1983).

Basically, the decay mechanism proposed for carbonate-bearing materials involves the reaction of $CaCO_3$ with $SO_2$, $H_2SO_4$, $(NH_4)_2SO_4$, or $NH_4HSO_4$ to form anhydrous calcium sulfate (Yocom and Baer, 1983; Stevens et al., 1980) which is hydrated to form gypsum ($CaSO_4.2H_2O$), a more soluble salt highly susceptible to surface erosion. Recently, Cheng and Castillo (1984) used optical microscopy, scanning electron microscopy, and ion-probe analytical data to present a calcite decay mechanism involving $SO_2$, $CO_2$ (in the presence of $O_2$ and $H_2O$), and $NO_3^-$. This mechanism indicated that not only $SO_2$, but also $CO_2$ and $NO_3^-$, contribute to degradation of calcareous materials by forming compounds other than gypsum. Some gypsum in solution can penetrate the intergranular space of marble while the rest can be washed away (Gauri and Holdren, 1981). Like gypsum, other substances in the capillaries and interstices can undergo volume changes due to changes in humidity, rainfall, and temperature.

Other modes of damage to $CaCO_3$-bearing materials are possible. Tomback (1982) has classified several mechanisms of stone deterioration caused by several meteorological factors.

The calcite reaction with acidic pollutants may explain the unnaturally accelerated decay of stone buildings and monuments that has been observed in highly industrial areas with adverse air quality resulting from local sources. The accelerated damages reported on the Acropolis buildings contructed of pentelic marble (almost pure $CaCO_3$) (Yocom, 1979) and a sculpture on the west frieze of the Parthenon (Plenderleith and Werner, 1971) in Greece, and a sandstone sculpture (circa 1702) in West Germany (Winkler, 1982) were believed to be due to the interaction of oxidized $SO_2$ with the $CaCO_3$ of the materials.

Some quantitative studies of atmospheric pollution damage to stones have been reported. The differences in the observed deterioration of sandstone exposed in varying locations in Germany have been attributed to trends in local air quality (Luckat, 1981; cited by Yocum and Baer, 1983). Schreiber (1982) developed damage functions for Baumberg sandstone and Krensheim shell limestone in terms of $SO_2$ uptake rates; however, the statistical fit of the functions to the data was not good (Baumberg sandstone, $R^2 = 0.36$; Krensheim shell limestone, $R^2 = 0.80$). This suggests that other variables (physical and chemical properties of stone, rainfall, other pollutants) can potentially contribute to stone degradation. A study of tombstones in national cemeteries in the United States (Baer and Berman, 1983) indicated that grain size, local air quality, and total precipitation significantly affect the marble headstone damage rates.

Marble erosion data collected from nine air monitoring sites in the St. Louis, Missouri, area have been studied by Haynie (1983) with respect to the possible effects of total gaseous sulfur compound concentrations, levels of total gaseous $NO_x$, oxidants, time-of-wetness, wind speed, and temperature. Time-of-wetness was found to be the only statistically significant factor, accounting for 98.74 percent of the variability in the marble deterioration rate. $SO_x$ did not significantly affect marble erosion rates. A different result, however, was obtained by Husar et al. (1985) who analyzed the weathering rates of fine-grain marble tombstones in two cemeteries in the New York City vicinity. A linear relationship found between weathering rates and $SO_2$ concentrations suggested that $SO_2$ is an important factor for the marble deterioration. The investigator admitted that there was considerable error in the plotted data points. There was a great deal of uncertainty in the estimated $SO_2$ concentration and it was assumed that the meteorological conditions did not differ very much for the two cemeteries during 1930 through 1980.

In St. Augustine, Florida, Rosenow (1985) recently finished a study on the acid-rain-induced deterioration of Castillo de San Marcos National Monument which was constructed of coquina blocks. Coquina is a grainy and porous, sponge-like structure made up of sea shells (Donax shells) and other ingredients, such as calcareous limestone. Synthetically prepared rain water (pH 4.57 and 4.85), in addition to $HNO_3$ (pH 4.0) and $H_2SO_4$ (pH 4.0) solutions and deionized water as a control, were allowed to pass through the coquina columns and the collected leachates were analyzed for pH, calcium, magnesium, alkalinity, and other important ions, and compared with levels from pH 5.6 rain. Equilibrium calculations indicated that ocean spray and inland acid rain are both significant factors affecting coquina deterioration. However, no conclusion was made as to whether or not the effect of acid rain predominated over that of ocean spray.

Further studies are still needed to be able to develop more accurate damage functions for other materials involving several environmental factors and atmospheric pollutants. A computerized literature survey and inquiries of Webster and Kukacha (1984) revealed very little qualitative or quantitative information are available on acid rain deposition effects on Portland cement concrete.

Painted Surfaces--Paint is composed of pigments (e.g., titanium dioxide and zinc oxide) which impart color, and which provide film-forming properties. The vehicle contains resins, binders, solvents, and some additives. On painted surfaces, the pigment, with some fillers and extenders ($CaCO_3$ and silicate), and the vehicle protect the underlying surface and enhance the appearance of the exposed surface. Damage results from the cumulative effect of conditions which include various combinations of temperature, moisture, sunlight, and pollutant concentrations. To date, no field exposure study has been conducted to account for the influence of all environmental and meteorological factors and to accurately quantify the specific contribution of $SO_2$ effect relative to other factors. Similarly, the numerous possible combinations of factors cannot be duplicated in the chamber studies.

Attempts have been made to derive damage functions for paints exposed to gaseous pollutants. Chamber data of Haynie *et al*. (1976) were analyzed by Spence *et al*. (1975) who found no correlation of $SO_2$ and humidity with vinyl and acrylic oil coating. For the oil-based paint, a multiple regression analysis yielded the following relationship:

$$E = 14.3 + 0.0151\ SO_2 + 0.388\ RH \qquad (4.4\text{-}4)$$

where: $E$ = erosion rate (μm/yr),
$SO_2$ = $SO_2$ concentration (μg/$m^3$), and
$RH$ = mean of annual relative humidity (%).

This bivariate statistical model (Equation 4.4-4) suggests that paint damage is significantly more sensitive to changes in relative humidity than to changes in $SO_2$ concentration.

Significant differences in damage functions were observed in comparing experimental results of some investigators. For instance, the coefficients of the equations developed by Campbell *et al*. (1972) in the

Sherwin Williams study were substantially lower than those reported by Haynie et al. (1976). The lack of agreement between the results of the two chamber studies coupled with the seemingly unrealistic estimates from the developed functions (Stankunas et al., 1983) demonstrates the limitations and difficulty in applying the function to damage analysis. Both damage functions were based on erosion rates derived from mass loss which may not be a reliable measure of material damage in the context of the need for repair or replacement due to failure. Erosion of the paint film is not known to affect loss of film adhesion or to promote film substrate delamination. Occasionally, actual paint damage may be indicated by peeling or rusting. For exterior household paints, the shrinking and expansion of wood together with freezing of moisture trapped between paint layers can cause normal failure which may not be related to atmospheric pollutants.

Although chamber studies have shown a minor role associated with $SO_2$ in the deterioration of some paints, results of some field studies demonstrated that natural factors appeared to override the impact of acidic deposition. In a field study in St. Louis where several environmental variables were measured, household paint damage was not significantly affected by $SO_2$ (Haynie and Spence, 1983), indicating that other factors exerted more important effects on paint damage under outdoor atmospheric conditions.

Climatic and air quality data were recorded during a 30-month exposure of two types of white exterior household paints (latex and oil base) in St. Louis, Missouri, area. Paint deteoriation was evaluated by measuring the rate of surface erosion. After analyzing the data, Haynie and Spence (1984) concluded that both paints are eroded primarily by the effects of time-of-wetness, temperature, and sunlight, and that $SO_2$ has no effect at the ambient levels to which the paints have been exposed. Further critical examination of available data from laboratory and field studies of erosion damage to paints led Haynie (1986) to suggest much more information is needed to accurately assess the damaging effects of acid depositon on paints. Results of past field studies were not adequate to establish whether or not a relationship exists between paint damage and acid deposition.

Other Materials (Paper, Textiles, Leather, and Photographic Materials)--The majority of materials composed of organic compounds are potentially susceptible to acidic deposition, especially in the presence of ultraviolet light and other oxidants ($O_2$ and $O_3$). Humidity is important when organic hydrolysis is the dominant deterioration mechanism. Glucosidic bonds in cellulose, a polymeric carbohydrate present in paper and linen, are known to be cleaved by acid hydrolysis. Early experiments conducted by Langwell (1952; 1953) and Hudson and Milner (1961) demonstrated the role of $SO_2$ in the deterioration of paper. Due to acidity and $SO_2$ sorption, old books and wall papers have been observed to deteriorate (Hudson, 1967; Spedding and Rowlands, 1970). Photographic materials (paper, acetate film, and gelatin) have been reported to be adversely affected by significant quantities of gases such as $H_2S$, $SO_2$, and to a lesser extent by $NO_x$, peroxides, and $O_3$ (Eastman Kodak, 1979). Weyde (1972) described a simple test to identify oxidizing gases responsible for damage to silver photographic materials in the indoor atmospheres of archives.

Acidic pollutants can chemically attack textile materials, resulting in depolymerization and subsequent loss of tensile strength. Studies of Brysson _et al_. (1967), Zeronian (1970), and Zeronian _et al_. (1971; 1973) showed relatively higher loss of tensile strength of cotton, rayon, and nylon fabrics due to $SO_2$ exposure. In the presence of light and acidity, $SO_2$ damage to silk was greater (Leene _et al_., 1975). Fading and discoloration of some colored fabrics, accompanied by loss of fiber strength, were attributed to the combined presence of $SO_2$ and $NO_2$ (Beloin, 1973; Harrison, 1975).

Collagen in leather can be damaged by a process involving a metal-ion catalyzed conversion of absorbed $SO_2$ to $H_2SO_4$. Using tagged $^{35}SO_2$, Spedding _et al_. (1971) demonstrated that $SO_x$ can be adsorbed evenly on the leather surface. $SO_2$ attack, however, may be limited by the gas-phase diffusion. Some investigators (Innes, 1948; cited by Yocum and Baer, 1983; Smith, 1964) have previously described the sequence of chemical deterioration of leather. The hydrolytic weakening of leather causes cracking and ultimately transforms the leather to a red-brown powder (Spedding _et al_., 1971; Yocom and Grappone, 1976).

In most of the studies and experiments conducted to date, high concentrations of $SO_2$ were used to evaluate potential damage to textiles, leather, and photographic materials. No accurate damage functions were reported to isolate the effect of $SO_2$ from the effects of other strong oxidizing gases and other important environmental factors.

_Culturally Significant Materials_--Inorganic and organic materials are present in museums, libraries, archives, architectural monuments, and other works of art which are potentially susceptible to acidic deposition damage under favorable environmental conditions. The mechanisms of deterioration of these materials by atmospheric pollutants, $SO_2$ in particular, are generally comparable to those previously described for metals, masonry, and paper. In an indoor environment, sorption of $SO_x$ and $NO_x$ typically precedes the reaction causing the damage. A direct relationship between pollutant sorption and damage has led major museums and libraries to install scrubbers to remove acidic gases (Yocom and Baer, 1983).

Damage to culturally significant structures such as important architectural monuments and historical edifices due to $SO_2$ and other weathering agents in heavily polluted atmospheres has been reported in Europe (Yocom and Upham, 1977; Luckat, 1976), India (Gajendragalcar, 1977), and Japan (Kadokura and Emoto, 1974). Medieval stained glass was observed to undergo accelerated deterioration (Korn, 1971) which was found to be caused by the combined action of $SO_2$ attack and leaching by condensed water (Newton, 1974). It is not certain whether the leaching effect predominates over $SO_2$ deposition.

The process of degradation of historical and important works of art is commonly believed to have taken place over a long period of time. The actual damage observed today is viewed by most researchers as a cumulative effect of slow damage rates associated with acidic deposition and other environmental factors. This type of damage is generally regarded as irreversible because it is difficult to repair and restore cultural structures to their original state and condition.

#### 4.4.1.4 Implications

Various physical and chemical mechanisms have been presented to account for the effects of acidic deposition in the materials damage process. Because of the inherent limitations of the experimental approaches, statistically derived functions quantifying the dose-response relationship between acidic deposition and materials damage have considerable uncertainty.

The data gathered so far are still insufficient to provide a more defensible basis to accurately quantify the incremental contribution of acidic deposition to materials degradation. In some field tests, meteorological and air quality data were inadequately measured, thereby precluding proper quantification of $SO_2$-induced effects during the statistical analysis. Coupled with the questionable statistical validity of some damage functions is the manner by which the actual damage of the materials is determined. Mass loss of metals and painted surfaces is not necessarily an appropriate measure of damages. For instance, damage to paint is usually in the form of substrate delamination or loss of film adhesion and not a uniform loss of thickness derived from mass loss.

materials damage attributable to acidic deposition alone would be slight or perhaps negligible within Florida. Meteorological and other environmental factors such as high humidity and relatively long sunshine exposure would be expected to be dominant factors in materials degradation within Florida. With regard to historically important cultural structures, even a minor acceleration in damage rates would be a concern, but an acidic deposition effect has not been demonstrated either in Florida or under atmospheric conditions similar to Florida's.

### 4.4.2 INDIRECT EFFECTS ON PLUMBING MATERIALS

The potential for acidification of surface waters as a result of acidic deposition is addressed in Section 4.3. Considerably less research attention has been focused on the potential acidification of ground waters, although the factors influencing impacts on soils (refer to Section 4.2) exert important controls on the acidification of shallow water-table aquifers. The technical literature indicates that acidification of both ground and surface waters may result from acidic deposition in watersheds whose soils, geologic substrates, and natural waters have a low buffering capacity. These surface and ground waters may be used as potable water supplies.

Middleton and Rhodes (1984) reviewed several studies that provide qualitative evidence of a possible link between acidic deposition and degradation of drinking water quality. Consequently, the potential of acidic deposition to increase water corrosivity to distribution systems and plumbing materials has been a concern to the water works industry (Reed and Henningson, 1984).

#### 4.4.2.1 Mechanism of Corrosion

Waters with relatively low pH (<6.0) have been observed to increase the corrosion of metal and other plumbing materials in potable water system (Ahmadi, 1981; Pisigan, 1981; Schock and Gardels, 1983). To understand better the influence of acidity on material damage in the piping system, a brief discussion of the mechanism of aqueous metal corrosion is presented. Corrosion is basically an electrochemical process involving oxidation and reduction reactions on the metal surface. These electrode reactions can be represented for iron (Fe) metal in contact with water with dissolved chemicals as follows:

Anode (oxidation):

$$Fe \dashrightarrow Fe^{+2} + 2e^-$$

$$2Fe^{+2} + 1/2\ O_2 + 5H_2O \dashrightarrow 2Fe(OH)_3 \text{ (or hydrated oxides)} + 4H^+$$

Cathode (reduction):

$O_2 + 4H^+ + 4e^- \text{--->} 2H_2O$ (acidic solution)

$O_2 + 2H_2O + 4e^- \text{--->} 4OH^-$ (neutral to basic solution)

In a typical acidic water with dissolved oxygen, further increase in acidity can enhance the cathodic process and, in turn, the anodic reactions which consume the metal. Deposited corrosion products (iron oxides or hydroxides) can dissolve due to higher acidity, thus exposing the bare metal to further corrosive attacks.

In asbestos-cement pipes, the basic deterioration mechanism is dissolution of calcium-based compounds accompanied by asbestos fiber leaching to the water.

### 4.4.2.2 Corrosion in Water Distribution Systems

Generally, physical factors (temperature, velocity), chemical factors (pH, oxygen, salt, and other dissolved compounds), and biological factors (bacterial action) influence corrosion of plumbing materials used in water distribution systems. Important chemical factors promoting corrosion (e.g., low pH, low alkalinity and buffer capacity, high concentration of $Cl^-$ and $SO_4^{-2}$, and appreciable amounts of $O_2$ and $Cl_2$) have been discussed and summarized by Singley et al. (1984) and Kirkmeyer (1983).

Water corrosivity is traditionally evaluated by analyzing pH, Ca, alkalinity, temperature, and total dissolved solids (TDS) which are used together with other parameters in calculating various indices such as the Langelier Index (Langelier, 1936), Ryznar Index or Stability Index (Ryznar, 1944), Larson's Ratio (Larson, 1966), Riddick Corrosion Index (Riddick, 1944), Casil Index (Loschiavo, 1948), Calcite Saturation Index, and Aggressiveness Index (AI) (Millette et al., 1980). AI is applied only to asbestos-cement (AC) pipe deterioration. Kirkmeyer (1983) theoretically analyzed the effects of acidic deposition on these corrosion indices and reported that acidic deposition changes the value of each index toward increased corrosivity. Kirkmeyer's analysis was qualitative and appears to be based on the concept that the effect of acidic deposition is to increase the concentrations of $H^+$ and $SO_4^{-2}$ in water delivered through the distribution system. This is a gross oversimplification of the actual relationship between acidic deposition and the quality of water in potable supply distribution systems.

Taylor and Symons (1984) applied some of these indices to hundreds of raw water supplies in the eastern United States to evaluate the potential effects of acidic precipitation and concluded that soft, low-pH and weakly buffered waters have been affected by acidic deposition. However, neither in the theoretical prediction of Kirkmeyer (1983) nor in the water quality analysis of Taylor and Symons (1984) was the incremental contribution of acidic deposition to the water's acidity or corrosivity considered.

Taylor and Symons (1984) also presented an interesting historical database from the Salem-Beverly, Massachusetts, water supply utility. The utility's raw water supply is a surface water body, Wenham Lake. Hardness, expressed in terms of milligrams of $CaCO_3$ per liter, averaged 25 prior to 1935 and 36 since 1935. Alkalinity and pH have remained virtually unchanged since 1935, and the calculated corrosivity indices remained relatively unchanged throughout the period from 1935 to 1980.

Turk and Peters (1978) concluded that their data on acid rain, pH, and dissolved metal concentrations would not support an estimate of the extent to which increased precipitation acidity and decreased pH of water had intensified the corrosion of pipes. Karalekas et al. (1975, 1977, 1982) and Karalekas (1980) investigated the extent of corrosion of lead pipes in the Boston area by soft and acidic waters. Acidic deposition has not been identified as the ultimate cause of the acidic character of the raw water supply, and lead concentrations in the tap water were reduced by adjusting the pH (pH >8.0) with NaOH and $NaHCO_3$ treatment.

The difficulty of assessing how much corrosion or material deterioration has occurred due to acidic deposition stems from the following:

1. Natural or "pristine" rain [as characterized, for example, by Galloway _et al_. (1982)] would be expected to be relatively corrosive;
2. Tools used in evaluating water's corrosivity are not adequately reliable as indicated by a critical conceptual analysis of the various corrosion indices (Singley _et al_., 1984), experimental results for iron and galvanized steel (Pisigan and Singley, 1985a, 1985b), and asbestos leaching observed in waters judged to be non-aggressive according to AI value (Kanarek _et al_., 1980); and
3. Corrosion is a complex process involving interaction of several factors and may not be simply affected by acidity alone.

### 4.4.2.3 Metal Leaching

Metallic ions can be leached into the water during corrosion and dissolution of deposited corrosion products once the solution near the metal-water interface becomes sufficiently acidic. Generally, the level of leached metallic ions are relatively higher in acidic waters conducted through iron pipes (Singley _et al_., 1984), galvanized steel coupons (Pisigan and Singley, 1985b), lead pipes (Sheiham and Jackson, 1981), and copper tubings (Cruse and Pomeroy, 1985). Fuhs and co-workers have studied the metal concentration in drinking water sources and tap water at various locations in the Adirondacks affected by acidic deposition (Fuhs and Olsen, 1979; Fuhs, 1981; Fuhs _et al_., 1982). Levels of lead and copper in some tap water samples were found to exceed drinking water standards. Studies of cistern systems by Young and Sharpe (1984) showed that the lead leached into the tap water is a corrosion product formed in acidic water (pH 3.40 to 5.29). A survey conducted in Sweden indicated that due to acidic deposition, untreated drinking water supplies have become acidified and attacked the cisterns and water pipes leading to leaching of copper, lead, cadmium, and zinc into solution (Stockholm Conference on Acidification of the Environment, 1982).

### 4.4.2.4 Corrosion Control Measures

Because it is economically impractical to replace the plumbing materials with the more corrosive-resistant metals and inappropriate to employ electrochemical techniques (which are typically used in industrial systems), water quality modification appears to be most appropriate in controlling corrosion in drinking water systems. Since the immediate impact of acidic deposition is increased acidity which can potentially enhance corrosivity of raw water supplies, the most obvious general solution is acid neutralization. Quite often the lowered alkalinity due to acidity has to be replenished and even raised. The water needs to be treated to remove metals, especially toxic ones. Several conditioning chemicals can be used to raise the pH and alkalinity and provide a sufficiently strong buffer capacity. Lime and caustic soda are typically used for pH adjustment, and sodium bicarbonate or carbonate is added to increase the carbonate alkalinity. In cases where $CaCO_3$ deposition is the chosen corrosion control method, $Ca(OH)_2$ treatment is done, particularly in water with sufficient carbonate alkalinity. A combination of $Ca(OH)_2$ and sodium bicarbonate treatment may be appropriate to soft acidic water with very low carbonate alkalinity. Sometimes the use of corrosion inhibitors (e.g., phosphates or silicates) may prove to be the best option. In implementing the strategy, monitoring of corrosion rates and periodic water quality analysis and effectiveness evaluations have to be conducted.

### 4.4.2.5 Implications

For acidic deposition to indirectly cause corrosion of piping in potable water distribution systems, a complex chain of events must occur. As discussed previously, corrosion is a complex phenomenon affected by a variety of chemical, physical, and biological factors. Isolating the incremental effect of acidic deposition would be difficult; indeed, studies that have been reported in the technical literature do not provide sufficient evidence to demonstrate that such effects have occurred. In some relatively atypical water supply systems, such as cisterns used to collect rainwater or individual spring-fed water supplies in the Adirondack Mountains, the data suggest that acidic precipitation may have exacerbated corrosion problems. Stated simply, acidic deposition must acidify the raw water supply or otherwise cause the supply to become more aggressive or corrosive; secondly, this raw water supply must not be treated to mitigate its aggressiveness; and thirdly, the distribution system must contain materials (e.g., lead solder or iron pipe) susceptible to corrosion.

Within the State of Florida, approximately 60 percent of the population is served by a public water supply derived from a limestone aquifer. Because of the massive neutralization capacity of these limerock formations, these supplies are not susceptible to acidification.

Approximately 10 percent of Florida's population is served by public water supplies from surface water sources, principally the Hillsborough and Peace Rivers. These surface water supplies are relatively hard and alkaline (alkalinity = 50 to 150 mg/L as $CaCO_3$; hardness = 70 to 200 mg/L as $CaCO_3$), are not particularly aggressive, and are not susceptible to significant modifications by acidic deposition.

Approximately 10 percent of the population is served by public supplies drawn from the Sand and Gravel Aquifer of the western panhandle or from undifferentiated surficial and intermediate aquifers which are primary ground water sources over much of the Atlantic coast region. These undifferentiated aquifers may consist of sand, shell, sandstone, or limestone. Compared to the Floridan and Biscayne Aquifers, the undifferentiated aquifers and the Sand and Gravel Aquifer would tend to be more susceptible to acidification. Nonetheless, no data are available indicating that these ground water sources have been affected by acidic deposition, and the effectiveness of soils in neutralizing acidic precipitation (refer to Section 4.2) suggests that significant effects on the quality of these aquifers are unlikely.

Approximately 20 percent of Florida's population derives its drinking water from individual domestic wells. Data on the source and quality of water from domestic wells are less available than for major public supplies, particularly related to the amount of the state's population deriving its drinking water from shallow domestic wells in surficial sand deposits or alluvial sand and gravel deposits which would be more susceptible to incremental corrosion caused by acidic deposition than wells drawing from limestone aquifers. These users are predominantly in rural or suburban fringe areas. The potential for corrosion problems resulting from acidic deposition for these residents is also presumed to be very low because of the neutralizing capacity of soils and aquifer materials in most areas of Florida, but data are insufficient to characterize the risk at this time.

In summary, at least 70 percent of Florida's population is served by water supplies with virtually no potential for acidification. Of the remaining 30 percent of the population, 10 percent is serviced by public water supplies drawn from ground water sources whose neutralization/buffering capacity is somewhat uncertain based on readily available data. Public water suppliers would be expected to test and treat their water supplies if there is an indication of a corrosive potential. The remaining 20 percent of the state's population derives drinking water from individual domestic wells. Many of these wells tap limestone aquifers and are immune to any effects of acidic deposition. Incremental corrosion of piping by acidic deposition in potable water delivery systems is plausible only for individual domestic walls drawing from shallow sand aquifers. Even for this portion of the state's population, effects are very unlikely in the context of the neutralizing capacity of soils as indicated by the Lake McCloud studies.

## 4.5 SUMMARY OF ECOLOGICAL EFFECTS OF ACIDIC DEPOSITION IN FLORIDA

The previous sections of this chapter have presented the results of research into the nature and extent of ecological effects associated with acidic deposition in Florida. The focus of this presentation has been on research specific for Florida's ecological resources and has drawn upon results from the Florida Acid Deposition Study, research conducted by other researchers on aquatic and terrestrial systems in Florida, and from research conducted in the northeastern United States, Canada, western Europe, and Scandinavia of a nature considered relevant for the Florida experience. The underlying objective of each section of this chapter was to develop the framework required to address fundamental research questions relating to the acidic deposition phenomenon in Florida (see Table 1.2-1). These questions are addressed specifically in the sections that follow.

- What are the chemical/physical relationships between acidic deposition and lake sensitivity and which lakes are potentially sensitive to current levels of acidic deposition?

Aquatic systems in Florida potentially sensitive to acidic deposition have several geochemical and hydrological features in common. Lakes with the greatest likelihood for undergoing changes in response to acidic deposition are those with (1) lakewaters with low ANC, (2) watershed soils dominated by acidic soils with low CEC, low base saturation, and minimal ability to adsorb sulfate, and (3) hydrologic budgets dominated by precipitation directly to the lake surface.

Soils characteristics perhaps represent the most fundamental variable for examining sensitivity on a regional basis. Lake hydrology followed by lakewater ANC can be used sequentially to further define the overall population of lakes with the greatest perceived sensitivity. Again, it must be emphasized that each lake categorized by the above criteria may not be sensitive because of differing biological and chemical characteristics (e.g., the presence of high concentrations of organic color).

Lakes characterized by all three of the above features may be found among the many seepage lakes characteristic of the sandhills of the highlands and ridge physiographic regions of the panhandle and peninsular Florida (Figure 4.5-1); these lakes have no surface inlets or outlets and derive the bulk of their hydrologic inputs from precipitation directly to the lake surface. As a result, lakewater chemistry of these systems is extremely dilute and reflects rainfall chemistry (in terms of ionic strength and ANC) more closely than other aquatic systems in Florida. For example, conductivity of precipitation in Florida approximates 10 µS/cm on the average and ranges as high as 50 to 60 µS/cm; many softwater seepage lakes have conductivities on the order of 20 to 50 µs/cm, with conductivities of less than 20 µS/cm reported for some lakes in the panhandle and north-central Florida. The precise number of seepage lakes in Florida is unknown but may total 2,000 or more of Florida's more than 7,300 lakes. Preliminary results of the National Lake Survey conducted by EPA indicates that approximately 1,600 of the lakes located primarily in highlands regions are seepage lakes.

An important variable is the relative contribution of seepage from the shallow ground water table to the overall hydrology of seepage lakes. Despite the rather poor buffering characteristics and acidic nature of the soils, acidic deposition falling within the watersheds of seepage lakes appears to be almost completely neutralized by ion exchange and some nitrate and sulfate retention; as a result, seepage of ground water into these systems can be an important source of ANC. Lakes with greater inseepage fluxes should be correspondingly less sensitive to acidic deposition. Because of the very high infiltration capacity of the sandy soils characteristic of these watersheds, surface runoff is virtually nonexistent. Thus overall long-term relative contribution of the

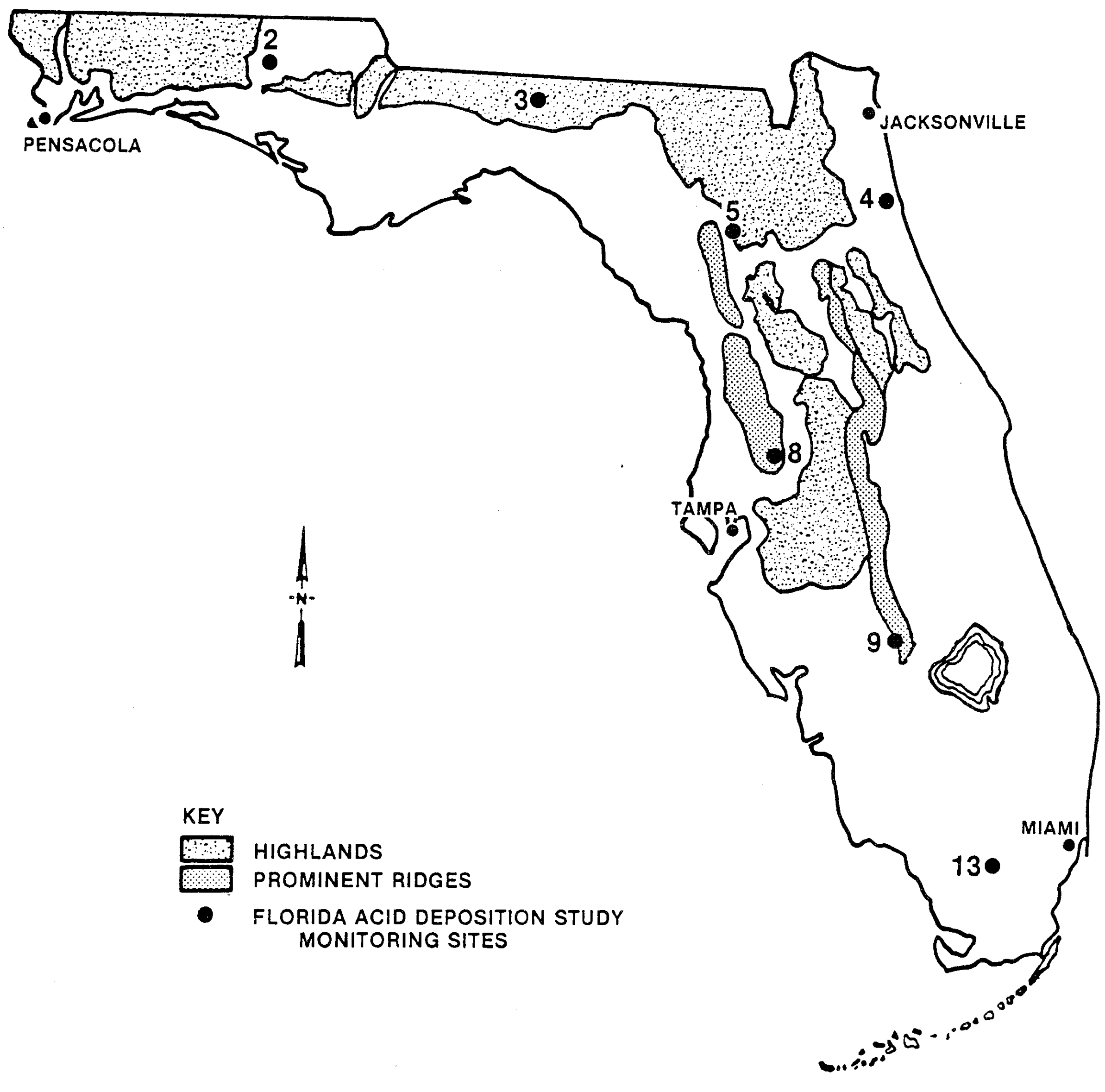

Figure 4.5-1
PHYSIOGRAPHY OF FLORIDA

SOURCES: Florida State University, 1981; ESE, 1986.

ENVIRONMENTAL SCIENCE
AND ENGINEERING, INC.

watershed to seepage lake hydrology simply reflects the difference between precipitation and evaporation from the lake surface; lakes with proportionally more precipitation than evaporation tend to discharge more water to and receive less inseepage from the shallow ground water table than lakes receiving less relative amounts of precipitation. In Florida, the net difference between precipitation and evaporation decreases as a general gradient from north to south, implying that ground water inputs to seepage lakes in the highlands of south-central Florida are more significant than corresponding inputs to seepage lakes in northern Florida. Thus potential sensitivity to acidic deposition lies along a gradient extending from north to south, with seepage lakes in the highlands of the panhandle potentially more sensitive than similar lakes in the highlands of north- and south-central Florida.

Seepage lakes in Florida in all likelihood approximate so-called direct response (as opposed to delayed response or capacity protected) systems in regard to changes in rainfall acidity. In other words, because precipitation dominates the hydrology of these lakes (~90 percent of the inputs), seepage lakes may be expected to respond rapidly to changes in atmospheric deposition. The rapidity of response of seepage lakes compared to other aquatic systems is also consistent with the mobile anion hypothesis; i.e. the principle of electroneutrality dictates that cation (e.g. protons, base cations such as calcium and magnesium, and aluminum) mobilization and transport in watersheds must be accompanied by an equivalent quantity of anions. Processes such as adsorption or vegetative uptake which limit the mobility of sulfate in particular (since sulfate is the dominant anion in Florida precipitation) promote a delayed watershed response. The sulfate time of travel in watersheds (and hence the time scale of response to acidic deposition) reflects the hydrologic flowpath and the sulfate retention characteristics of the soil; however, because the flux of sulfate in seepage lakes is dominated by direct precipitation rather than flow through the watershed, seepage lakewater chemistry responses to changes in atmospheric sulfate loading should be more rapid than for lakes with similar residence times but derive a significant portion of their water from surface runoff and ground water.

Apart from the relative chemical contributions of different hydrologic flowpaths, temporal response of lakes to changes in acidic deposition is a direct function of lake hydraulic residence time. Residence time ($\tau_w$) is simply the ratio of lake volume to outflow. For seepage lakes, outflow consists entirely of seepage outflow; by normalizing the seepage outflow by the surface area of the lake, the residence time of seepage lakes reduces to a function of the normalized outflow and mean depth of the lake:

$$\tau_w = \bar{z}/Q_o$$

where: $Q_o$ = seepage outflow rate (m/yr) normalized to the lake surface area, and
$\bar{z}$ = mean depth of the lake (m).

Thus, all other factors considered equal (i.e., neglecting sediment-water interactions in particular), shallow lakes should respond more rapidly to acidic deposition than deep lakes; similarly, seepage lakes in regions with relatively greater amounts of precipitation than evaporation will respond more quickly than seepage lakes in regions where the net difference between precipitation and evaporation is less. For lakes in the Trail Ridge of north-central Florida, $\tau_w$ is approximately $\bar{z}/0.35$; by comparison, $\tau_w$ for lakes in the Highlands Ridge of south-central Florida is approximately $\bar{z}/0.24$. As a result, the timeframe of response of seepage lakes in north-central Florida (excluding watershed effects) will be approximately 50 percent more rapid than for similar lakes in south-central Florida; assuming that these lakes respond to perturbations within 3 residence times (cf. Sonzogni *et al.*, 1976) indicates a timeframe of response of approximately 26 and 38 years. It should be understood that the timeframe of response discussed here is long-term (i.e., years) changes in atmospheric deposition rather than short-term variations; in this context, perturbations are more properly considered as step function shifts in deposition rates. For seepage lakes in the Western Highlands of the panhandle, seepage outflow rates probably exceed rates in north-central Florida resulting in correspondingly more rapid response times.

A final important set of processes regulating the response of lakes to acidic inputs is the interaction of the bottom sediments with overlying lakewater. Sediment interactions with overlying lakewater may be regarded as an areal process (i.e., x $m^2$ of sediment interacting with y $m^3$ of lakewater); thus, the greater influence of the bottom sediments on lakewater chemistry in shallow lakes may offset the enhancement of sensitivity to acidic deposition imposed by a shorter hydraulic residence time (cf. Rawson, 1955; Fee, 1979).

Sulfate reduction, which is a microbially mediated process, is an important process contributing to in-lake neutralization of acidic inputs in poorly buffered, softwater seepage lakes. In addition, uptake of nitrate and ammonium by primary producers results in the generation and consumption, respectively, of ANC. Of these three biogeochemical processes, the sources and fluxes of ammonium in particular are not well quantified. Organic matter decomposition in the bottom sediments results in the release of $NH_4^+$ and ANC into the porewater; diffusion of $NH_4^+$ into the overlying water, however, can be a significant internal source of acidity to seepage lakes.

The magnitude of response of softwater seepage lakes with low ANC to acidic deposition is thus mediated by two principal factors: (1) lake hydrology and specifically inseepage contributions to ANC, and (2) the net balance of biogeochemical processes resulting in the depletion of sulfate, nitrate, and ammonium from the water column. Hydrology also dictates how rapidly seepage lakes will respond to acidic deposition, and low-ANC seepage lakes with short hydraulic residence time must be considered relatively more susceptible to acidification effects because of reduced seepage inputs and, by definition, a shorter timeframe of response. Which of these two factors is most important is not known but can be inferred from relative differences in $SO_4^{-2}$ enrichment ratios between south- and north-central Florida seepage lakes. $SO_4^{-2}$ enrichment ratios are higher for south-central Florida seepage lakes, which would suggest that north-central Florida lakes have higher ANC owing to apparently higher $SO_4^{-2}$ reduction rates (and thus lower enrichment ratios). However, higher ANC is generally observed in south-central Florida lakes--a regional trend which is consistent with the relatively greater inseepage contibutions hypothesized for south-central Florida. Other factors such as urban development and geological differences also may be important. Detailed ion budgets are necessary to examine more fully the relative contributions of inseepage and $SO_4^{-2}$ reduction to the ANC dynamics of softwater seepage lakes.

- What are the chemical/physical relationships between acidic deposition and soil sensitivity and which soils are potentially sensitive to current levels of acidic deposition?

Increased losses of base cations and the mobilization of aluminum when base cation reserves are exhausted probably are the most significant effects of acidic deposition on soils. Using aluminum solubilization as the parameter defining sensitivity, the most sensitive soils are those which are already acidic, with low CEC and base saturation, such that aluminum and manganese solubilization is the principal mechanism buffering against changes in soil solution pH. Because charge balance considerations preclude cation transport in the absence of a mobile anion, $SO_4^{-2}$ adsorption can mitigate soil acidification effects; in other words, soils with low $SO_4^{-2}$ adsorption capacities are more likely to exhibit effects of acidification than soils with greater $SO_4^{-2}$ retention capabilities. Soils in Florida exhibiting these characteristics (i.e. low CEC, base saturation, and $SO_4^{-2}$ adsorption) include principally the highly leached and deep acidic sands (entisols and ultisols) of the Western Highlands of the panhandle and the Central Ridge of peninsular Florida (Figure 4.5-2).

- How are lakes likely to respond to current levels or changes in current levels of acidic deposition?

Seepage lakes with low pH, minimal or no concentrations of ANC present in the water column, and low concentration of DOC (i.e., clearwater lakes) are in all likelihood the most sensitive aquatic systems in Florida. By virtue of being a seepage lake, watershed hydrologic inputs are small and atmospheric inputs assume more significance in the overall ANC budget relative to other systems characterized by a greater degree of interaction with the watershed soils. [In this case, sensitivity is applied to reflect principally biological response. Buffering in low-pH lakes (i.e., pH 5 or less) includes $H^+$ and solubilization of the toxic metal aluminum; relatively small changes in lakewater pH will occur for these lakes compared to low ANC lakes at pH levels above 5].

The response to current levels of acidic deposition or changes in current deposition rates to these lakes, which are located principally in the acidic deep sands of the Western Highlands of the panhandle and the Central Ridge of peninsular Florida, is not well understood. For the most part, acidic deposition-related research for Florida lakes has focused on several limited surveys to delineate the chemical and biological characteristics of seepage systems. From these surveys biological and chemical responses to acidification have been inferred. These surveys have been augmented to some extent by (1) manipulation studies conducted in situ via enclosure studies in Lake McCloud, a seepage lake in north-central Florida, in which changes in pH (both increases and decreases) were investigated, and (2) laboratory investigations of the interaction of lake sediment and lakewater in response to acidic inputs. In addition, results from a few limited

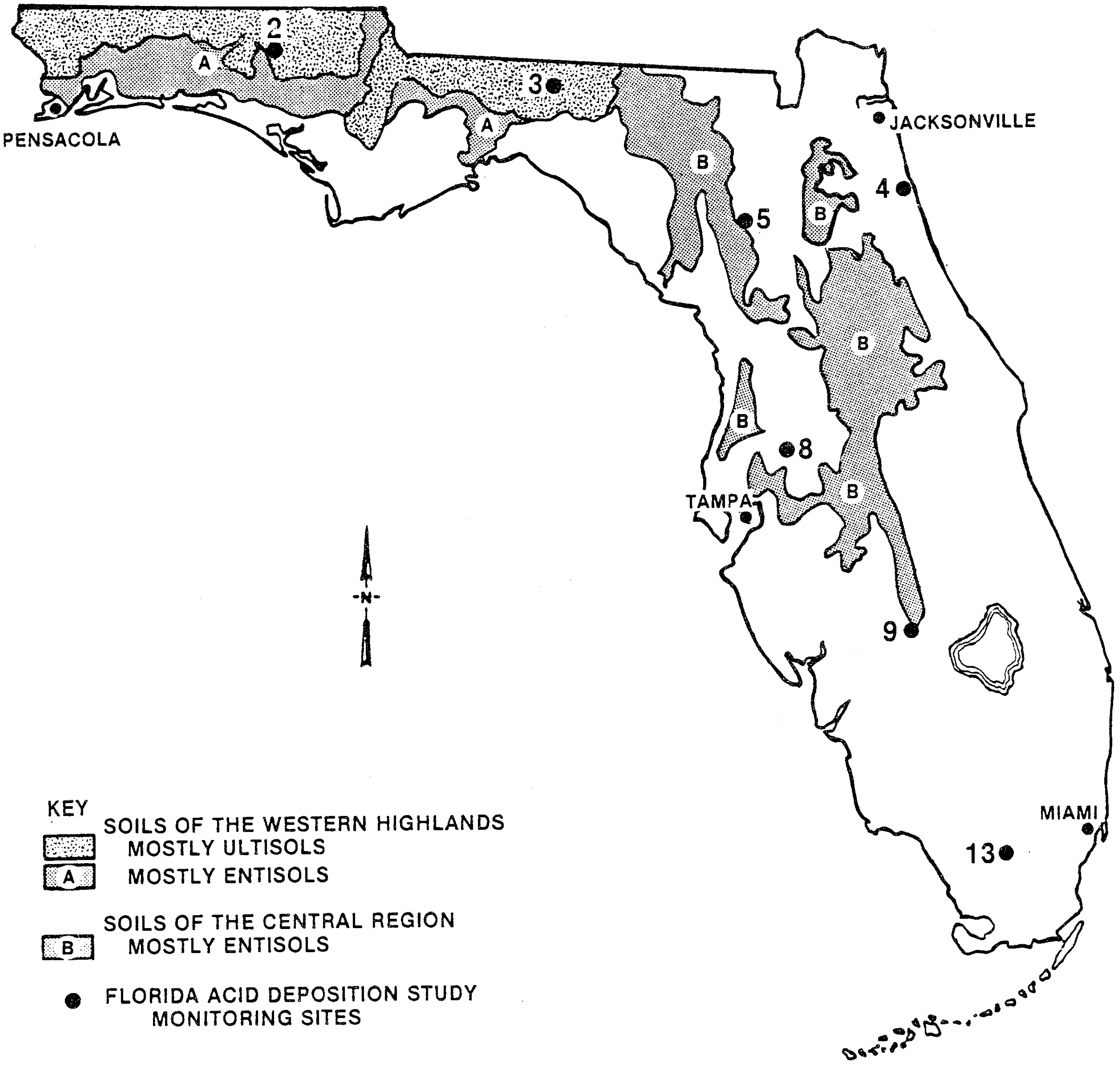

Figure 4.5-2
SOIL TYPES OF FLORIDA

SOURCES: Florida State University, 1981; ESE, 1986.

ENVIRONMENTAL SCIENCE
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investigations of direct biological response to acidification are available to infer biological response.

Preliminary results of the NLS conducted by EPA suggest that Florida (and part of southern Georgia) contain approximately 1,600 seepage lakes located principally in the highlands and ridge region of Florida. Of these lakes, a relatively large number are apparently poorly buffered with low pH; preliminary estimates indicate 43 percent of the seepage lakes have ANC concentrations less than 40 µeq/L and 37 percent have pH levels less than 6.0. In addition, 28 percent of these seepage lakes are estimated to contain ANC concentrations less than 0.

The likelihood of response to acidic deposition is a function of lakewater ANC, lake hydrology, and internal biogeochemical processes as well as the rate of acidic deposition. Hydrologic factors (short hydraulic residence time and low inseepage rates), depositional patterns, and internal biogeochemical considerations all suggest that seepage lakes in Western Highlands of the panhandle are the most likely to exhibit some response to acidic deposition. Moreover, preliminary NLS results confirm a general north-south gradient of increasing lakewater ANC concentrations described in earlier surveys and indicate that a large fraction of lakes in the Western Highlands and the Trail Ridge of north-central Florida have low ANC (<40 µeq/L).

Because of the paucity of historical data, whether lakes in the Western Highland have been affected by current levels of acidic deposition is unknown. Comparisons of historical lakewater chemistry data for several lakes in the Trail Ridge suggest minor declines in lakewater ANC and pH and increases in lakewater excess $SO_4^{-2}$ concentration between 1957 and 1979. Lakes Brooklyn, Magnolia, and Lowry all showed losses of ANC from about 25 or 30 µeq/L to <5 ueq/L. However, the analytical precision of the methods used to measure ANC (approximately 20 µeq/L) approximates and tends to obscure the significance of the estimated differences. The largest apparent declines in pH were observed for Lakes Brooklyn and Magnolia; during this period, lakewater pH of both lakes fell 0.5 unit to pH 5.0 and 5.2, respectively. No cause and effect relationship between acidic deposition and changes in lakewater pH and ANC have been established, and the influence to which hydrologic variations may have affected trends in chemical composition has not been definitively evaluated.

Similar historical trends in lakewater chemistry have been observed for another lake in the Trail Ridge, Lake McCloud, between 1968 and 1982. Lakewater pH in Lake McCloud has declined from about pH 4.85 in 1968-1969 to pH <4.6 in 1981-1982, a reduction in pH which equates to an approximate doubling of proton concentrations. Corresponding increases in lakewater excess sulfate were also observed and suggest that acidic deposition may have contributed to the decline. However, the significance of the reported change in $SO_4^{-2}$ concentrations is not well established. Differences in analytical techniques used between the 1968 and 1982 studies indicate the estimated increase in $SO_4^{-2}$ concentrations is probably overestimated. Furthermore, the ionic balance for 1968 data is poor (cation/anion ratio = 0.81), and the calcium concentrations reported for 1968 appear anomalously low compared to other constituents. Apart from the limited data on these four lakes in the Trail Ridge, no other data are available to evaluate a response to current levels of acidic deposition. Additional historical data on Lakes Geneva and Kingsley between 1957 and 1979 show increases in lakewater excess $SO_4^{-2}$ concentrations; however, both of these lakes are strongly influenced by residential development within their watersheds and receive runoff and septic tank leachate from these developments. As a result, ANC concentrations more than doubled in Kingsley Lake during this period (from 94 to 216 μeq/L) and pH increased from 6.3 to 6.7. Likewise, ANC in Lake Geneva increased from 12 to 130 μeq/L, and pH has increased from 5.4 to 6.1.

Apart from apparent declines in lakewater pH and ANC in several softwater lakes in the Trail Ridge, no other apparent effects related to current levels of acidic deposition have been observed. In the event that levels of acidic deposition increase, accelerated leaching and export of $Ca^{+2}$ and $Mg^{+2}$ from the watershed to receptor lakes can be anticipated, accompanied by increasingly smaller quantities of ANC and correspondingly larger quantities of $SO_4^{-2}$ as the counterion. ANC generation by $SO_4^{-2}$ reduction should increase as lakewater $SO_4^{-2}$ inputs increase, offsetting to some extent proton inputs. Nevertheless, some reduction in lakewater pH can be anticipated, the magnitude of which depends on the composition of acidic deposition, the hydrology of the lake, the ability of the lake to remove $SO_4^{-2}$ via $SO_4^{-2}$ reduction, and the ability of the watershed to contribute ANC. Mobilization of aluminum from watershed soils does not appear to be significant until rainfall pH is depressed below 3.7. Similarly, reduction of lakewater pH to 3.7 should result in solubilization of aluminum from the sediments and concomitant increases of lakewater aluminum to potentially toxic concentrations (>200 µg/L).

Several biological effects can be expected with increasing lake acidification. Reduction of lakewater pH below 6.0 to 5.5 will result in replacement of bluegreen algae by green algae as the dominant species group. Below pH 5.0, increases in relative abundance of pyrrophytes may occur. Species richness or the number of phytoplankton species will be reduced as pH is depressed below 6.0. Effects of pH reduction on algal productivity in Florida lakes are not known conclusively although it seems unlikely that lake acidification to pH 3.7 will result in reductions in algal abundance (i.e., biomass). Lake survey results demonstrate a positive relationship between algal abundance and lakewater pH; however, similar relationships can be derived for nutrient concentrations and a causative link between pH and a decline in productivity (using chlorophyll-a concentrations to define productivity) has not been established. Furthermore, algal abundance is at least as strongly correlated with watershed factors indicative of nutrient loading as with pH. These results are supported by manipulation studies conducted at Lake McCloud which indicate that productivity is not affected by changes in pH and that the availability of nutrients is the determining factor.

Some changes in the macrophyte community may also occur including the loss of a few species of macrophytes found only in relatively high pH waters and a reduction in the total number of species. Increased concentrations of cadmium, copper, lead, and zinc are likely to accumulate in macrophyte tissues, although these levels are quite low relative to potential toxicity at higher trophic levels. Macrophyte abundance appears to be independent of pH in softwater oligotrophic lakes, and reductions in lakewater pH to least pH 4.2 should have little effect.

As with phytoplankton, increasing lake acidification may result in a reduction in zooplankton diversity although the reductions probably will not be as extensive as declines observed in similar temperate systems. Some replacement of species in response to changes in pH will occur. Copepods appear to perform well at increasingly lower pH levels approaching pH 4.6 to 4.7 and increase in relative abundance at the expense of rotifers. Further reduction in pH to 3.6, however, may result in the virtual elimination of copepods and substantial reductions in overall zooplankton abundance. For one major copepod species (Diaptomus floridanus) found in acidic software lakes in Florida, the threshold level below which the toxic response increases markedly appears to be pH 4.0 to 4.2.

Results of two limited surveys of the distribution of Florida fish as a function of surface water pH indicate that minor declines in species abundance will occur with reductions of surface water pH to approximately 4.0. Performance (as reflected by condition factor) of largemouth bass (Micropterus salmoides) appears to be more a function of algal biomass rather than pH to levels as low as pH 4.5. Survey results suggest that Florida fish are more resistant of low pH than members of the same species found in temperate lakes, possibly because of: (1) natural selection operating over many generations of exposure to low pH; (2) higher levels of primary productivity; (3) climatic differences; and (4) lower lakewater concentrations of aluminum. Below pH 4.0, fish response in Florida lakes is largely unknown. The only published results documenting potential effects at this pH level are for bioassays conducted in the laboratory for redear sunfish (Lepomis micropholus) which demonstrate that a reduction of pH from 4.0 to 3.5 results in complete mortality within 24 hours. It should be noted that the redear sunfish apparently performs poorly in acidic waters and is not an important species in lakes with pH below 6.5 (ESE, 1984) although it has been reported in swamp waters with a pH range 3.9 to 5.7 (Dickinson, 1948). Preliminary results of bioassays on the largemouth bass indicate a similar threshold level for acute toxicity (~pH 3.7, Crisman, 1985). Long-term or chronic effects of exposure to pH 4.5 and below have not been studied for Florida fish.

Finally, the question arises as to what pH levels would be expected in softwater seepage lakes in Florida in the absence of acidic deposition. Paleolimnological investigations examining the sedimentary distribution of chironomid head capsules and diatom assemblages presently are being analyzed to evaluate historical trends and precultural pH levels in several Florida seepage lakes (Crisman, 1985). These data are not finalized, however; in their absence, attempts to address historical pH levels are speculative. Nevertheless, two physical and geochemical factors suggest that many Florida seepage lakes are naturally acidic. Florida soils are quite old, highly weathered and very acidic, reflecting leaching occurring over thousands of years in response to internal processes (e.g., production of carbonic acid due to the decomposition of organic matter) and leaching resulting from rainfall in excess of water losses due to evapotranspiration and surface runoff. Because of the large reservoir of acidity in these soils, soil solution pH in the absence of acidic deposition almost certainly would be low in ANC and acidic. Moreover, rainfall pH in the absence of anthropogenic inputs of strong acids is acidic (<pH 5.6). Given that (1) direct inputs of precipitation and seepage are virtually the only hydrologic sources supporting seepage lakes, and (2) both of these inputs should be acidic, it seems likely that low ANC and low pH (<pH 6) levels would be characteristic of many seepage lakes under natural circumstances.

- How are soils likely to respond to current levels or changes in current levels of acidic deposition?

Soils in Florida with the least ability to neutralize acidic inputs are deep highly weathered and acidic sands found in the highlands and ridge physiographic regions of the state. These soils have very limited cation exchange capacities and only a minor fraction of the total cation exchange capacity is available to neutralize acidity via ion exchange with base cations. Furthermore these soils have little ability to adsorb sulfate, at least within the surficial horizons. There is no evidence to suggest that current levels of acidic deposition are promoting soil acidification to a measurable extent. Because of their acidic character, these deep sands are probably not susceptible to large changes in pH or large relative losses of base cations, at least at current levels of acidic deposition. However, the effect of small reductions of base content in these soils on particularly forest growth where base cations are tightly recycled is unknown. Clearly, increasing inputs of acidity will accelerate the flux of base cations from the soil over long periods of time. Whether the reservoir of available base cations will be reduced by this accelerated flux or will be maintained by enhanced weathering rates has not been studied for Florida soils.

Mobilization of aluminum is inversely related to soil pH and is perhaps the most significant potential effect on soils related to acidic deposition. There is no evidence to suggest that current levels of acidic deposition result in mobilization of aluminum to any significant degree. Increasing amounts of acidic deposition, however, can release potentially toxic concentrations of aluminum into the soil water of soils already acidic. Field studies in Florida with a very poorly buffered entisol sand demonstrate significant amounts of aluminum mobilized when the pH of simulated throughfall was lowered below pH 3.6 to 3.0 (ambient throughfall pH at the study site was greater than pH 4.6). Although significant aluminum solubilization for this particular soil was not observed when exposed to pH 3.6 simulated throughfall, the chronic effects of this level of acidic deposition on nutrient dynamics are not well defined.

- What are the long-term trends of soil chemistry in Florida?

There are currently no data available for Florida soils from which a direct or explicit determination of long-term trends in soil acidification in relation to acidic deposition can be made. This problem is compounded by the extreme heterogeneity of soils which makes comparisons of small differences in soil chemistry for even a particular soil in a particular watershed virtually meaningless without a relatively large number of samples to establish statistical limits of confidence. Nevertheless, some inferences regarding the likelihood of soil acidification induced by acidic deposition can be drawn for Florida soils by regarding the soil as a reservoir of base cations which is slowly depleted as a consequence of natural weathering processes. Acidic deposition may accelerate this leaching process (i.e. soil acidification). Johnson (1985) submits that some perspective on the contribution of acidic deposition to soil acidification is gained by consideration of the cation capacity of the soil in relation to cation loss rates. Although measurable increases in soil acidification rates attributable to acidic deposition may be discerned (however no such measurements exist for Florida soils), changes in soil acidity are not likely to be measured because of the long timeframe that even young soils have been undergoing acidification due to natural processes (greater than 10,000 years). Florida soils are relatively old (at least 25,000 years old and as much as 1,000,000 years old) and highly weathered and, as a consequence, extremely acidic; in view of the inherently large reservoir of acidity, it seems rather improbable that measured increases in soil acidity as a consequence of acidic deposition have occurred.

- What are the long-term trends of lake chemistry in Florida?

Because of their shallow nature, small lakes in Florida for the most part can be considered well-mixed and therefore homogeneous, thus facilitating a comparison of historical and current measurements of lakewater chemistry. This analysis has been performed for a 20-year period between 1957-1979 for several lakes in the Trail Ridge lake district in north-central Florida. Several lakes exhibited apparent declines in ANC from approximately 25 µeq/L to essentially 0 ANC; the decrease in anions represented by the loss in ANC was roughly offset by equivalent increases in nonmarine or excess $SO_4^{-2}$. However, the significance of these reported changes in $SO_4^{-2}$ and ANC cannot be demonstrated conclusively for several reasons. Changes in ANC and $SO_4^{-2}$ are low and, with respect to ANC, approximate the limits of analytical uncertainty. Moreover, analytical biases inherent in the various analytical techniques that evolved and were used during this time frame uniformly serve to overestimate any apparent historical differences. In addition, assuming the validity of these reported changes, it is not known with certainty whether these changes in lakewater chemistry can be attributed to acidic deposition; extreme changes in hydrology because of variations in precipitation occurred during this period and this effect must be accounted for. Nevertheless, examination of historical changes in Lake McCloud (also in the Trail Ridge) suggests that progressive acidification may be occurring in this lake. During the 14-year period between 1968 and 1982, $H^+$ concentrations essentially doubled (from pH 4.85 to less than 4.6) in

Lake McCloud with concomitant increases in excess $SO_4^{-2}$. Using chloride concentrations to normalize the data indicates that changes in hydrology observed over the 14-year period of record cannot account for the chemical changes in the lake. Again, as discussed for the Trail Ridge lakes database, there is uncertainty implicit in the results for Lake McCloud because changes in analytical techniques tend to exaggerate apparent differences in $SO_4^{-2}$. In addition, the estimated change in $H^+$ between 1968 and 1982 approximates the variability observed in Lake McCloud over a 2-year period.

Similar temporal trends have not been observed in the Highlands Ridge seepage lakes of south-central Florida. In part, the absence of any temporal trends may reflect a more limited historical record (1967 to 1978) from which trends may be established. However, several other factors may account for the apparent difference between lakes in the Trail Ridge and Highlands Ridge lake districts: (1) Highlands Ridge lakes appear to have longer hydraulic residence times and correspondingly higher inseepage rates, resulting in higher inputs of ANC; (2) excess $SO_4^{-2}$ loadings are lower and rainfall pH is higher in south Florida relative to north Florida; and (3) the Highlands Ridge lakes are characterized by higher ANC concentrations and thus are better able to assimilate acid loadings.

- What are the potential effects of current levels of acidic deposition to agricultural crops and terrestrial systems? In addition, what are the responses of agricultural crops and terrestrial systems to changes in deposition?

It is unlikely that current levels of acidic deposition are adversely affecting agricultural crops. No unexplained yield declines can be attributed to acidic deposition. Literature reviews of more than 85 studies using simulated acid rain on test species have revealed only five cultivars that are negatively affected by ambient pH levels (Irving, 1983 and 1985; Jacobson and Troiano, 1983). Only one crop, a soybean cultivar Amsoy, which is not widely grown was considered to be tested under natural field conditions (Irving, 1985). Other factors that reduce the probability that ambient levels of deposition affect crop yields are (1) the short time that most crops are exposed to atmospheric deposition (less than 1 year), and (2) the periodic amendments of lime and fertilizers to cropland which neutralize soil acidity and replace any leached nutrient cations.

Some studies report significant yield reduction when test species are exposed throughout the growing season to simulated acid rain with pH levels below 3.0. It can be inferred from these studies that yields from some crops may be reduced if the VWM pH of rain dropped to levels below 3.0.

The effects of current levels of acidic deposition on terrestrial systems are not well understood and apparently depend on interactions with atmospheric oxidants, heavy metals, various forms of abiotic and biotic stress, and the plant species that are dominant in the system. Severe declines have been reported for conifers in high-elevation forests in northern temperate climates. Some researchers suspect that acidic deposition is a factor in these declines, but no causal link has been demonstrated. Growth reductions have been reported in pines on the mid-Atlantic coastal plain and in the southern piedmont and in conifers generally in the southern Appalachians. Causes of declines may differ between and within different regions. There are no reports of tree growth reduction or other effects on Florida forests that can be attributed to atmospheric deposition. The response of such systems to changes in deposition cannot be predicted because the effects of acid deposition on these systems are not known.

- What are the potential effects of acidic deposition and precursor emission to manmade materials in Florida?

During the course of this study, it was determined that state-of-the-art research methods were inadequate to address this question definitively. Consequently, the Florida Acid Deposition Study did not include any original reserach in this area. Any attempt to estimate or predict potential effects based on studies reported in the literature should be approached with caution due to the inherent limitation of the experimental procedures employed and questionable applicability of statistical procedures used, resulting in considerable uncertainty, and potential inappropriateness of dose-response relationships that have been reported linking acidic deposition with materials damage. Virtually all available research results fail to relate damage rates to routine replacement or maintenance cycles to evaluate whether reported damage rates have any practical significance. Reported research results imply, however, the ambient levels of $SO_2$ reported for Florida (2 to 26 $\mu g/m^3$; DER, 1983) would not be expected to cause substantial materials damage. Most studies indicate damage only at higher $SO_2$ levels, while under Florida's conditions, atmospheric moisture (in terms of humidity or time of wetting by dew or rain) appears to be a more important variable than $SO_2$ in affecting metals damage rates.

The potential effects of acid deposition on other materials (particularly those $CaCO_3$-bearing materials) is also hard to quantify in the absence of accurate damage function even though the physicochemical basis of the damage appears to be adequately understood. Deposition of acid precursor gases along with their acidic species could potentially favor dissolution of $CaCO_3$ in masonry, including architectural monuments and statuary, via a displacement reaction which yields a more soluble gypsum salt. Other environmental factors including atmospheric $CO_2$, precipitation amount and intensity, and freeze/thaw cycles could be expected to affect this proposed mechanism. Overall, acidic deposition can potentially increase metal corrosion and materials damage rates; however, the magnitude of these incremental effects might be immeasurably low when the influence of a variety of environmental factors is taken into account.

- How are changes in acidic deposition levels and precursor emissions likely to influence manmade materials?

Based on the review of available literature concerning the inherent uncertainty and limitations of damage functions, potential increase or decrease in materials damage associated to changes in deposition of acidic pollutants and precursor species would be difficult to predict. Any attempt to evaluate materials damage using unreliable damage functions developed from inadequate databases would probably lead to inaccurate damage quantitation especially when we note the fact that key dose-response relationships reported in the literature do not apply under Florida conditions. Any potential damages occurring under current levels are probably not measurable since they would be masked by more significant damage rates due to other, largely natural causes. Therefore, a reduction in deposition rates and/or acid precursors levels would not be expected to result in a noticeable reduction in damage rates. However, it is impossible to determine how much deposition rates and acid precursor concentrations would have to increase before measurable damage would occur.

## 4.6 REFERENCES CITED

The following references are cited in Section 4.0.

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# 5.0 INTEGRATION OF PROGRAMS

## 5.1 INTRODUCTION

In Sections 2.0, 3.0, and 4.0, the results obtained from a 3½-year research effort on acidic deposition in Florida are presented. Specifically, the objective of this research effort was to assess and/or develop information on acidic deposition concerning its magnitude, variability, sources, and effects in Florida. Through an analysis of the data and information gathered over this 3½-year period, specific key research questions were addressed within the three major study areas of Acid Deposition Monitoring, Source Attribution, and Ecological Effects. Taken separately, the answers to these key research questions generally define, within specified limits, the current knowledge of the acidic deposition phenomena in Florida. However, in order to gain a perspective on the potential magnitude of this phenomenon on the state as a whole, the data and information within each study area must be integrated (see Figure 5.1-1). This final section presents such an integration that has as its focus the following key questions:

1. What are the current levels of total acidic deposition in Florida?
2. At these levels, what are the potential environmental impacts?
3. How certain are these impacts?
4. If there are potential impacts, what are the likely sources contributing to total acidic deposition?
5. What is the overall uncertainty of these results?
6. What areas require additional data to refine the uncertainty in the knowledge of acidic deposition in Florida, its sources, and effects?

The answers to these key study questions are presented in four sections. Subsection 5.2 presents the current knowledge of total acidic deposition in Florida. This question forms the baseline from which all other questions will be addressed and where a significant amount of research

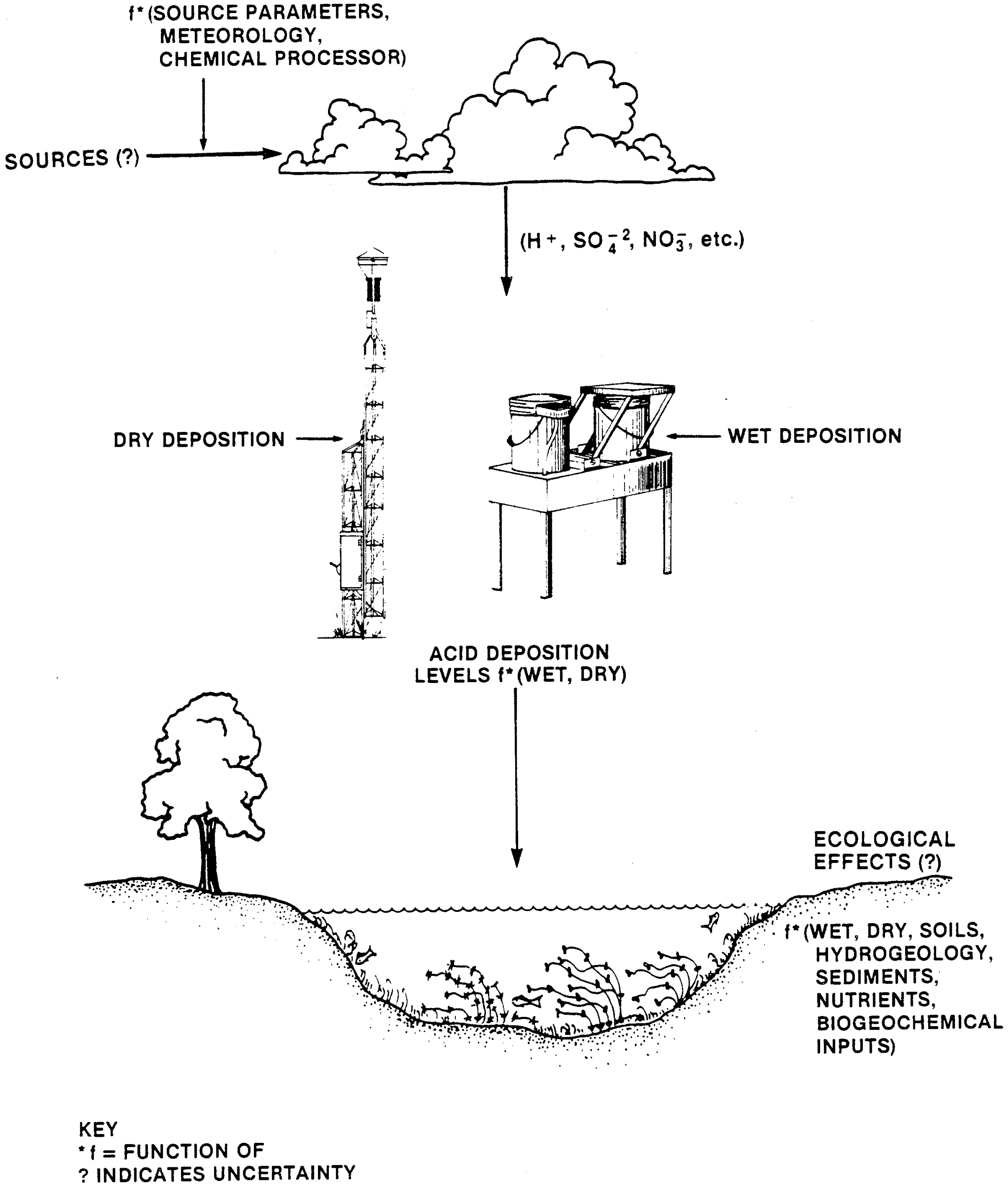

Figure 5.1-1
INTEGRATION

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was devoted. Yet there are uncertainties associated with the research efforts, particularly as they relate to dry deposition.

Section 5.3 addresses the central theme of these key study questions: the potential for environmental impacts due to acidic deposition (Question 2). Primarily, the focus was to assess the potential for environmental impacts to the most sensitive ecological resources at the current levels of acidic deposition and attempt to assess if there is some threshold where effects would be detectable above natural variation. While the focus of this analysis was to assess the most sensitive ecological resources, it must be recognized that all of Florida's natural resources were considered during the course of the study. During initial investigations, the potential sensitivity of a variety of resources was screened, leading to a focus in subsequent research on resources at relatively greater risk. The detailed discussions thus focus on potentially sensitive resources. Additionally, the uncertainties associated with the knowledge of potential ecological impacts are addressed (Question 3).

Section 5.4 addresses Question 4 relating to the potential sources of total acidic deposition in Florida. Specifically, the focus will be to make an assessment of those sources likely to contribute to potential impacts.

Section 5.5 addresses the final two key study questions centering on the major uncertainties and suggested research that could address these uncertainties.

As a focal point for this discussion, Florida can be divided into three general regions: the panhandle, northern peninsula, and southern peninsula (see Figure 5.1-2). This division, although not along definitive boundaries, was found to be appropriate for three reasons. First, results of the aquatic effects analysis (Subsection 4.3) suggest

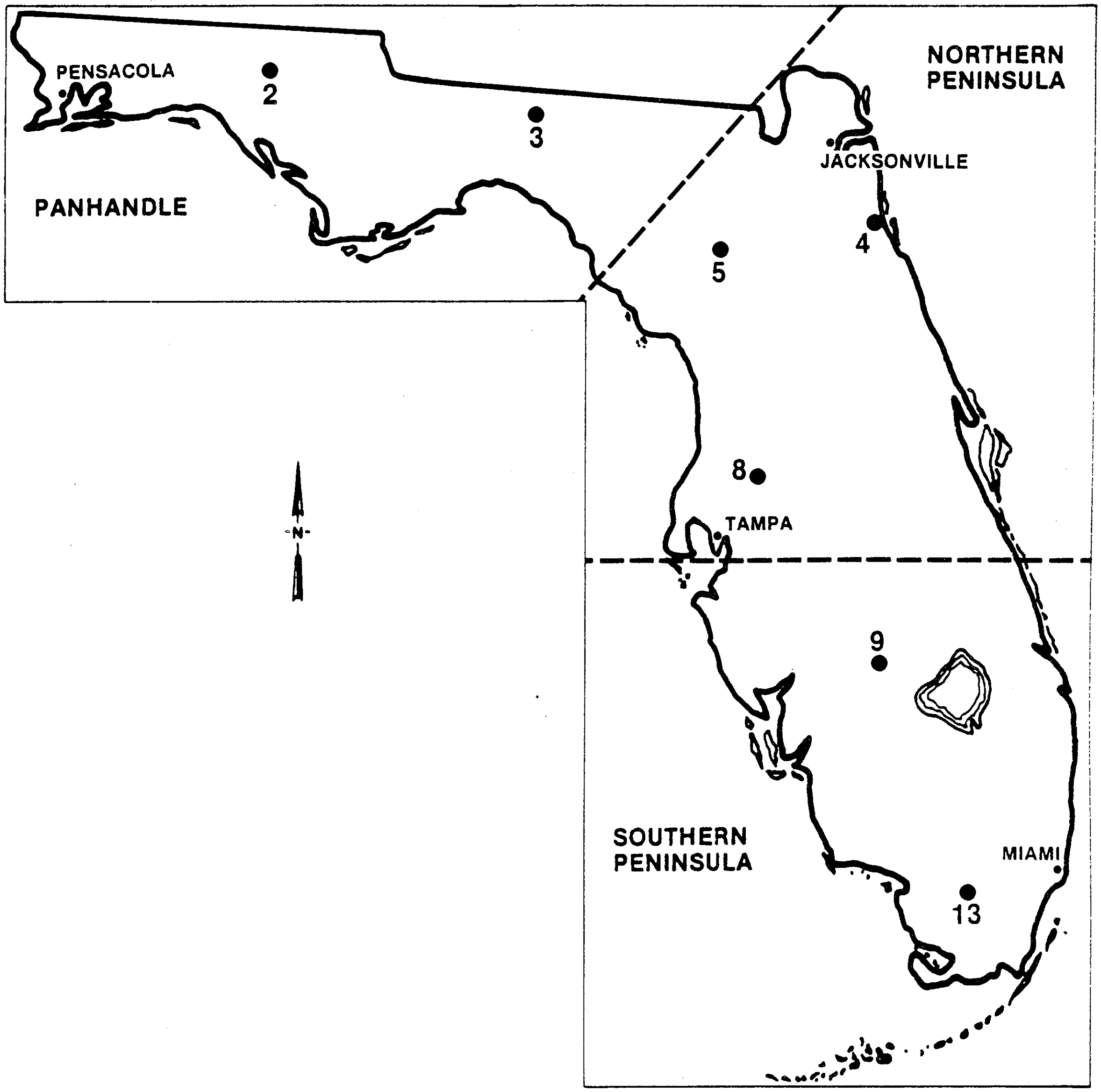

Figure 5.1-2
LOCATION OF RECEPTOR REGIONS AND WET/DRY DEPOSITION MONITORING SITES

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the following general order of sensitivity among Florida lakes: seepage lakes located in the Trail Ridge and Highlands physiographic provinces of the panhandle and northern peninsular Florida are potentially more sensitive than other types of lakes or lakes in other areas. Note that sensitivity, in this context, refers only to the relative likelihood of chemical response due to acidic deposition. Nothing is implied here concerning the likelihood, or expectation, of biological effects, either positive or negative. Nor should this ranking be construed to mean that all panhandle lakes are uniformly sensitive or that all panhandle lakes are more sensitive than southern peninsular lakes. The natural resources of all three regions are far too heterogeneous to warrant any such conclusion.

Second, results of the Acid Deposition Monitoring Program indicate three regimes of precipitation chemistry across the state. The spatial distribution of these regimes varies slightly for excess $SO_4^{-2}$, $NO_3^-$, and $H^+$, but the overall picture is one of higher concentrations/depositions in the northern peninsular and panhandle regions than in the southern peninsular regions. Ambient concentration data for particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ show relatively low spatial variability for oxidation products and relatively high variability for the gaseous precursors. Using ambient air concentration data as a surrogate for dry deposition, the overall pattern suggests lower deposition in the southern peninsula than either the panhandle or the northern peninsula.

Finally, further support for division of the state stems from the Source Attribution Program. Trajectory calculations for panhandle, northern peninsular, and southern peninsular receptors showed distinct patterns of atmospheric transport for each receptor. This, in turn, suggests that potential sources of acidity vary from one part of the state to the next. Thus, treating Florida as a single geographical unit may be misleading, especially when the relationship between sources and potentially sensitive receptors is being evaluated.

## 5.2 ACID DEPOSITION MONITORING

The objective of this section is to assess current knowledge on the magnitude, variability, and uncertainty of acidic deposition in Florida. For the purpose of this presentation, acidic deposition includes both wet and dry deposition of acidifying substances, specifically $SO_x$ and $NO_x$. Due to major differences in the ability to quantify wet and dry deposition, wet deposition in Florida is evaluated first, followed by dry deposition.

### 5.2.1 WET DEPOSITION

The spatial and temporal variability of wet deposition within Florida over the 3-year monitoring period is shown in Table 5.2-1. Comparison of mean depositions across receptor regions shows a peak in excess $SO_4^{-2}$ for the northern peninsula, but relatively constant values for $NO_3^-$, $NH_4^+$, and $H^+$ deposition across the panhandle and northern peninsular regions. The southern peninsular region exhibits lowest deposition for all species; however, that of $NO_3^-$ is only marginally lower than elsewhere.

Inspection of coefficients of variation within receptor regions and across years shows that, with the exception of $NH_4^+$, interannual variability is larger than spatial variability. This suggests that the existing wet-deposition network yields reasonable estimates of deposition to sensitive areas (e.g., Trail Ridge lakes), even though monitors are not located in those areas. On the other hand, the relatively higher interannual variability suggests that meteorological and photochemical processes, combined with possible changes in emissions, significantly influence annual observations. The interannual variability in wet-deposition rates over the 3-year database shows considerable uncertainty remains in estimating "typical" annual deposition rates for Florida.

As a result, the monitoring data represent only an appropriate estimate of total acidic deposition rates over periods of a decade or longer.

Table 5.2-1. Spatial and Temporal Variability of Wet Deposition in Florida for the 3-Year Period from 10/01/81 Through 09/30/84

| Receptor Region | Analyte | Mean Annual Deposition (eq/ha) | Within-Region CV (%) | Across-Year CV (%) |
|---|---|---|---|---|
| Panhandle | Excess $SO_4^{-2}$ | 280 | 8 | 15 |
| | $NO_3^-$ | 140 | 4 | 11 |
| | $NH_4^+$ | 85 | 9 | 56 |
| | $H^+$ | 320 | 9 | 11 |
| Northern Peninsula | Excess $SO_4^{-2}$ | 315 | 10 | 16 |
| | $NO_3^-$ | 145 | 6 | 7 |
| | $NH_4^+$ | 90 | 33 | 27 |
| | $H^+$ | 330 | 6 | 22 |
| Southern Peninsula | Excess $SO_4^{-2}$ | 180 | 9 | 17 |
| | $NO_3^-$ | 120 | 4 | 14 |
| | $NH_4^+$ | 65 | 16 | 8 |
| | $H^+$ | 190 | 14 | 16 |

CV = standard deviation ÷ mean.

Source: ESE, 1986.

Results of the Ecological Effects Program suggest that the deposition rates over such long averaging times are more important than short-term fluctuations with respect to aquatic systems.

One source of uncertainty concerns the influence of point sources on localized wet deposition. The network design, in general, attempted to avoid the potentially complicating effects of local $SO_x$ and $NO_x$ emissions by locating sites at least 35 km from point sources that exceed 100 tons/yr. One of the three northern peninsular sites (Site 5), however, was within point-source exclusion zones and another northern peninsular site (Site 8) was within 50 km of a major source area with $SO_x$ and $NO_x$ emissions greater than 100,000 tons/yr. It is, therefore, appropriate to inquire whether site location strongly influenced deposition within this receptor region.

The areal distribution of $SO_2$ emissions used in the ENAMAP modeling is presented in Figure 5.2-1 and shows considerable variability across the state. When compared to excess $SO_4^{-2}$ deposition for the same period, CV for across-state $SO_2$ emissions (1.49) is over 4 times larger than the across-state CV for excess $SO_4^{-2}$ (0.34). This dissimilarity between the areal distribution of individual site depositions and emissions within the corresponding emission grids is reinforced graphically by Figure 5.2-2. Data for $NO_2$ emissions and $NO_3^-$ deposition show similar differences in across-state variability. Thse camparisons suggest that local $SO_x$ and $NO_x$ emissions did not appear to have a significant influence on observed wet deposition, and that sites located within or near exclusion zones were not significantly influenced directly by local sources. Nevertheless, the possibility of areal influences as large or the panhandle, northern peninsula, or southern peninsula of Florida cannot be ruled out. Indeed, excess $SO_4^{-2}$ deposition in the northern peninsula shows about a 15-percent higher deposition relative to the panhandle which is genrally supported by ENAMAP results.

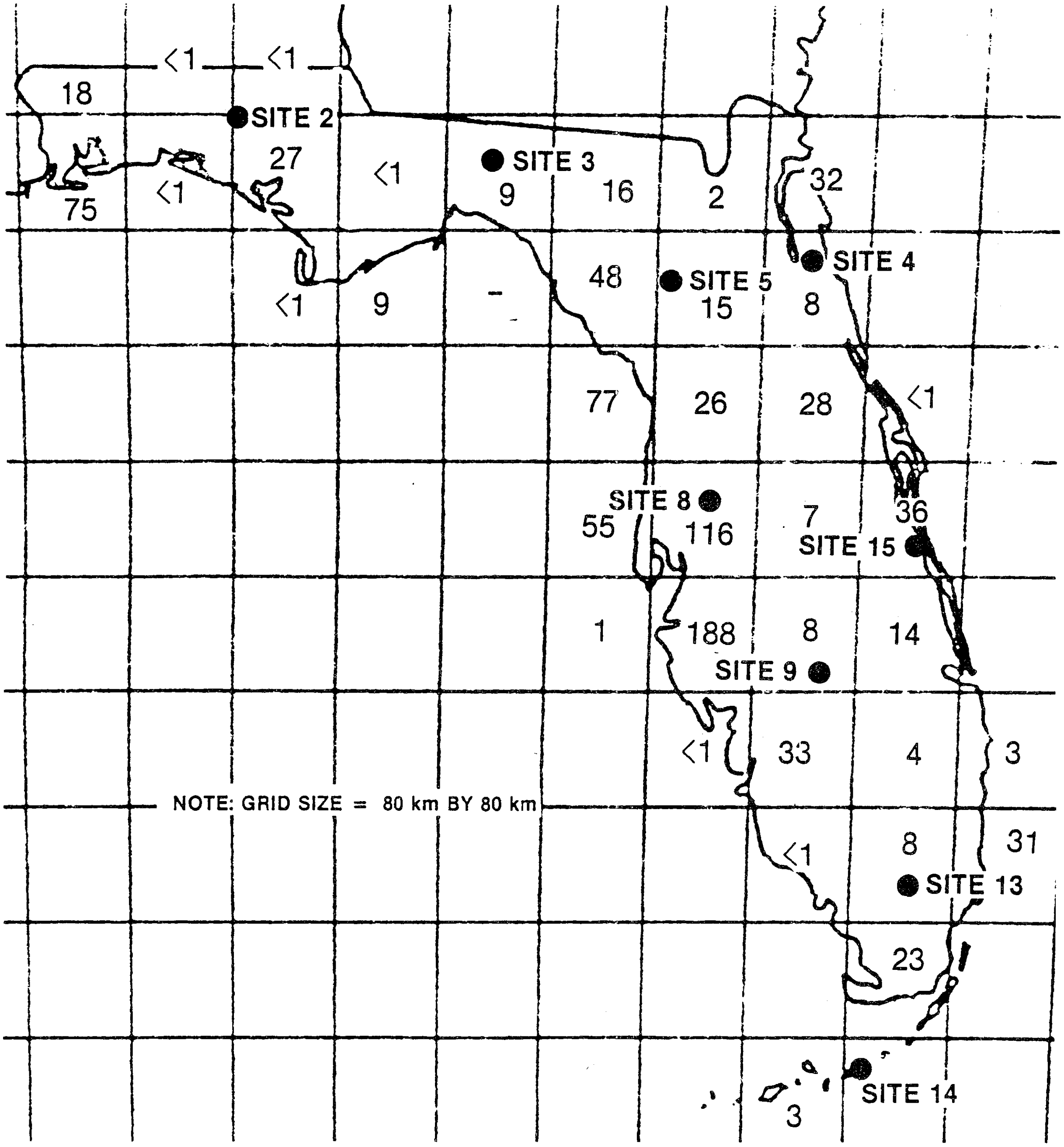

Figure 5.2-1
ESTIMATED ANTHROPOGENIC $SO_2$
EMISSIONS FOR FLORIDA BY ENAMAP 9/15/82
THROUGH 9/15/83

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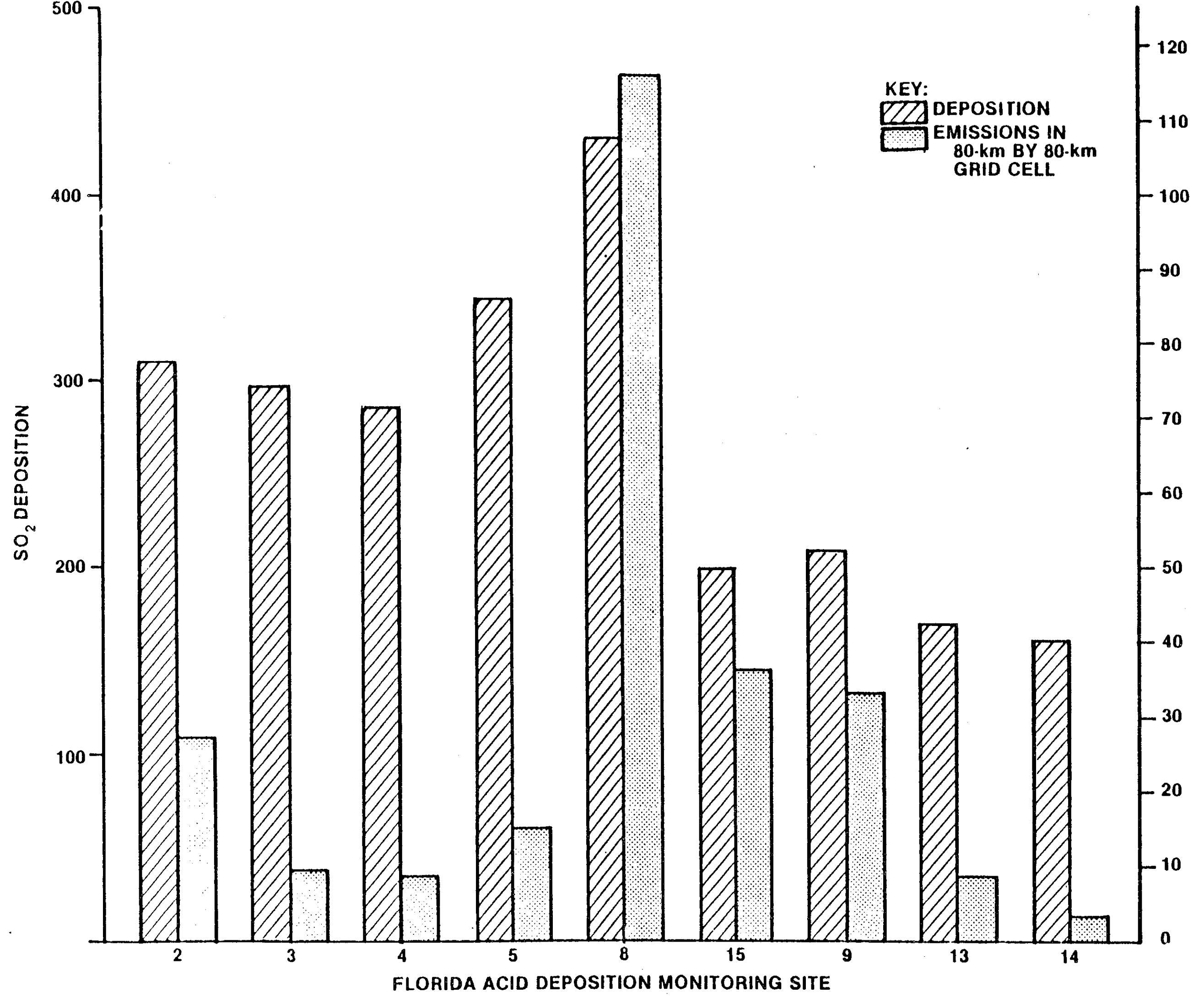

Figure 5.2-2
COMPARISON OF SITE DEPOSITION AND AREAL $SO_2$
EMISSIONS FOR 9/15/82 THROUGH 9/15/83

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Consistent with the within-region coefficients of variation, results of the meteorological classification of precipitation chemistry suggest that the influence of local sources may be less important than other factors in determining statewide patterns of wet deposition. Precipitation amounts associated with synoptic weather patterns were similar at Site 2 (panhandle) and Site 5 (northern peninsula), with the exception of the maritime high and the continental-Atlantic low categories. For Site 2, nearly 50 percent of total precipitation during the period from October 1, 1982, through September 30, 1983, consisted of relatively clean maritime high events, and less than 1 percent consisted of continental-Atlantic low events. For Site 5, in contrast, maritime high and continental-Atlantic low events accounted for approximately 22 percent and 12 percent, respectively, of total annual precipitation. Continental-Atlantic low events at Site 5 exhibited the lowest average pH of all synoptic classifications and the highest sulfate-to-nitrate ratio. If it is assumed that Sites 2 and 5 are representative of their respective receptor regions, then it is likely that variable influences of synoptic meteorology play a large role in the statewide pattern of wet deposition.

Results of ENAMAP simulations also suggest that $SO_4^{-2}$ wet deposition is a regional rather than a local phenomenon. Inspection of average predicted deposition across the panhandle, northern peninsula, and southern peninsula reveals a pattern similar to observed deposition. Average predicted deposition across the northern peninsula exceeds panhandle deposition and southern peninsular deposition by 22 percent and 85 percent, respectively. Corresponding values for the 3-year monitoring period are 13 percent and 75 percent, respectively. These results should not be construed as suggesting that local effects of emissions on wet deposition do not occur. The monitoring data do not adequately address this question. Rather, the above findings suggest that the current network design provides reasonable estimates of wet deposition to sensitive receptors.

The spatiotemporal variability of $H^+$, $NH_4^+$, excess $SO_4^{-2}$, and $NO_3^-$ in precipitation is depicted in Table 5.2-2. Results show that laboratory pH is similar across the northern peninsula (4.60) and the panhandle (4.64), but substantially higher in the southern peninsula (4.84). Similar to deposition results, this finding shows that highest concentrations of $H^+$ generally occur in the most sensitive receptor regions in the state (i.e., panhandle and northern peninsula). Implicitly, this suggests that the potential for concentration-related effects is also highest in these regions.

Unlike results for deposition, however, concentration data show that the relative importance of intersite and interannual variability changes from region to region. For the panhandle region, interannual variability is dominant for all parameters, suggesting that annual concentration and rainfall amount vary inversely to establish the relatively low interannual variability in depositions. For the northern peninsula, intersite variability dominates for $NH_4^+$ and excess $SO_4^{-2}$, whereas intersite and interannual variability are about equal for $H^+$ and $NO_3^-$. The southern peninsula region exhibits the lowest interannual variability (except $NH_4^+$) and the lowest concentrations of all analytes. This is consistent with results of the trajectory analyses and the meteorological classification of precipitation events, which showed relatively low variability of precipitation chemistry as a function of event type and trajectory direction.

### 5.2.2 DRY DEPOSITION

Due to the inherent uncertainties surrounding dry deposition, this section focuses on the variability of ambient concentration data rather than on the variability of dry-deposition estimates. The absolute rates of dry deposition, normally calculated as the product of an air concentration and a dry-deposition velocity, are relatively uncertain because the dry-deposition velocity is not known very precisely. If it can be assumed, however, that over an annual average, spatiotemporal

Table 5.2-2. Spatial and Temporal Variability of Precipitation Chemistry for the 3-Year Period from 10/01/81 Through 09/30/84

| Receptor Region | Analyte | Mean Annual Concentration* | Within-Region CV (%) | Across-Year CV (%) |
|---|---|---|---|---|
| Panhandle | pH | 4.64 | -- | -- |
| | $H^+$ | 22.8 | 7 | 26 |
| | $NH_4^+$ | 5.7 | 4 | 21 |
| | Excess $SO_4^{-2}$ | 20.9 | 4 | 10 |
| | $NO_3^-$ | 9.9 | 6 | 9 |
| Northern Peninsula | pH | 4.60 | -- | -- |
| | $H^+$ | 25.2 | 9 | 11 |
| | $NH_4^+$ | 6.5 | 39 | 10 |
| | Excess $SO_4^{-2}$ | 24.9 | 18 | 9 |
| | $NO_3^-$ | 11.2 | 9 | 9 |
| Southern Peninsula | pH | 4.84 | -- | -- |
| | $H^+$ | 14.6 | 16 | 2 |
| | $NH_4^+$ | 5.2 | 10 | 12 |
| | Excess $SO_4^{-2}$ | 15.1 | 14 | 1 |
| | $NO_3^-$ | 9.4 | 2 | 5 |

*All concentrations are µN except pH, which is unitless.

CV = Standard deviation ÷ mean.

Source: ESE, 1986.

variability in dry-deposition velocity is small compared with the variability in air concentration, then variability in dry-deposition rates will be reasonably characterized by the variability in ambient air concentrations.

The spatial and temporal variability of particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ within Florida are shown in Table 5.2-3. As noted in Section 2.0, two distinct patterns of mean concentrations are apparent within Florida. Particulate $SO_4^{-2}$ and, to a lesser extent, $HNO_3$ exhibit a north-south gradient through the state, whereas $NO_2$ and, to a lesser extent $SO_2$, show a peak in the northern peninsula receptor region. Mean concentrations of all species are lowest in the southern peninsula, implying the lowest rates of dry deposition. $HNO_3$ and $NO_2$ exhibit by far the lowest and highest variability, respectively, across receptor regions. Together with the rapid gas-phase oxidation of $NO_2$ (relative to $SO_2$) and the expectedly rapid dry deposition of $HNO_3$ (relative to $SO_4^{-2}$), the spatial concentration pattern suggests that the dry deposition of $NO_x$ is more of a local phenomenon than that of $SO_x$ deposition.

Comparison of within-region and across-year coefficients of variation in ambient air concentrations indicates that interannual variability is less than spatial variability for all species. With the exception of $NO_2$ in the panhandle receptor region, interannual variability is on the order of the expected uncertainty in the observational data. Assuming, again, that deposition velocities are relatively invariant over the receptor regions and over years, this observation suggests that the spatiotemporal behavior of dry deposition contrasts with that of wet deposition. Thus, estimates of dry deposition appear to be more sensitive to monitor location, but less subject to temporal variability.

Spatial and temporal variability of $SO_x$, $NO_x$, and total deposition for the three receptor regions is shown in Table 5.2-4. The results cannot be directly compared with the wet deposition and ambient concentration

Table 5.2-3. Spatial and Temporal Variability of Particulate $SO_4^{-2}$, $SO_2$, $HNO_3$, and $NO_2$ in Florida for the 3-Year Period from 10/01/82 Through 09/30/84

| Receptor Region | Analyte | Mean Annual Concentration (µg/m$^3$) | Within-Region CV (%) | Across-Year CV (%) |
|---|---|---|---|---|
| Panhandle | $SO_4^{-2}$ | 5.1 | 5 | 8 |
| | $SO_2$ | 2.8 | 10 | 5 |
| | $HNO_3$ | 1.1 | 6 | <1 |
| | $NO_2$ | 6.2 | 46 | 16 |
| Northern Peninsula | $SO_4^{-2}$ | 4.5 | 2 | <1 |
| | $SO_2$ | 3.3 | 29 | 2 |
| | $HNO_3$ | 1.0 | 8 | 6 |
| | $NO_2$ | 9.3 | 16 | 8 |
| Southern Peninsula | $SO_4^{-2}$ | 3.4 | 6 | 2 |
| | $SO_2$ | 2.1 | 43 | 7 |
| | $HNO_3$ | 0.9 | 12 | 2 |
| | $NO_2$ | 3.9 | 29 | 1 |

CV = Standard deviation ÷ mean.

Source: ESE, 1986.

Table 5.2-4. Spatial and Temporal Variability of Estimated $SO_x$ and $NO_x$ Deposition for the 3-Year Period from 10/01/82 Through 09/30/84

| Receptor Region | Analyte | Mean Annual Deposition (eq/ha) | Within-Region CV (%) | Across-Year CV (%) |
|---|---|---|---|---|
| Panhandle | $SO_x$ | 480 | 6 | 4 |
| | $NO_x$ | 340 | 24 | 2 |
| | Total | 820 | 13 | 2 |
| | $SO_x/NO_x$ | 1.41 | | |
| Northern Peninsula | $SO_x$ | 500 | 13 | 7 |
| | $NO_x$ | 400 | 18 | 3 |
| | Total | 900 | 9 | 4 |
| | $SO_x/NO_x$ | 1.25 | | |
| Southern Peninsula | $SO_x$ | 310 | 13 | 7 |
| | $NO_x$ | 250 | 16 | 5 |
| | Total | 560 | 14 | 6 |
| | $SO_x/NO_x$ | 1.24 | | |

CV = Standard deviation ÷ mean.

Source: ESE, 1986.

data previously presented (Tables 5.2-1 and 5.2-3) because combined wet and dry deposition of $SO_x$ and $NO_x$ can be estimated for only two of the three monitoring years.

As for wet deposition of $SO_x$ and $NO_x$, total deposition results show highest annual rates in the northern peninsula. In this case, however, the major difference between the northern peninsula and the panhandle can be attributed to $NO_x$ deposition, specifically dry $NO_x$ deposition. This is a direct consequence of higher observed $NO_2$ concentrations for the northern peninsula than the panhandle (see Table 5.2-3). $NO_x$ deposition also exhibits greater intersite variability than $SO_x$ for all receptor regions. The extremely low spatial variability of the wet $NO_x$ component (see Table 5.2-1) suggests that dry deposition of $NO_x$ may play an important role in the overall variability of both $NO_x$ and total deposition across Florida. This finding could be an artifact of monitoring location, i.e., $NO_x$ concentration and, by implication, dry deposition, could be biased due to variable proximity to area emission sources, especially highways.

Inspection of intersite and interannual coefficients of variation for $SO_x$ and $NO_x$ shows that temporal variability is less than spatial variability in all three receptor regions. Interannual values are uniformly less than 10 percent in all regions. Therefore, total deposition may be less variable, on a relative basis, than wet deposition. This is consistent with the continuous nature of the dry-deposition process, but is dependent upon the assumption of uniform annual average deposition velocities. Although data in Table 5.2-4 suggest relatively low temporal variability in dry deposition, this should not be equated to the absolute uncertainty in the estimates themselves. Uncertainties in dry deposition estimates are significant (probably a factor of 2) and will be addressed in Subsection 5.5.

## 5.3 EFFECTS ON ECOLOGICAL RESOURCES

This section addresses the likelihood of effects to ecological resources in response to current levels of acidic deposition observed within Florida.

### 5.3.1 AQUATIC EFFECTS

Significant biological effects are not likely to occur in Florida lakes unless lakewater pH levels are depressed below approximately pH 4. Lakes with the greatest likelihood for becoming acidified to these levels or below are those with (1) extremely dilute lakewaters with low ANC; (2) watershed soils dominated by acidic soils with low CEC, low base saturation, and minimal ability to adsorb sulfate; and (3) hydrologic budgets dominated by precipitation directly to the lake surface. Lakes characterized by all three features may be found among the many seepage lakes characteristic of the sandhills of the highlands and ridge physiographic regions of the panhandle and peninsular Florida (Figure 5.3-1); these seepage lakes have no surface inlets or outlets and derive the bulk of their hydrologic inputs from precipitation directly to the lake surface. As a result, lakewater chemistry of these systems is extremely dilute and, as a general rule, more poorly buffered than other aquatic systems in Florida. It should be understood that not all seepage lakes can be considered sensitive to acidic deposition. Seepage lakes most likely to exhibit some effects related to acidic deposition are those with extremely dilute lakewater chemistry and low ANC concentrations and are isolated or protected from cultural development (e.g. residential development and associated urban runoff and/or septic tank leachate and seepage effects) within their watersheds. An apparent example of the strong influence of cultural factors within a particular watershed on seepage lake chemistry can be drawn from the analysis by Hendry and Brezonik (1984) of historical trends of lakewater chemistry for a series of seepage lakes in the Trail Ridge in north-central Florida. Hendry and Brezonik described apparent declines in ANC concentrations in excess of 25 μeq/L (from 30 to less than 5 μeq/L) in

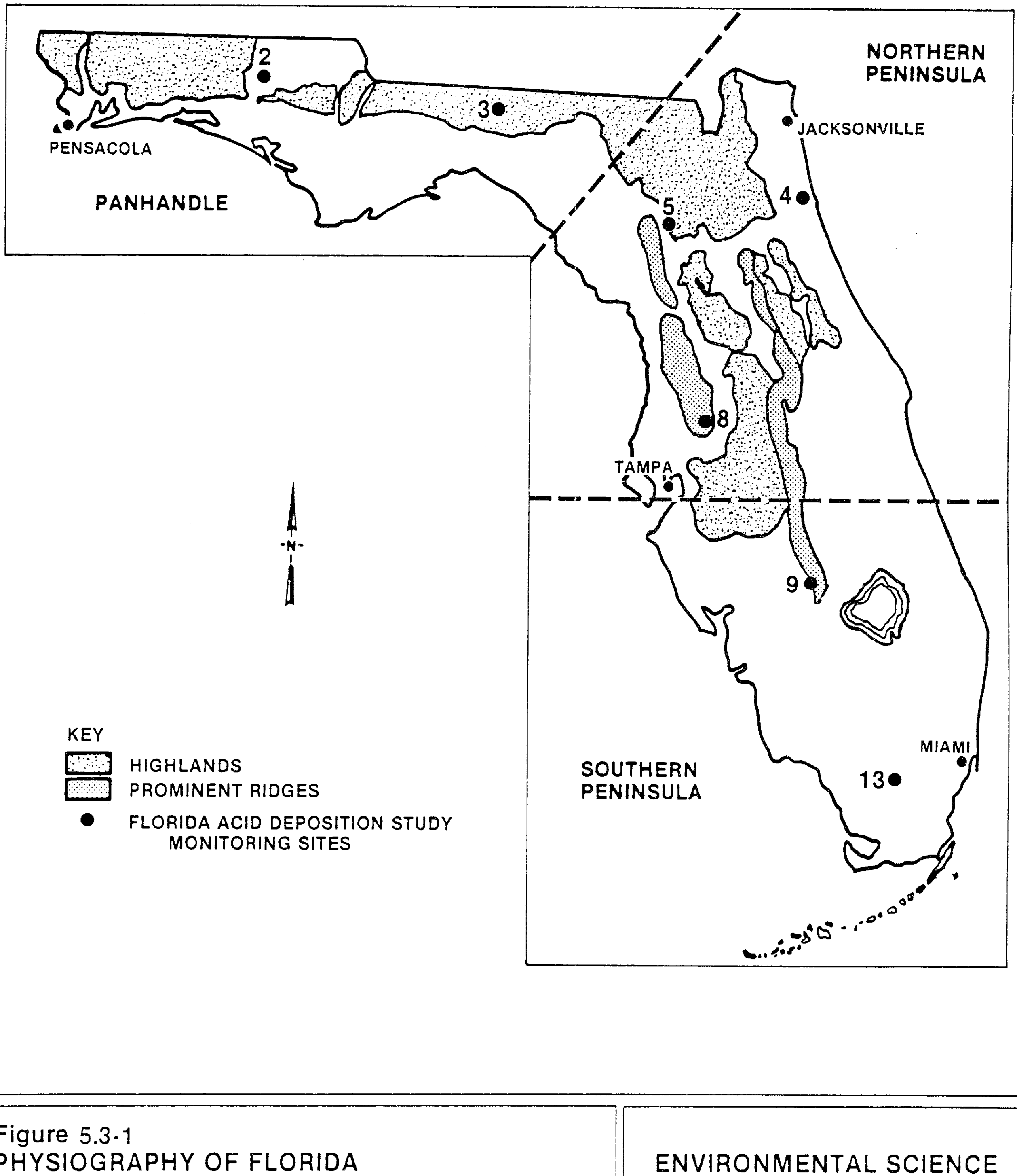

Figure 5.3-1
PHYSIOGRAPHY OF FLORIDA

SOURCES: Florida State University, 1981; ESE, 1986.

ENVIRONMENTAL SCIENCE
AND ENGINEERING, INC.

Magnolia and Lowry Lakes between 1957 and 1979. The watersheds of both lakes are largely undeveloped. By comparison, pH and ANC in Lake Geneva, which is extensively developed around the perimeter of the lake with residences (including septic tanks associated with this type of development), showed relative increases during the same period, most likely due to nutrient inputs.

Several large lake chemistry databases such as FLADAB have been established from which the frequency distribution of lakewater ANC and pH can be analyzed. Of the lakes included in FLADAB, 23 percent are fairly acidic (pH <6.0) and 17 percent have ANC concentrations less than 50 µeq/L (Tables 5.3-1 and 5.3-2). Existing large databases for Florida lakes such as FLADAB, however, are not well suited for examining the population of softwater seepage lakes in the highlands and ridge regions, and their relative distribution with respect to pH and ANC is not well established. Furthermore, critical parameters such as DOC are not routinely included. Nevertheless, these data probably indicate lower limits on the frequency distribution of lakes and the total population of lakes at or below a particular pH or ANC level is probably higher than inferred by FLADAB.

Sensitivity also can be affected profoundly by the presence of organic acids (humic substances) derived from decaying vegetation. Humic substances have acid dissociation constants ($pK_a$) between 3.5 and 6 and can buffer softwater lake pH in this range. Preliminary results from NLS for Florida and southeast Georgia show that the median concentration of ANC in colored (>30 PCU) lakes is approximately three times greater than ANC in clear lakes (146 µeq/L compared to 44 µeq/L). By comparison, median pH in colored lakes is somewhat lower (pH 6.57 compared to pH 6.77 in clear lakes) and illustrates the role of humic substances in regulating pH in softwaters. Humic substances or organic acids can also influence sensitivity because of their ability to form stable complexes with dissolved trace elements. Organic complexation can result in both

Table 5.3-1. Frequency Analysis of Lake pH of FLADAB Lakes by Lake Surface Area Group

| Surface Area Group* | pH | | | | | | Total Count |
|---|---|---|---|---|---|---|---|
| | <4.5 | 4.5-5.0 | 5.0-5.5 | 5.5-6.0 | 6.0-7.0 | >7.0 | |
| SA1 | 0 | 2 | 5 | 6 | 22 | 29 | 64 |
| SA2 | 0 | 1 | 13 | 14 | 44 | 46 | 118 |
| SA3 | 2 | 8 | 16 | 27 | 67 | 75 | 195 |
| SA4 | 0 | 0 | 8 | 11 | 31 | 54 | 104 |
| Total Count | 2 | 11 | 42 | 58 | 164 | 204 | 481 |
| | Percentage | | | | | | |
| SA1 | 0.00 | 0.03 | 0.08 | 0.09 | 0.34 | 0.45 | |
| SA2 | 0.00 | 0.01 | 0.11 | 0.12 | 0.37 | 0.39 | |
| SA3 | 0.01 | 0.04 | 0.08 | 0.14 | 0.34 | 0.38 | |
| SA4 | 0.00 | 0.00 | 0.08 | 0.11 | 0.30 | 0.52 | |

*SA = surface area
SA1 = <10 ha
SA2 = 10 to 50 ha
SA3 = 51 to 500 ha
SA4 = >500 ha

Source: ESE, 1986.

Table 5.3-2. Frequency Analysis of Lake Alkalinity of FLADAB Lakes by Lake Surface Area Group

| Surface Area Group* | Alkalinity (meq/L) <50 | 50-100 | 100-200 | 200-500 | >500 | Total Count |
|---|---|---|---|---|---|---|
| SA1 | 11 | 6 | 4 | 11 | 34 | 66 |
| SA2 | 21 | 17 | 17 | 32 | 43 | 130 |
| SA3 | 40 | 37 | 26 | 30 | 72 | 205 |
| SA4 | 14 | 16 | 12 | 17 | 45 | 104 |
| Total Count | 86 | 76 | 59 | 90 | 194 | 505 |
| | Percentage | | | | | |
| SA1 | 0.17 | 0.09 | 0.06 | 0.17 | 0.52 | |
| SA2 | 0.16 | 0.13 | 0.13 | 0.25 | 0.33 | |
| SA3 | 0.20 | 0.18 | 0.13 | 0.15 | 0.35 | |
| SA4 | 0.13 | 0.15 | 0.12 | 0.16 | 0.43 | |

*SA = surface area
SA1 = <10 ha
SA2 = 10 to 50 ha
SA3 = 51 to 500 ha
SA4 = >500 ha

Source: ESE, 1986.

considerably lower free (unbound) trace element concentrations and reduced toxicity. Of the estimated 1,600 seepage lakes present in Florida and southeast Georgia, the NLS results indicate approximately 50 percent are colored.

NLS should ultimately provide better estimates of the distribution of lakes with low ANC and low pH levels in sensitive regions of the state. Lake sampling during the NLS, which included 141 lakes from Florida, was conducted at random from the population of lakes (>4 ha) within regions considered to be most sensitive to acidic deposition and focused principally on the highlands of Florida. Based on preliminary results from the survey, DOC and ANC generally appear to be lowest in the panhandle, which appears to have a preponderance of lakes with ANC concentrations less than 40 µeq/L, and gradually increase along a southerly gradient. The NLS results also suggest a greater frequency of low-ANC, low-pH than indicated by FLADAB and similar databases. Preliminary NLS results indicate, for example, that 54 percent of the population of lakes sampled in the regions of Florida and southern Georgia included in the survey have ANC concentrations less than 200 µeq/L compared to an observed frequency of 44 percent of the FLADAB lakes. Application of the NLS database with land use and hydrologic data ultimately should result in an improved understanding of the distribution of potentially sensitive lakes and seepage lakes in particular.

The extent or degree to which softwater seepage lakes respond to acidic deposition is functionally related to lake hydrology and internal biogeochemical processes. Although seepage lake hydrology is dominated by precipitation, shallow ground water inputs (i.e., inseepage) are an important source of lakewater ANC. Infiltrating and percolating ground water does contain ANC despite being acidic, and lakes which receive comparatively small amounts of inseepage are more likely to be affected by acidic deposition than seepage lakes with relatively low discharge and higher inseepage rates. The relative contribution of inseepage to overall seepage lake hydrology is ultimately an inverse function of the difference between precipitation and evaporative losses. Thus because of regional differences in evaporation and precipitation, lakes in the Western Highlands and the Trail Ridge of north-central Florida are less influenced by seepage inputs and more likely to exhibit a response to acidic deposition than lakes in south-central Florida.

Internal biogeochemical processes which mediate lakewater ANC changes to acidic deposition include sulfate reduction in the sediments and nitrate and ammonium uptake by primary producers. Sulfate reduction and nitrate uptake contribute to ANC generation, whereas ammonium uptake is an acidifying process. All three of these chemical species occur in rainfall, and it is useful to examine the regional deposition rate of these species in the context of in-lake ANC generation and consumption. Total wet deposition of the acid species ($H^+$ and $NH_4^+$) is lowest in southern peninsular Florida, approximating 255 eq/ha compared to 405 eq/ha-yr and 420 eq/ha-yr in the panhandle and northern peninsular Florida, respectively (Table 5.2-1). Deposition of $H^+$ and $NH_4^+$ are nearly balanced by sulfate and nitrate in the panhandle (within 12 percent); by comparison, a larger relative excess (19 percent) of sulfate and nitrate occurs in northern peninsular Florida. This cation deficit in terms of biogeochemically reactive species is important because it represents an excess of ANC-contributing species in wet deposition.

Considering only internal processes, the balance between acid species ($NH_4^+$ and $H^+$) and base species ($NO_3^-$ and $SO_4^{-2}$) indicates that changes in lakewater ANC (in either direction) will not occur if $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ are completely removed from the water column. Comparison of dry and wet deposition with lakewater ion enrichment (i.e., normalized to $Cl^-$) ratios indicates, however, that $SO_4^{-2}$ is not removed from the water column to the same degree as $NH_4^+$ and $NO_3^-$; thus the regional differences in the ionic composition of wet deposition suggest a greater potential for lake acidification occurring in the panhandle than in northern peninsular Florida. The relative difference between acid ($NH_4^+$ and $H^+$) and base ($SO_4^{-2}$ and $NO_3^-$) species is even more pronounced for southern peninsular Florida (30 percent), indicating further that Highlands Ridge softwater seepage lakes are less susceptible to acidification than similar systems in north-central Florida and the panhandle. Weathering of calcium carbonate and subsequent release into the atmosphere as fine particles is undoubtedly contributing to the observed gradient in anion excess deposition increasing from north to south; calcareous outcrops are more a prevalent feature of southern peninsular Florida. This observation is directly supported from data and analyses from the precipitation chemistry monitoring network which indicated that excess $Ca^{+2}$ deposition decreased significantly from south to north.

Hydrology dictates the rapidity as well as the magnitude of response by which softwater seepage lakes are influenced by acidic deposition. Because seepage lakes are precipitation-dominated, the time frame of response can be approximated by the hydraulic residence time. As a first approximation, seepage lakes may be assumed to approach a new state of dynamic equilibrium in response to sustained changes of acidic deposition within three residence times. Because precipitation is generally higher and evaporation lower in northern peninsular Florida and the panhandle compared to the southern peninsula, residence times are shorter and response times are more rapid for the more northern lakes in the state. In general, seepage lakes in south-central Florida will require about 50 percent more time to equilibrate to changes in acidic deposition than comparable lakes in north-central Florida.

The aggregated effect of regional differences in hydrology and atmospheric inputs of biogeochemically important species contributing to in-lake regulation of ANC is summarized in Table 5.3-3. From all perspectives, seepage lakes in the panhandle must be considered most likely to undergo changes in lakewater chemistry in response to current

Table 5.3-3. Regional Summary of Hydrologic Parameters and Atmospheric Inputs (Wet Deposition) of Biochemically Reactive Species Important in Regulating ANC in Florida Seepage Lakes

| | Total Acid Loading* (eq/ha-yr) | Anion Excess† (eq/ha-yr) | Base/Acid Ratio** | Seepage†† Inputs | Rapidity of Response*** |
|---|---|---|---|---|---|
| Panhandle | 405 | 50 | 1.12 | <1 | <1 |
| Northern Peninsular Florida | 420 | 79 | 1.19 | 1 | 1 |
| Southern Peninsular Florida | 255 | 76 | 1.30 | 1.5 | 1.5 |

*Total acid loading equals $\Sigma(H^+, NH_4^+)$.

†Anion excess equals $\Sigma(SO_4^{-2}, NO_3^-) - \Sigma(H^+, NH_4^+)$.

**Base/acid ratio equals $[\Sigma(SO_4^{-2}, NO_3^-) - \Sigma(H^+, NH_4^+)] / \Sigma(H^+, NH_4^+)$.

††Relative inputs for lakes with similar morphometry (in particular, mean depth). For example, based on net differences in precipitation and estimated evaporative losses, seepage inflow rates in southern peninsular Florida seepage lakes are approximately 1.5 times inflow rates for seepage lakes in northern peninsular Florida.

***Relative time of response for lakes with similar morphometry based on estimated hydraulic residence times, $_w$. For example, $_w$ for seepage lakes in southern peninsular Florida is approximately 1.5 x $_w$ for seepage lakes in northern peninsular Florida. Thus seepage lakes in southern peninsular Florida are predicted to respond to acidic deposition 1.5 times more slowly than northern peninsular seepage lakes.

Source: ESE, 1986.

levels of acidic deposition. Total acid ($H^+$ and $NH_4^+$) deposition rates are highest in the panhandle and the northern peninsular, and seepage inputs are lowest for panhandle lakes. Furthermore, biogeochemical processes must consume or remove a larger proportion of the anions currently deposited and $SO_4^{-2}$ in particular to offset acid inputs. Finally, seepage lakes in the panhandle as a general class of lakes are predicted to respond somewhat more rapidly than lakes in the northern peninsula. Conversely, seepage lakes in southern peninsular Florida are more capable of assimilating current acidic deposition rates than similar lakes in northern Florida because of regional differences in hydrology, acid loading rates, and the chemical composition of rainfall. The effects of dry deposition on this regional perspective are unknown, largely because of the lack of ambient air data for $NH_3$ and $NH_4^+$ as well as uncertainties in deposition velocities. From model analyses of the role of in-lake processes on ANC dynamics, it is apparent that ANC in softwater lakewater is strongly influenced by $NH_4^+$ release from the sediments, and by the same token, additional external inputs from any deposition. In addition, the internal dynamics of $NH_4^+$ in softwater Florida lakes is largely unknown but is almost certain to vary to an appreciable degree from lake to lake.

Effects to aquatic systems in Florida as a result of current levels of acidic deposition have not been demonstrated conclusively. The strongest evidence of any sort of chemical and biological response related to acidic deposition is apparent reductions in lakewater pH for Lake McCloud, which is a seepage lake located in the Trail Ridge of north-central Florida. Lakewater pH in Lake McCloud has declined from about pH 4.85 in 1968-1969 to less than pH 4.6 in 1981-1982 and equates to an approximate doubling of proton concentrations. Corresponding increases in lakewater nonmarine or excess sulfate concentrations implicate acidic deposition as a possible cause of the apparent decline. Changes in precipitation and evaporation also can affect seepage lake chemistry; however, the fact that chloride concentrations remained essentially constant in Lake McCloud over the period of record suggests that hydrologic variability was not responsible for all of the observed changes in lakewater chemistry. Finally, it should be emphasized that the significance of the decline is uncertain; changes in ANC approximate the analytical uncertainty of the methods used for analysis. In addition, changes in analytical techniques for both sulfate and ANC serve to promote an overestimation of any historical changes.

The possibility of a causal relationship between current levels of acidic deposition and chemical changes in Lake McCloud can be examined to some extent by evaluating historical deposition rates and the response time of the lake inferred from its hydraulic residence time. Although monitoring data indicate that acidic deposition rates have remained relatively constant over the past decade, current rates of deposition are possibly higher than levels observed in the mid-1950s (Hansen et al., 1981; Barrie and Hales, 1984). If deposition rates have indeed increased, the timeframe of Lake McCloud approaching a steady-state response to the changed loading rates will approximate 20 to 30 years ($\tau_w$ = 7-10 years). Thus the change in lakewater chemistry observed between 1968 and 1982 in Lake McCloud could reflect changes in atmospheric loading rates occurring in the mid-1950s and later; however, the absence of historical precipitation and lakewater chemistry predating 1968 precluded a definitive assertion of cause and effect.

Coupled with the uncertainty that chemical changes attributable to acidic deposition have occurred in some seepage lakes is the uncertainty concerning the likelihood and extent that further chemical changes will occur. An absolute lower limit on lakewater pH can be calculated by assuming that no neutralization of acidic deposition occurs within the watershed or by in-lake processes. Using Lake McCloud as an example for this analysis, lakewater concentrations of chloride indicate that evapoconcentration in the lake results in nearly an order of magnitude increase (~8.6x, cf. Tables 2.3-1 and 5.3-1 in ESE, 1985) over rainfall concentrations including dry deposition inputs. Assuming that lakewater proton concentrations in Lake McCloud ultimately will reflect a similar concentrative effect yields a lower limit on pH of 3.7 (excluding dry deposition). In reality, over 90 percent of acidic inputs to Lake McCloud currently are neutralized, and lakewater pH will ultimately reflect a balance between: (1) the acidifying effects of proton deposition, evapoconcentration, and ammonium deposition and release from the sediments; and (2) the generation of ANC by sulfate reduction and nitrate uptake as internal processes and ANC contributions from the watershed as a result of sulfate retention and weathering. Whether Lake McCloud (and similar softwater seepage lakes) is in a transitional state with respect to pH and will reach some steady-state (or dynamic-equilibrium) pH below 4.5 but above 3.7 is unknown. The hydrology of seepage lakes and the interaction of the poorly buffered soils of these watersheds with seepage lake chemistry in Florida are largely not understood. Furthermore, the internal cycle of ammonia in seepage lakes appears to be a significant process regulating lakewater pH in softwater seepage lakes and has not been studied to any extent.

Insufficient data are available to allow a definitive assessment of aquatic biota effects in response to acidic deposition in Florida. Research in Florida to date has largely been restricted to several cross-sectional surveys of softwater lakes across a gradient in pH and ANC. These surveys have been used to characterize aquatic communities as a function of lakewater pH and have been supplemented to some extent by: (1) several limited laboratory studies designed to evaluate acute toxicity effects of low pH and/or aluminum solubilization, and (2) *in situ* studies conducted at Lake McCloud in which pH levels in enclosures were manipulated. There are no long-term biological data available documenting changes in aquatic community structure as a result of declines in pH of any particular lake in Florida. Thus biological response can be only inferred.

In general acidification of softwater lakes in Florida should result in a simplification of community structure (i.e., reductions in species diversity). Reduction of lakewater pH below 6.0 to 5.5 will result in the replacement of bluegreen algae by green algae as the dominant species group. Some decline in the number of phytoplankton species can be anticipated with reductions in lakewater pH below 6.0. In all likelihood, algal productivity will not be adversely affected with pH declines to as low as pH 3.7.

Macrophytes are also likely to exhibit a simplification in community structure should lakewater pH levels decline, reflecting the loss of a few species of macrophytes found only in relatively high-pH waters. Also, some enrichment of trace elements in macrophyte tissues, including copper, cadmium, lead, and zinc, is likely to occur. Macrophyte abundance appears independent of pH in softwater lakes, and reductions in lakewater pH to as low as pH 4.2 should have little effect.

Increasing lake acidification may also result in a reduction in zooplankton diversity, although the reductions probably will not be as extensive as declines observed in similar temperate systems. Some species replacement is expected in response to changes in pH. Drastic changes in zooplankton community structure are likely should reduction of lakewater pH to approximately 3.6 occur, including the virtual elimination of copepods and substantial reductions in overall zooplankton abundance. At what specific pH between 4.6 and 3.6 these effects become evident is unknown.

Minor declines in the numbers of species of Florida fish are probable with reductions of surface water pH to approximately 4.0. Limited surveys of the distribution of Florida fish as a function of pH suggest that Florida fish including some game fish are more tolerant of low-pH regimes than members of the same species found in temperate lakes, possibly because of: (1) natural selection operating over many generations of exposure to low pH; (2) higher levels of primary productivity; (3) climatic differences; and (4) lower lakewater concentrations of aluminum. Below pH 4.0, fish response in Florida lakes is largely unknown, although acute toxicity at approximately pH 3.7 has been reported in laboratory tests for two species of fish, the largemouth bass (Micropterus salmoides) and the redear sunfish (Lepomis microphＯlus). Although the reported pH range for the redear sunfish extends as low as pH 3.9 in highly colored swamp waters, this species is not an important member of the aquatic community below pH 6.5.

### 5.3.2 TERRESTRIAL EFFECTS

Acidic deposition may exert two types of effects on terrestrial resources: indirect or direct. Indirect effects are mediated by the reaction of acidic deposition with the soil matrix and may develop through changes in organic matter availability, loss of nutrients, the mobilization of potentially toxic metals, or the modification of terrestrial community relationships such as interactions between vegetation and bacteria. Direct effects arise from exposure of foliar surfaces to strong acid and may include the response of vegetation to nitrate and sulfate inputs inherently part of acidic deposition. Regional differences in direct effects ultimately reflect the spatial distribution of acidic deposition. Regional sensitivity to indirect effects is a function of both depositional patterns and the distribution of soils.

Soils in Florida with the least ability to neutralize acidic inputs are deep highly weathered and acidic sands found in the highlands and ridge physiographic regions of the state. These soils have very limited cation exchange capacities and only a minor fraction of the total cation exchange capacity is available to neutralize acidity via ion exchange with base cations. Furthermore, these soils have little ability to adsorb sulfate, at least within the surficial horizons. Because of their acidic character, these deep sands are probably not susceptible to large changes in pH or large relative losses of base cations. However, the effect of small reductions of the base content in these soils, particularly on forest growth where base cations are tightly recycled, is unknown. Clearly, increasing inputs of acidity will accelerate the flux of base cations from the soil over long periods of time. In addition, mobilization of aluminum is inversely related to soil pH, and increasing amounts of acidic deposition could release potentially toxic concentrations of aluminum into the soil water of soils already acidic.

Chemical and biological effects related to current levels of acidic deposition on terrestrial ecosystems found in the Highlands and Trail Ridge regions (and other parts of Florida) have not been demonstrated. Essentially no historical data are available to establish a baseline for comparing changes in soil chemistry or forest productivity in response to long-term changes in acidic deposition to current levels. Because of the paucity of data, the question of whether or not current levels of acidic deposition are resulting in effects to soils in particular cannot be answered definitively. However, because of their acidic character, the deep, highly weathered sands of the Highlands and Trail Ridge regions are probably not susceptible to large changes in pH or large relative losses of base cations. Irrigation studies at Lake McCloud with acidified, simulated throughfall indicate that significant changes in aluminum solubilization and soil solution pH do not occur until throughfall pH is depressed and sustained below pH 3.6. Because of the mitigating or neutralizing effects of canopy processes in the McCloud watershed on rainfall pH (Roof, 1985), which in turn implies that effects will not be perceived unless rainfall pH is less than 3.6, it seems unlikely that significant soil acidification effects are currently occurring in the McCloud watershed. Current levels of rainfall pH in northern Florida approximate 4.6 (Table 5.2-2), and less than 0.2 percent of the rainfall events in this region are depressed below pH 3.7.

The likelihood of soil effects in the panhandle and southern peninsular Florida can be examined by considering deposition rates of protons and ammonium (since ammonium uptake has an acidifying effect and its presence in rainfall and dry deposition is largely the result of neutralization of acid by gaseous ammonia) as an estimate of the total acid burden received by terrestrial systems. Total wet deposition of $H^+$ and ammonium is virtually identical for both the panhandle and northern peninsular Florida (405 and 420 eq/ha-yr, respectively; Table 5.2-1); by comparison, wet deposition of these two species is nearly 40 percent lower in southern peninsular Florida. Superimposing these results on the distribution of the most poorly buffered soils in Florida indicates that the soils with the greatest likelihood of exhibiting acidic deposition effects are the ultisols and entisols of Western Highlands of the panhandle and the entisols of the Central Ridge in northern peninsular Florida (Figure 5.3-2). Nevertheless, the inherently acid nature of the soils in these two regions as a result of extensive (natural) weathering occurring over thousands of years suggests that the likelihood of perceptible increases in soil acidification over the next several decades is rather low.

Experiments involving the application of acid rain simulants to young, potted trees indicate no adverse effects on growth at ambient pH levels. These experiments indicate that the thresholds for such effects could be as low as pH 2 or pH 3 in some cases. The frequency of rainfall pH $\leq$3.0 in Florida is extremely low as evidenced by the frequency distribution of laboratory pH over a 3-year period for sites located in Gainesville (Site 5) and Archbold (Site 9) (Table 5.3-4). In fact, at Gainesville over the 3-year period, about 1 percent of the observed rainfall events had pH as low as 3.5, whereas at Archbold about 1 percent of the observed rainfall events had pH less than 3.7. Acidic events with pH $\leq$3.7 are also generally associated with low rainfall volumes. These data, taken by themselves, would suggest that adverse effects to Florida's forest

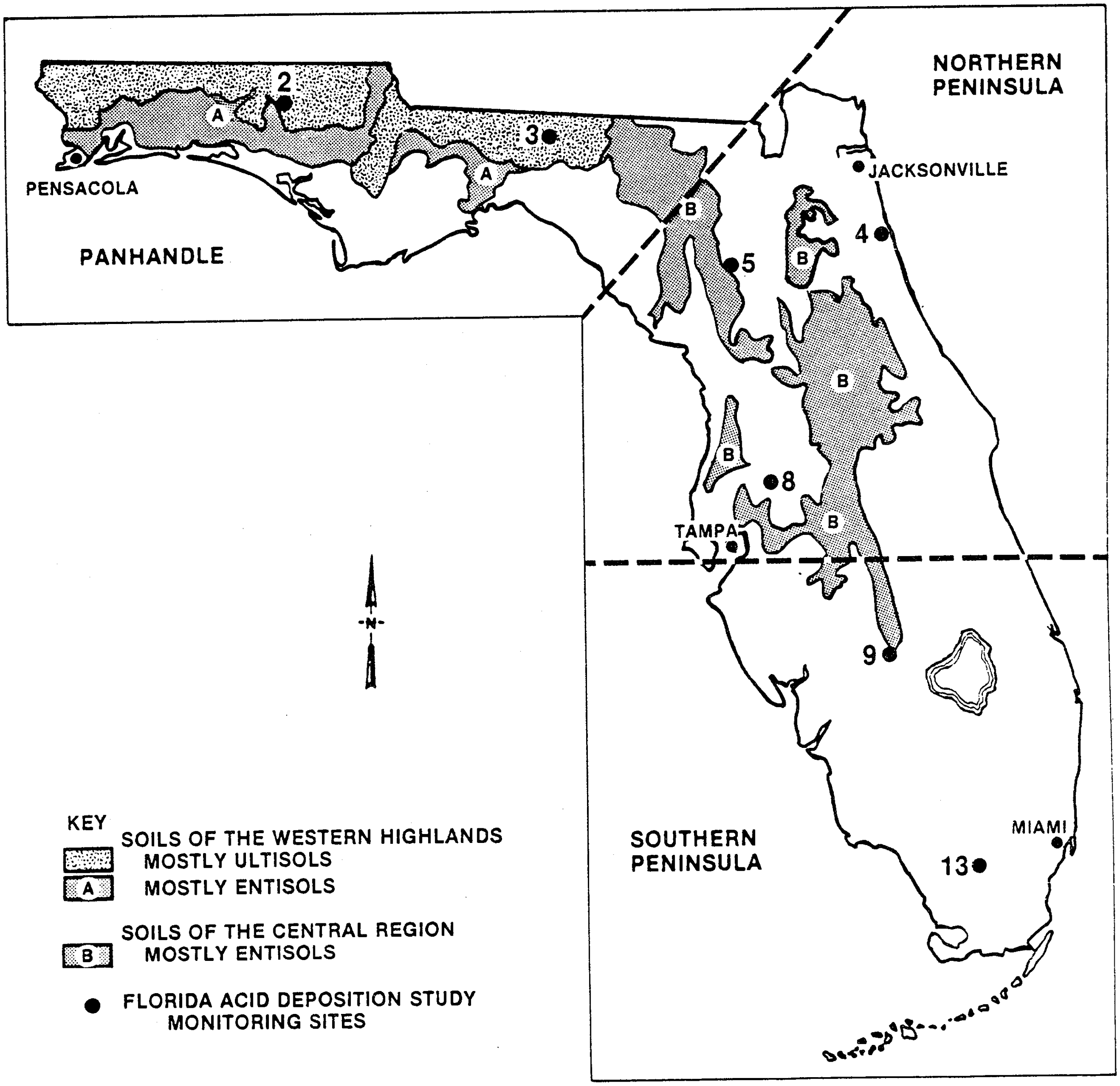

Figure 5.3-2
SOIL TYPES OF FLORIDA

SOURCES: Florida State University, 1981; ESE, 1986.

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Table 5.3-4. Frequency Distribution of 3-Year Mean Laboratory pH for Gainesville (Site 5) and Archbold (Site 9)

| Site | | pH Class<br>≤3.5 | <br>>3.5<br>≤3.7 | <br>>3.7<br>≤4.0 | <br>>4.0<br>≤4.5 | <br>>4.5 |
|---|---|---|---|---|---|---|
| Gainesville<br>5 | Occurrence (%) | 1 | 2 | 8 | 35 | 54 |
| | Rainfall (%) | <<1 | <1 | 3 | 18 | 79 |
| Archbold<br>9 | Occurrence (%) | <<1 | <1 | 2 | 16 | 81 |
| | Rainfall (%) | <<1 | <<1 | <1 | 8 | 92 |

Source: ESE, 1986.

resources are unlikely. However, short-term controlled laboratory tests do not include the multiplicity of factors that occur in the real world.

Hypotheses implicating acidic deposition in observed forest declines in the United State and Europe assume that trees are damaged by the interaction of acidic deposition over time with abiotic and biotic stresses. Until the reasons for observed forest declines in other regions and the role of anthropogenic atmospheric deposition in these declines are better understood, it is not possible to predict either the potential long-term effect of present levels of acidic deposition or the threshold levels that would adversely affect forests in Florida.

Information about the effects of acid deposition on crops is based on experiments in which simulated acid rain is applied to test species either in the field or in a controlled environment. Such experiments, which are generally short-term, are applicable to crops which are harvested annually. Results of experiments on the same species vary. Species tested in field experiments generally show yield reductions at lower pH levels than potted plants of the same species tested in a controlled environment. Many field tests indicate that rain with pH 3.0 throughout the growing season would be required to reduce yields of some crops. As shown in Table 5.3-4, rainfall pH as low as 3.0 is extremely infrequent. Effects on agronomic soils are unlikely because croplands are amended with fertilizers to raise pH and nutrients to optimum levels. Therefore, it can be stated with reasonable certainty that acidic deposition is not significantly impacting crop yields in Florida and is not likely to have a significant effect on crop yields in the future.

## 5.4 SOURCE ATTRIBUTION

As noted in Subsections 2.9 and 5.2, $SO_4^{-2}$ and $NO_3^-$ are both important contributors to total acidic deposition within the state, with $SO_4^{-2}$ contributing about 60 percent of the total acidic deposition. Subsections 4.5 and 5.3 indicate that, of all categories of effects evaluated, the potential for damage to aquatic systems in Florida as a result of acidic deposition has been documented more extensively than the potential for damage to other resources. The most sensitive aquatic systems appear to be the seepage lakes of the Trail Ridge Highlands of northern peninsular Florida and of the Western Highlands of the panhandle. For such systems, the potential for any effect to occur appears to be related to the total acidic deposition (the sum of $NO_3^-$ and $SO_4^{-2}$ over a period of a decade or more). This subsection presents preliminary estimates of the contribution of several major categories of sources to total acidic deposition in Florida. Uncertainties in source-receptor relationships derived from atmospheric deposition models are unknown (refer to Subsections 3.1.2.3, 3.1.3.3, and 3.4.2 for discussions of model limitations and uncertainty). Therefore, the data presented below are merely illustrative of the type of results obtained from model simulations.

The main sources of $SO_x$ and $NO_x$ found in Florida's atmosphere are summarized in Figures 5.4-1 and 5.4-2. It is apparent that nearly half of both of these acid precursors in Florida's atmosphere are imported from out-of-state sources. Florida's electric generating utilities contribute approximately 35 percent of Florida's atmospheric $SO_x$ and 20 percent of its atmospheric $NO_x$. Nonutility point sources (principally industrial sources) contribute approximately 10 percent of the atmospheric burden of each of these precursors. Transportation-related sources, principally automobiles and trucks, contribute approximately 25 percent of the $NO_x$ in Florida's atmosphere. The contribution of natural biogenic emissions is approximately 5 percent for both $SO_x$ and $NO_x$.

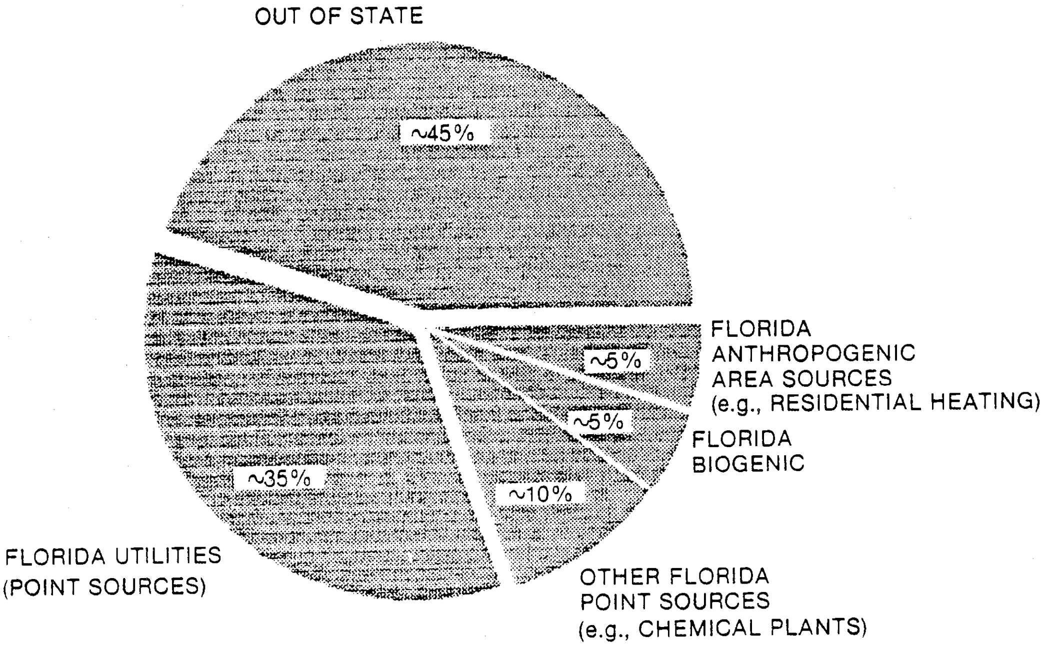

Figure 5.4-1
SOURCES OF SULFUR IN FLORIDA'S ATMOSPHERE

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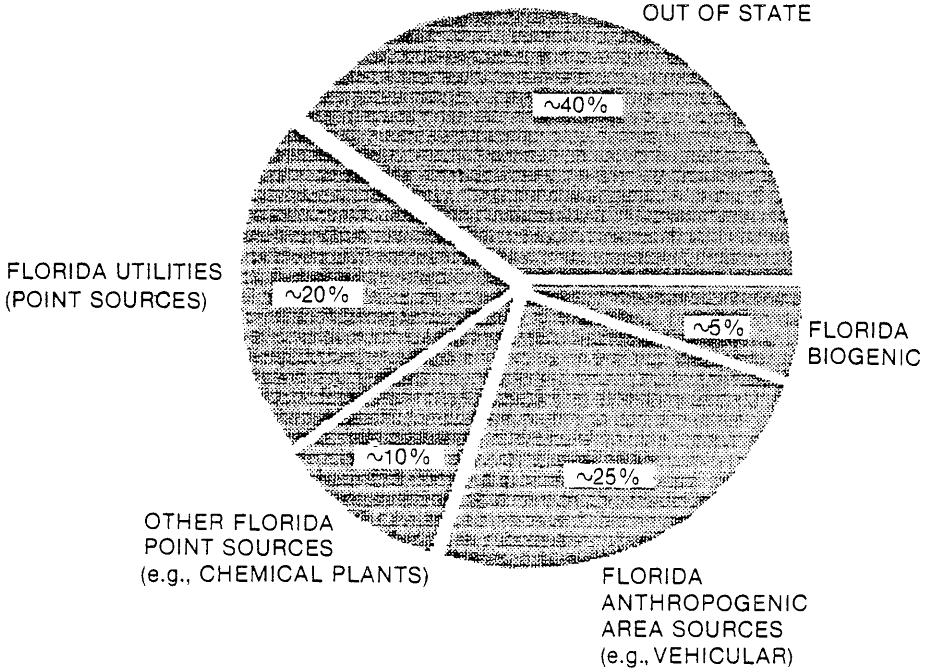

Figure 5.4-2
SOURCES OF NITROGEN IN FLORIDA'S
ATMOSPHERE

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Figures 5.4-1 and 5.4-2 illustrate estimates of the contribution of major source categories to atmospheric levels of important acid precursors. The contribution of each source to total acid deposition is closely related to the contributions to $SO_x$ and $NO_x$ in the atmosphere, although acid precursors from some source types may deposit more efficiently than others (i.e., disproportionate to their contribution to air concentrations) because of their release height. The major factors controlling the relative efficiency of deposition from different source types are the source emission height and the source-to-receptor distance. Ground-level sources deposit more efficiently by dry-deposition processes than do elevated sources. Gaseous $SO_2$ from distant sources may be converted during transport to secondary contaminants such as particulate $SO_4^{-2}$. The particulate $SO_4^{-2}$ is not deposited by dry processees very efficiently but is scavenged by precipitation relatively efficiently.

To address these and other phenomena controlling transport, transformation, and deposition, a computer model (ENAMAP) was applied to estimate the contribution of major source types and regions to sulfur deposition in Florida. The model was not applied to $NO_x$ because of substantially greater uncertainties in emission rates and atmospheric transformation and deposition processes controlling $NO_x$. Consequently, in order to estimate the contribution of various source types to total acidic deposition, it is necessary to assume that the contribution of each source category to total $NO_x$ deposition in Florida is proportional to its contribution to atmospheric $NO_x$. This approach is likely to result in an underestimate in the contribution of local sources, particularly local ground level sources. The contribution of each source type to $SO_x$ deposition is based primarily on the computer model results. Only anthropogenic sources were simulated by the model so the contribution of biogenic emissions has been estimated in proportion to its contribution to atmospheric $SO_x$.

Figure 5.4-3 presents the calculated contribution of major source types to total acidic deposition in Florida. Approximately 40 percent of total deposition in the state is attributable to out-of-state sources. Approximately 30 percent is attributable to Florida utilities. Other Florida point sources contribute approximately 15 percent of total acidic deposition. Florida area sources (principally transportation) contribute 15 percent of total acidic deposition. Biogenic emissions contribute less than 5 percent to total acidic deposition.

The preceding presentation of source categories to total acidic deposition reflects their relative contribution to deposition over the state as a whole. In keeping with the integrative focus of the section, the contribution of source categories to the potentially sensitive receptors of the Trail Ridge Highlands of northern peninsular Florida and the western highlands of the panhandle region are also considered. It may be expected that the pattern of source contributions as a whole to the state might be somewhat similar to the source contributions to northern peninsular Florida because of its central location. The panhandle could be expected to be influenced by out-of-state sources to a greater extent than the statewide average might indicate.

The contribution of source categories to sulfur depositions in the major geographic regions of Florida can be addressed by reference to the ENAMAP model results. The representative reproduction of spatial patterns of deposition within Florida (see Subsection 3.3.2.3) indicates that its results can be disaggregated meaningfully to this extent, although only in Florida. ENAMAP results indicate that out-of-state sources account for approximately 60 percent of total sulfur deposition in the Florida panhandle, whereas Florida utilities account for approximately 25 percent. In the Florida panhandle, nonutility point sources were calculated to contribute about 10 percent of total sulfur deposition, with anthropogenic and biogenic area sources comprising the remaining 5 percent.

## 5.5 UNCERTAINTY AND RESEARCH RECOMMENDATIONS

### 5.5.1 ACID DEPOSITION MONITORING

The Florida acid deposition monitoring network provides highly reliable data on wet deposition of acidic contaminants. The database is limited in its ability to address the key research questions, principally because of the 3-year duration of the study. Substantial interannual variations in wet deposition were observed over the 3-year data record; the record is too short to determine climatic norms or trends reliably or to definitively address the cause of the observed variability. Monitoring of acid deposition within Florida should be maintained long enough to determine climatic norms and the existence of environmentally significant trends.

Total deposition of acidifying substances results from both dry and wet deposition processes. Although wet deposition is measured reliably by the Florida network, dry-deposition rates cannot be measured reliably with demonstrated monitoring technology. In an attempt to account for dry deposition as a component of total acidic deposition, air chemistry was also monitored by the network. Dry-deposition rates are normally calculated as the product of air concentration and the dry-deposition velocity. Dry-deposition velocities depend on meteorological conditions, contaminant physical and chemical properties, and surface properties. Dry-deposition velocities are highly variable from place to place and hour to hour. Estimates of dry deposition are uncertain largely because dry-deposition velocities are uncertain. Dry-deposition velocities of sulfur and nitrogen species appear to decrease in the following order: $HNO_3 > SO_2 \geq NO_2 >> SO_4^{-2}$.

However, additional research is needed to understood the major variables controlling dry deposition. Other factors also contribute to uncertainty in dry-deposition rates. Air concentrations, particularly of precursor gases, vary spatially over Florida. The Florida network, even though it was designed to characterize regional processes by selecting sites generally 35 km or more from major local sources, exhibits significant spatial variability in air concentrations of precursor gases. Concentrations of precursor gases are presumably higher near major sources and, consequently, the Florida network probably underestimates dry deposition of acid precursors which occurs preferentially near local sources. An alternative method for estimation of dry-deposition rates involves the use of computer models. The ENAMAP model used in this study is designed to simulate regional-scale processes and would not be expected to estimate dry deposition near local sources very accurately. The monitoring network cannot account for dry deposition near local sources because the network was designed to monitor regional deposition and avoid the effects of local sources. These fundamental contrasts are reflected in the fact that ENAMAP estimated higher statewide average dry deposition rates than were estimated from the monitoring network (Subsection 2.3.1.5) even though both estimates relied on the same dry-deposition velocities and ENAMAP had underestimated $SO_2$ air concentrations at the monitoring sites by 20 percent. From a mass-balance perspective (i.e., considering total statewide dry deposition), the ENAMAP results are probably more realistic since they account for dry deposition near local sources. In the context of regional total deposition in areas isolated from local sources, the estimates based on the monitoring network are more reliable because they are based on observed air concentrations.

Uncertainties regarding the dry-deposition rates can be reduced by (1) fundamental research on the dry-deposition process, particularly for nitrogen species, and/or (2) further refinement and application of models; a variety of modeling approaches may be useful besides the ENAMAP approach taken here.

Direct monitoring of dry deposition is probably not feasible at the state of the art, but further development in the field should be evaluated at regular intervals to determine whether direct monitoring is advisable at a later date.

Data gaps and uncertainties remain regarding the nitrogen mass balance in Florida's atmosphere. These uncertainties can affect the reliability of deposition estimates and evaluation of the likelihood of effects. In particular, monitoring of atmospheric $NH_3$ would reduce these uncertainties.

## 5.5.2 ECOLOGICAL EFFECTS

### 5.5.2.1 Aquatic Effects

Of the various processes contributing to the regulation of seepage lakewater chemistry, the principal factor is hydrology. The amount of water discharged by a seepage lake controls the hydraulic residence time and thus the rapidity of lake response to perturbations in acidic loading rates. Furthermore, because seepage lakewater chemistry is sensitive to seepage inputs from the shallow ground water table, the pH and ANC dynamics of seepage lakes will ultimately reflect a balance between precipitation and seepage inputs. On a regional scale, some perspective on both the relative contribution of inseepage to seepage lake hydrology and the hydraulic residence times of seepage lakes is provided by long-term differences between average precipitation and evaporative losses from the lake surface as estimated by pan evaporation measurements. For individual seepage lakes, however, the subsurface hydrology (i.e., seepage inputs and outputs) is poorly understood and not well studied. In addition, virtually no data exist on the chemical quality of seepage inputs to softwater seepage lakes apart from the limited data collected by Baker (1984) for Lake McCloud. The applicability of Lake McCloud seepage chemistry to other aquatic systems in Florida has never been verified. Thus the physical and chemical dynamics of seepage inputs (including seepage chemistry changes in response to changes in acidic deposition) to seepage lakes represents an area of major uncertainty regarding the effects of acidic deposition on aquatic systems.

Internal or in-lake processes such as sulfate reduction and nitrate and ammonium uptake by primary producers contribute to the production and consumption of lakewater ANC. Consequently, the magnitude of the response of poorly buffered, softwater lakes to acidic deposition is mediated by internal biogeochemical processes as well as by hydrologic factors. Sulfate dynamics have been studied to some extent in the laboratory and *in situ* via mesocosm or enclosure studies and the removal of sulfate by sediments and concomitant production of ANC is well documented for several softwater seepage lakes in Florida. In part, the production of ANC in the sediments is the result of ammonification of organic matter [i.e., the release of ammonia ($NH_3$) during the degradation of organic matter]; however, the flux of ammonium ($NH_4^+$) from the sediments into overlying lakewater has an acidifying effect which is unquantified in softwater lakes. Further research on the development of a diagenetic model accounting for the major ANC-regulating processes in softwater lake sediments including sulfate reduction and ammonification would reduce this uncertainty.

General trends in the chemical and spatial distribution of softwater lakes have been established using relatively large databases such as FLADAB. Databases such as FLADAB, however, are not well suited for examining the distribution of softwater lakes because of the inherent bias towards inclusion of highly productive lakes or lakes that have been disturbed by cultural activity, principally via the introduction of nutrients and, to some degree, ANC. As a result, FLADAB and similar databases probably underestimate the number of low-ANC, low-pH lakes. This deficiency may be resolved to some extent by the National Lake Survey which applied a random sampling regime to allow statistical inferences regarding the distribution of poorly buffered lakes in principally the highlands and ridge physiographic regions of Florida. Because of the susceptibility of small seepage lakes to cultural disturbances and land use practices within their watersheds, an accurate determination of the number of lakes potentially at risk to acidic deposition must incorporate land use and hydrologic information.

Aquatic biota effects at current levels of acidic deposition can be only inferred at present from lake surveys conducted across a gradient in pH and several limited direct effects studies. Consistent with other studies conducted in temperate lakes of North America and Scandinavia, survey results in Florida suggest that progressive lake acidification will lead to simplification (or loss of species) of the aquatic community. However, the inference that declines in productivity coupled with reductions in lakewater pH (based on correlations between algal and zooplankton abundance and lakewater pH) is confounded by coincident correlations with trophic-state variables. These correlations neither substantiate nor refute a causal link between productivity and lakewater pH. Nevertheless, support for the acid-induced oligotrophication hypothesis is weakened by mesocosm studies in Lake McCloud which suggest that algal productivity is more a function of nutrient concentrations than lakewater pH.

Several major research programs should be considered, including:

- Studies on the hydrology of seepage lakes, including stable isotope studies to evaluate evaporative effects on the hydrologic balance, should be undertaken. Flow rates and chemical characteristics of inseepage in particular need to be examined directly. This research should also be extended to include further evaluation of the effects of acidic deposition on weathering contributions and how changes in acidic deposition will affect weathering inputs to seepage lakes.
- Process oriented *in situ* studies on biogeochemical processes mediating the ANC response of softwater seepage lakes to acidic deposition should be performed. A particular need is research on the internal dynamics of $NH_4^+$ and $SO_4^{-2}$ in softwater lakes and examination of $NH_4^+$ release from sediments as an ANC-consuming process.
- Long-term monitoring of the chemistry and hydrology of selected seepage lakes should be performed to evaluate possible trends and effects of lake acidification. Biological community characterization and monitoring should also be included.
- The spatial and numerical distribution of poorly buffered softwater lakes in Florida should be analyzed, including land use and hydrologic data to identify localized watershed influences on lakewater ANC and pH. Some of these data should be provided by the final results of NLS.

- Dry deposition, including $NH_3$ and $NH_4^+$ deposition, should be studied.

### 5.5.2.2 Terrestrial Effects

The absence of appropriate historical monitoring data to establish reference points for evaluating changes precludes a definitive evaluation as to whether current levels of acidic deposition are resulting in measurable soil acidification of poorly buffered soils in Florida. The likelihood of significant increases in soil acidification related to acidic deposition can be inferred by considering the highly acidic character of the most poorly buffered soils as a result of extensive weathering occurring over thousands of years. The large reservoir of acidity inherent in these soils suggests that perceptible increases in soil acidity are rather unlikely, a conclusion which is supported by irrigation studies in the poorly buffered watershed of Lake McCloud. Nevertheless, it is evident that acidic deposition does contribute to accelerated rates of base cation leaching. It is uncertain whether forest systems in Florida will compensate for enhanced nutrient leaching rates by more rapid uptake rates to maintain the tight cycling of nutrients characteristic of nutrient poor systems. Should uptake rates fail to keep pace with leaching rates, the base cation reservoir of the forest will diminish, and declines in productivity may occur.

Uncertainties regarding the interaction of acidic deposition with soils could be reduced by further research, including:

- A long-term monitoring database on soil chemical characteristics (e.g., CEC, pH, base saturation, $SO_4^{-2}$, etc.) at undisturbed sites throughout the state should be developed with a focus on the highlands and ridge physiographic regions. Because of the uncertainty regarding long-term effects on soil microbial activity, enzymatic assays should be included as monitoring parameters at several sites sampled at a high rate of frequency.

- The long-term effect of acidic deposition on base cation cycling and loss rates from acidic, poorly buffered forest soils within the highlands or ridge physiographic regions should be studied. These studies should assess whether acidic deposition promotes the further acidification of soils and reduction of available cations or will result in weathering of primary minerals at rates sufficient to maintain base cation availability.
- Long-term studies on aluminum mobilization in acidic, poorly buffered soils should be undertaken.

### 5.5.3 SOURCE ATTRIBUTION

The limitation of the Source Attribution Program and the uncertainties in its conclusions have been addressed throughout this report. Specifically, Subsections 3.1.3.3 and 3.3.2.4 provide detailed discussions of such limitations. In general, it can be stated that uncertainties in source-receptor relationships are unknown. The purpose of this section, therefore, is to highlight areas where research can be focused to reduce model uncertainty.

Total deposition results first presented in Subsection 2.3.1.5 indicate that the major processes contributing to total acidic deposition may be ranked as follows:

> Wet deposition of acidic sulfur $\geq$ dry deposition of acidic nitrogen $\geq$ dry deposition of acidic sulfur > wet deposition of acidic nitrogen.

Even the least important process, wet deposition of $NO_3^-$ species, contributes approximately 15 percent to total deposition, so each process is important. The attribution of source contributions to sulfur deposition was emphasized in the source attribution program for several reasons. It contributes more to total acidic deposition than does nitrogen. Available models represent the atmospheric chemistry of $SO_x$ more realistically than can be achieved for $NO_x$; and little research has been reported on $NO_x$ deposition parameters relative to $SO_x$. Thus, it could be anticipated that attempts to model $SO_x$ would be more successful than an attempt to simulate $NO_x$ source receptor relationships. Nonetheless, the result of greater research attention to $SO_x$ than $NO_x$ (by the general acid rain research community, as well as in this study), is that the greatest uncertainties limiting attribution of total acidic deposition to major source categories result from uncertainties in the contribution of source categories to the dry deposition of $NO_x$.

Uncertainties regarding the contribution of source categories to total acidic deposition via the dry deposition of $NO_x$ result from the following factors:

1. Uncertainty in emissions;
2. Uncertainty in the long-term average dry-deposition velocity;
3. Probable negative bias by relying on monitoring network designed to represent regional air chemistry; and
4. Assumption that deposition is proportional to source for $NO_x$, probably underestimating the effect of local sources.

Uncertainties in ENAMAP estimates of source contributions to sulfur deposition derive from the following sources:

1. Emissions;
2. Simplified representation of complex atmospheric processes (e.g., layer average transport winds, linear transformation rates, linear wet deposition, no microscale, no cloud chemistry, etc.);
3. Lack of spatial resolution in input meteorological data; and
4. Lack of meteorological data over ocean (refer to Subsection 3.3.3.3 for illustration of the effects of this type of error).

A variety of measures of model performance were presented throughout Subsection 3.3.2 and interpreted further in Subsection 3.4. The results presented do not support an estimate of the uncertainty in model estimates of source attribution.

Source contributions to nitrogen wet deposition are less reliable than either of the sulfur terms, but at least the total amount of wet $NO_3^-$ deposited has been determined with reasonable reliability by the monitoring network. This situation is contrasted with that for dry deposition for $NO_x$ where not only the contribution of sources, but also the total amount deposited was in serious question.

Uncertainty arises from the following sources:

1. Emissions,
2. Assumption that wet deposition is proportional to contribution to atmospheric $NO_x$,
3. Cloud chemistry, and
4. Precipitation scavenging.

Uncertainty increases substantially in any attempt to attribute deposition in sensitive receptor regions such as the Western Highlands or Trail Ridge, and attribution to specific utilities or stacks is completely inappropriate. The wind data and the calculations using that data, in both the air mass trajectory analyses and the ENAMAP model, cannot reliably relate specific point sources to specific receptors (e.g., lakes). Such use of these modeling techniques would be inappropriate and inconsistent with their design and objectives. The implications of such investigation could not be supported scientifically.

To improve source attribution estimates beyond the findings of this study will require an improvement in ability to estimate dry deposition, particularly of nitrogen species. It is not clear, however, that either available modeling techniques or the fundamental understanding of $SO_x$ and $NO_x$ transformation and deposition processes have advanced far enough to warrant such an undertaking.

## 5.6 REFERENCES CITED

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# 6.0 CONCLUSIONS

The data and analyses developed within the Florida Acid Deposition Study have significantly increased the current knowledge about the acidic deposition phenomenon in Florida through research in three major areas: acid deposition monitoring, source attribution, and ecological effects.

The objective of this research was to assess and/or develop information on acid deposition concerning its magnitude, variability, sources, and effects in Florida.

In developing the plans of study to meet this research objective, the study focused on providing Florida-specific information from which certain key research questions could be addressed. The extent to which each research area was investigated was based upon the ability to obtain definitive Florida-specific results, the complexity of the acid deposition-related phenomena that were to be addressed, the desire to draw from national, regional, state, and university research efforts, as well as available time and funding. Although all research areas were not investigated to the same degree, each key question was addressed. The data and information developed during the study will provide the foundations for future research, even for those research areas where definitive information was not developed.

A qualitative measure of the achievements made during the course of the study for each major research area is presented in Table 6.0-1. As shown, direct evidence was developed primarily in the area of acid deposition monitoring. Substantial amounts of data were developed to address the magnitude of wet deposition in Florida as well as spatial and short-term temporal variability and chemical relationships. Although dry deposition was not directly monitored, monitoring was established for measuring ambient air concentrations of acid precursors from which dry deposition could be estimated. This study was also one of the first

Table 6.0-1. Accomplishments of the Florida Acid Deposition Study

| Research Area | Direct Evidence Developed | Limited Direct Evidence Developed | Indirect Evidence Developed | Literature Review Only |
|---|---|---|---|---|
| Acidic Deposition | | | | |
| 1. Wet—magnitude | X | | | |
| 2. Dry—magnitude | | | X | |
| 3. Spatial variability | X | | | |
| 4. Temporal variability | | | | |
| a. Short term | X | | | |
| b. Long term | | X | | |
| 5. Chemical relationships | X | | | |
| 6. Organic acids | | X | | |
| Ecological Effects | | | | |
| 1. Lakes | | | | |
| a. Chemistry | | X | | |
| b. Biology | | | X | |
| 2. Terrestrial | | | | |
| a. Soils | | X | | |
| b. Forests | | X | | |
| c. Crops | | X | | |
| 3. Materials | | | | X |
| Source Attribution | | | | |
| 1. Florida anthropogenic emissions | X | | | |
| 2. Biogenic emissions | | X | | |
| 3. Source contributions | | | X | |

Source: ESE, 1986.

regional-scale networks to provide concurrent precipitation chemistry and ambient air data from which dry deposition could be estimated using deposition velocities and interrelationships developed. The monitoring network operated over a 3½-year duration using standard techniques to establish a short-term database and to provide a foundation for assessing long-term trends. At the time of this report, the network (7 stations) has continued to operate and is funded through 1986. At a minimum, a 5½-year database will be available for future analyses.

Process-oriented soil and lake sediment studies were conducted in the ecological effects area. Direct foliar effects studies were also performed for three Florida plant species (i.e., slash pine, citrus, and tomato). Acid response on aquatic biota was inferred from data available for Florida fish species and other studies and literature; however, no experimental studies were performed. A literature review of material effects was conducted, but no experimental studies were performed on this topic.

The achievements made in the Source Attribution Program focused on applying existing modeling techniques to assess the contribution of acidic species to Florida. Substantial data were developed on emissions and drawn from the acid deposition monitoring efforts. Nonetheless, the currently available source attribution techniques have considerable uncertainty. Specifically, the source attribution relationships developed are at best only representative for the specific period evaluated and would not be appropriate for predicting changes in deposition as a result of emission changes.

The studies and analyses performed within the Florida Acid Deposition Study have led to a greater understanding of the acidic deposition phenomenon in Florida. While much of the information contained in this final report addresses key research questions within each research area, certain overall conclusions have been reached regarding the importance of acidic deposition to Florida. These major conclusions concerning the magnitude and variability, the effects and sources of acidic deposition in Florida are listed below.

## 6.1 MAGNITUDE AND VARIABILITY

- The Florida acidic deposition monitoring network results over a 3-year period, when compared with data from the eastern United States, show that pH in Florida averaged approximately 4.6 while precipitation pH in the northeastern and midwestern United States averaged about 4.3 for the same period. These differences in pH indicate that Florida's precipitation is roughly half as acidic as that of the northeastern and midwestern United States. $SO_4^{-2}$ deposition in Florida precipitation was approximately 14 kg/ha-yr as opposed to approximately 24 kg/ha-yr in the northeastern and midwestern United States. Similarly, $NO_3^-$ deposition in Florida precipitation was about 8 kg/ha-yr compared to about 14 kg/ha-yr observed in the northeastern and midwestern United States. In a broad sense, these data demonstrate a decrease in acidity and related parameters (i.e., $SO_4^{-2}$ and $NO_3^-$) from north to south. This gradient was also observed in Florida's precipitation chemistry.

- Over the 3-year period evaluated, the data and analyses indicate a north-south gradient in observed concentration and deposition patterns of acidity and related parameters in Florida. However, this gradient is not uniform, especially throughout the panhandle and northern peninsula of Florida. Statistically significant differences were found among sites, with the highest concentrations and depositions of $H^+$ and $NO_3^-$ observed at Sites 2, 5, and 8. For $SO_4^{-2}$, the highest significantly different concentrations were observed at Sites 5 and 8, and the highest significantly different depositions were observed at

Sites 2, 5, and 8. The lowest concentrations and depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$ were observed at Sites 9 and 13 located in the southern peninsula of Florida. The observed pattern appears to be somewhat influenced by meteorology and site location.

- Ambient air concentrations of particulate $SO_4^{-2}$, $HNO_3$, $SO_2$, and $NO_2$ observed over a 2-year period suggest distinct, and statistically different, spatial patterns. A statistically significant pattern in concentrations of particulate $SO_4^{-2}$ and $HNO_3$ was observed and indicated a north-south gradient in these acid precursors of $SO_4^{-2}$ and $NO_3^-$ in precipitation. Ambient $SO_2$ and $NO_2$ concentrations were not uniform, suggesting influences from local sources superimposed on a north-south gradient.

- Differences in seasonal concentrations and depositions were observed over the 3-year period. Summer (April through September) was generally significantly (about a factor of 2) higher than winter (October through March) in both concentrations and depositions of $H^+$, $SO_4^{-2}$, and $NO_3^-$. These differences were greater for sites located in the panhandle and northern peninsula than for sites located in the southern peninsula. Rainfall amount, which is higher in the summer, appears to influence this seasonal variability.

- Data from the mid-1970s suggest that acidity in Florida has not increased during the last 10 years. Data on acidic deposition in Florida prior to the mid-1970s are not sufficient to draw definitive conclusions regarding trends.

- During the 3 years analyzed, concentration and deposition of laboratory $H^+$ and excess $SO_4^{-2}$ decreased in the panhandle and northern peninsula of Florida by 30 percent and 20 percent, respectively. This decrease was statistically significant between the first and third years. For sites located in the southern peninsula, the decrease in laboratory $H^+$ and excess $SO_4^{-2}$ was less than that observed for the more northern sites. Concentrations and depositions of $NO_3^-$ remained relatively constant over the 3-year period with no statistically significant differences observed.

- The variability in Florida's rainfall acidity is closely related to the concentrations of excess $SO_4^{-2}$, $NO_3^-$, $NH_4^+$, and excess $Ca^{+2}$. Excess $SO_4^{-2}$ was found to be the most important rainfall parameter in accounting for the variability in acidity, and excess $Ca^{+2}$ or $NH_4^+$ was the second most important. $NO_3^-$ was typically the least important parameter. These relationships were found to be site-specific.

- Statistically significant relationships were obtained between rainfall amount and laboratory $H^+$, excess $SO_4^{-2}$, $NO_3^-$, and excess $Ca^{+2}$. Concentrations of these parameters were found to decay rapidly with increasing precipitation amount.

- The potential acids and bases contributing to net rainfall acidity were found to vary as a function of parameter and site location. Excess $SO_4^{-2}$ as $H_2SO_4$ and $NO_3^-$ (as $HNO_3$) were found to contribute about 2/3 and 1/3 of the total potential acidity, respectively. Excess $SO_4^{-2}$ became a decreasingly important contributor to acidity from north to south, whereas the reverse was observed for $NO_3^-$. The importance of $NH_4^+$ and excess $Ca^{+2}$ as potential bases increased from north to south. $NH_4^+$ was slighly higher in importance as a base than excess $Ca^{+2}$ for north Florida, whereas excess $Ca^{+2}$ was more important than $NH_4^+$ for south Florida.

- Precipitation and ambient air chemistry was found to vary as a function of synopotic meteorological conditions. The observations were not uniform across the state, suggesting that different meteorological conditions influence precipitation and air chemistry differently across the state.

## 6.2 EFFECTS

- Significant biological effects are not likely to occur in Florida lakes unless lakewater pH levels are depressed below approximately pH 4.0. As a general class, lakes with the greatest likelihood for becoming acidified to these levels or below are seepage lakes which, by definition, have hydrologic budgets dominated by precipitation directly to the lake surface. Seepage lakes potentially sensitive to acidic deposition may be further defined as those with (1) extremely dilute lakewaters with low ANC and DOC, and (2) watershed soils dominated by low CEC, low base saturation, and minimal ability to adsorb sulfate. Current estimates indicate an upper-limit estimate of approximately 2,000 out of Florida's 7,600 lakes are seepage lakes.

- The NLS conducted by EPA estimates that approximately 50 percent of the seepage lakes located in Florida and southeast Georgia are relatively colored. Organic acids (which impart the yellow-brown color characteristic of colored waters) can contribute measurably to the pH and ANC regime of softwater lakes and, if present in sufficient quantities, will constitute the predominant buffering system. The magnitude of the effect of organic acids on lakewater pH depends on (1) the amount of DOC derived from decaying vegatation in the watershed exported to the lake, and (2) the degree of neutralization of DOC inputs as a result of ion exchange and weathering reactions with watershed soils and lake sediments. In addition, organic acids can modify lake sensitivity to acidic deposition by forming stable complexes with aluminum and reducing its toxicity to aquatic organisms. The magnitude of these effects in Florida lakes, however, is virtually unknown and requires further analysis.

- Watershed influences (via ground water or seepage inputs) are important contributors to the ion balance and chemistry of seepage lakes although the hydrologic influence is generally small (approximately 10 percent). The amount of seepage to seepage lakes in general is governed by the difference between evaporation and precipitation. Lakes characterized by greater differences in evaporation and precipitation generally receive more inseepage and thus more ANC from the watershed compared to lakes which receive greater amount of precipitation.

- Internal or biogeochemical processes resulting in the removal of $H^+$, $SO_4^{-2}$, $NO_3^-$, and $NH_4^+$ also appear to contribute significantly to the ANC and pH dynamics of seepage lakes. The extent and rate at which seepage lakes may be influenced by rainfall pH thus integrates in-lake processes, hydrologic, and watershed factors as well as deposition.

- The seepage lakes likely to be most susceptible to acidic deposition are located in the western highlands of the panhandle and the highlands of north-central Florida. This perceived differential in sensitivity reflects several factors:

  1. Total (wet) deposition of $H^+$ and the potentially acid specie $NH_4^+$ in the panhandle and north-central Florida exceeds total deposition in south-central Florida by 60 percent or more.

2. Atmospheric deposition of fine calcareous particles is hypothesized to be a relatively more significant source of acid neutralization in south-central Florida compared to more northern portions of the state.

3. Regional gradients in precipitation and evaporation suggest that ground water inputs constitute a less significant fraction of the hydrologic budget of seepage lakes in the panhandle compared to south-central Florida. This implies comparatively lower ANC contributions from the watershed in panhandle lakes. Lakes in north-central Florida are expected to have ground water inputs intermediate between panhandle and south-central Florida lakes.

4. Preliminary survey results indicate that DOC (or organic acid) and ANC concentrations are lower in panhandle seepage lakes compared to south-central Florida seepage lakes. Results are currently not available for north-central Florida lakes.

- Limited historical data suggest that changes symptomatic of progressive lake acidification may have occurred in several clear and relatively undisturbed seepage lakes in north-central Florida. Apparent declines in ANC and pH accompanied by concommitant increases in nonmarine sulfate have been noted. However, the actual significance of these apparent historical trends is uncertain for several reasons. For each of these parameters, the magnitude of the change is rather small and approximates the limits of analytical uncertainty. Differences in analytical techniques for sulfate and ANC that have evolved with time are biased toward overestimation of any apparent historical change in concentration of these constituents. The influence of changes in lake levels due to normal variations in precipitation is also unclear.

- Several surveys of a limited number of Florida lakes indicate that the diversity (or numbers of species) of phytoplankton, zooplankton, and macrophytes is correlated with pH; i.e., lakes with higher pH tend to have greater diversity of these organisms compared to more acidic lakes. These correlations infer that, for a particular lake, some reduction in diversity is likely to occur with a reduction in lakewater pH. Based on similar evidence, minor declines in the numbers of species of Florida fish are probable with reductions in surface water pH to approximately 4.0. Limited acute toxicity studies indicate significant biological effects are not likely occur in Florida lakes unless lakewater pH levels are depressed below approximately pH 4.0. However, the limited availability of appropriate data necessitates further research before the biotic response to incipient changes in Florida seepage lakewater chemistry attributable to acidic deposition can be conclusively established.

- Certain soils in Florida have limited ability to neutralize acidic inputs. These soils, which predominate in the highlands and ridge physiographic regions of the state, are inherently acidic in nature, resulting from extensive weathering over thousands of years. Thus, at current levels of acidic deposition, increases in acidification of these soils over the next several decades is not likely to be measurable.

- Preliminary evidence has documented declines in growth rates of commercial forests in the southeast. Causes have not been conclusively established and may include drought, pests, disease, management practices, and air pollution including ozone as well as acidic deposition.

- Within Florida over the past decade, net annual growth of pine has increased and is contrasted with the general decline observed in other regions of the southeast. Coincident with increases in growth in Florida has been an observed increase in pine mortality rates which has been attributed principally to diseases such as fusiform rust. It is not possible to predict the potentail effect of acidic deposition on forests in Florida until the reasons for the forest declines in other regions are better understood.

- Current levels of acidity are not likely to have a significant effect on future crop yields in Florida.

- Overall, acidic deposition can potentially increase metal corrosion and materials damage rates; however, the magnitude of these incremental effects might be immeasurably low when the influence of a variety of environmental factors (e.g., humidity, sunlight, sea spray) is taken into account.

- There is little information available to support an estimate of the effects of acidic deposition on exposed cultural materials. The available studies indicate that, under Florida's climatic conditions, current levels of acidic deposition probably cause small, and perhaps unobservable, effects.

## 6.3 SOURCES

- The total anthropogenic statewide $SO_2$ and $NO_x$ emissions, including point and area sources, are approximately 937,000 and 810,000 tons per year (tons/year), respectively. For $SO_2$ emissions, the emissions from point sources contributed 91 percent to the total, with the contribution from utilities accounting for 68 percent of the total emissions. The quantity of $NO_x$ emissions from point sources was 52 percent of total emissions which was similar to the quantity from area sources (48 percent of total $NO_x$ emissions). Utility sources accounted for 32 percent of total $NO_x$ emissions.

- Preliminary results from field monitoring indicate that biogenic sulfur emissions are from approximately 1 to 5 percent of total emissions.

- From ENAMAP modeling, Florida anthropogenic sources were estimated to account for 66 percent of sulfur deposition in Florida, and out-of-state sources were estimated to account for 34 percent. Florida utilities were estimated to account for 44 percent of the sulfur deposition in Florida. Florida sources are not an important contributor to sulfur deposition in any out-of-state region, contributing at most 7 percent of all sulfur deposited in any state, about 2 percent to the southern Appalachians, and less than 1 percent to the Adirondacks.

- Mass-balance modeling indicated that anthropogenic sources located in Florida contribute 50 percent of the $SO_x$ deposition. Utility sources in Florida contribute 35 percent of the $SO_x$ deposition. For $NO_x$, anthropogenic sources in Florida were estimated to contribute 53 percent of $NO_x$ deposition; utility sources in Florida were estimated to contribute 17 percent of total $NO_x$ deposition. There are, however, inherent errors which would directly translate to uncertainties in the calculated contributions. The exact magnitude of individual errors is not known, and their cumulative effect may be quite large.

- Taken together, the ENAMAP and mass-balance modeling results suggest that a major portion of Florida's acidity is attributable to out-of-state sources (about 40 percent). The estimated contribution of Florida utilities to total acidic deposition in Florida is about 30 percent. Area (vehicular) sources and other point sources were estimated to contribute about 15 percent each.

## 6.4 RECOMMENDATIONS FOR FUTURE RESEARCH

The uncertainties associated with this study's findings suggest that the uncertainty in predicting ecological effects is greater than the uncertainty in predicting changes in source attribution which is much greater than the uncertainty in acid deposition measurement. These relative uncertainties suggest that additional information will be necessary to develop more definitive relationships between acidic deposition and sources, particularly as they relate to sensitive ecological resources.

Based on the current knowledge of the acid rain phenomenon in Florida, the following areas of additional studies are suggested to those interested parties that may wish to extend the efforts made by this study:

1. Measurement of wet deposition and ambient air concentrations of acid precursors;
2. Ambient measurement of $NH_3$ and particulate $NH_4^+$;
3. Additional analyses of the monitoring data collected;
4. Biogeochemical and hydrologic processes of seepage lakes (as a minimum, the chemical progress of selected seepage lakes should be monitored); and
5. Forest effects of species found in Florida.