

ACIDITY, NUTRIENTS AND MINERALS IN ATMOSPHERIC PRECIPITATION  
OVER FLORIDA: DEPOSITION PATTERNS, MECHANISMS,  
AND ECOLOGICAL EFFECTS.

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BY

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# TABLE OF CONTENTS

## PAGE

ABSTRACT  
ACKNOWLEDGEMENTS

## SECTIONS

1. SUMMARY OF CONCLUSIONS	1- 1
2. RECOMMENDATIONS	2- 1
3. INTRODUCTION	3- 1
4. NUTRIENT AND MINERAL DEPOSITION BY RAINFALL	4- 1
HISTORICAL NUTRIENT DATA	4- 1
SAMPLING PROCEDURES AND ANALYTICAL METHODS	4- 2
RESULTS AND DISCUSSION	4- 8
NUTRIENTS	4- 9
MAJOR MINERALS	4-28
MINOR MINERALS	4-42
5. THE ACIDITY OF RAINFALL IN FLORIDA	5- 1
EXPERIMENTAL METHODS	5- 1
SPATIAL TRENDS IN ACIDITY AND RELATED PARAMETERS	5- 3
WET, BULK, AND DRY DEPOSITION OF ACIDIC AND BASIC SPECIES	5-31
TEMPORAL PATTERNS IN PRECIPITATION ACIDITY	5-39
SOURCES OF ATMOSPHERIC SULFUR IN FLORIDA	5-47
ACID RAINFALL IN FLORIDA: A PERSPECTIVE	5-52
6. EFFECTS OF ACIDIFICATION ON FRESHWATER LAKES IN FLORIDA	6- 1
PREVIOUS STUDIES ON EFFECTS OF ACID PRECIPITATION ON	
AQUATIC ECOSYSTEMS	6- 1
DESCRIPTION OF THE STUDY REGIONS AND LAKES	6-19
SAMPLING AND ANALYTICAL METHODS	6- 19
RESULTS OF LAKE STUDY: WATER CHEMISTRY	6-22
RESULTS OF LAKE SURVEY: BIOLOGICAL COMMUNITIES	6-36
PHYTOPLANKTON AND CHLOROPHYLL A	6-36
ZOOPLANKTON	6-48
BENTHIC INVERTEBRATES	6-67
FISH	6-83

PAGE

7. REFERENCES

7- 1

APPENDICES

A-1

APPENDIX I ANALYTICAL METHODS

A-1

APPENDIX II VOLUME-WEIGHTED MEAN CONCENTRATIONS AND  
ANNUAL DEPOSITION RATES FOR EACH SITE DURING THE  
PROJECT PERIOD

A-3



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## ABSTRACT

Nitrogen deposition via atmospheric precipitation averaged  $0.75 \text{ g/m}^2\text{-yr}$  (range = 0.32-1.13) at 24 sampling sites over the state of Florida during the one year period May 1, 1978 to April 30, 1979. Comparable values for total phosphorus are 17-111 and  $50 \text{ mg P/m}^2\text{-yr}$ . Highest deposition rates occurred in agricultural areas and lowest rates in coastal and forested areas. Concentrations of N and P forms were higher in summer (convective) rains than in winter (frontal) events. Wet-only input accounted for 68 and 81% of the total (wet plus dry) deposition of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$ , but dry fallout was more important for organic nitrogen (53% of total input) and especially for phosphorus (80% of total input). Inorganic forms [ $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , soluble reactive (ortho) phosphate] accounted for most of the nitrogen and phosphorus in rainfall. Statewide deposition rates of nitrogen and phosphorus are below the loading rates associated with eutrophication and water quality degradation. The average nitrogen loading from bulk precipitation approached the "permissible" loading criterion of Vollenweider, and both nitrogen and phosphorus loadings exceeded permissible loading criteria at a few agricultural sites. Whereas the atmosphere is an important source of nitrogen for nutrient budget purposes, it is less so for phosphorus, especially if dry fallout of locally-derived dust particles is not considered.

The acidity of rainfall in Florida has increased markedly in the past 25 years, and average concentrations of nitrate and sulfate have risen correspondingly. Annual average pH values less than 4.7 now occur over the northern two-thirds of the state, and all but the extreme southern areas of

the state have acidic rainfall. Summer rainfall has average pH values 0.2-0.3 units lower than winter rainfall; excess sulfate concentrations are higher at most sites during summer. Sulfuric acid accounts for about 70% of the observed acidity and nitric acid accounts for the remainder. The spatial variation in hydrogen ion content of Florida bulk precipitation was accounted for by the following two variable regression model:

$$[H^+] = 6.1 + 0.54 [SO_4^{2-}]_{xs} - 0.35 [Ca^{2+}]_{xs}, R^2 = 0.75$$

where subscript xs refers to nonmarine-derived material. Ammonium and nitrate ions are more evenly distributed (geographically), and do not account for the observed spatial trends in acidity. Local (within-state) emissions of  $SO_2$  (and  $NO_x$ ) seem to control the acidity of Florida rainfall. The annual deposition of  $H^+$  is about 250-500 equivalents per hectare over the interior portions of northern Florida; this range is about one-third to one-half the deposition rate for  $H^+$  over the northeastern United States.

The pH levels of softwater lakes in north-central Florida have declined by up to 0.5 units over the past 20 years; no changes have been observed in softwater lakes of south-central Florida. Aluminum levels increase with decreasing pH, but maximum levels found (100-150  $\mu g/L$ ) probably are not high enough to cause fish toxicity problems. A trend of decreasing chlorophyll a with decreasing pH was observed in a survey of 20 softwater lakes; total phosphate levels also decreased with decreasing pH, but this trend does not entirely explain the pH-chlorophyll a trend. The major change in phytoplankton populations with change in pH was a replacement of blue-green algae by green algae under acidic conditions. Species numbers and phytoplankton abundance also declined with decreasing pH, but the data set exhibited much scatter. Although trends were noted in zooplankton and benthic invertebrate populations along a pH gradient, both species composition and total abundance

trends were relatively subtle. Results indicate that acidic conditions (as low as pH 4.6-4.7) do not have major impacts on community structure in Florida lakes.



## CHAPTER 1. SUMMARY AND CONCLUSIONS

The results of this project can be summarized into the following major conclusions. For details on the findings and the facts on which they are based, the reader is referred to the main body of the report (Chapters 4 to 6).

### ATMOSPHERIC LOADINGS OF NUTRIENTS AND MINERALS

1. Bulk precipitation is an important source of nitrogen for both terrestrial and aquatic systems. Average annual loadings of total nitrogen\* for 24 sampling sites in Florida ranged from 0.3 to 1.1 g/m<sup>2</sup>-yr during the study period, with a grand (statewide) mean of 0.75 g/m<sup>2</sup>-yr. About 70% of the nitrogen was in inorganic forms (ammonium and nitrate) that are readily available for plant growth. Deposition rates were highest in rural agricultural areas (0.88 g/m<sup>2</sup>-yr) and lowest in coastal areas (0.58 g/m<sup>2</sup>-yr).

2. Concentrations of all nitrogen forms in bulk precipitation were higher in summer convective showers than in winter frontal rains; statewide ratios of summer/winter concentrations ranged from 1.4 (nitrate) to 1.9 (ammonium and organic N). These results reflect a combination of higher biogenic emissions from soils during warmer weather, greater fixation of NO<sub>2</sub> by lightning in summer, and more efficient washout by turbulent convective showers.

3. Wet deposition (rainfall) accounted for about 70% of the total inorganic nitrogen in bulk precipitation but only about 50% of the organic N deposition. The balance represents dry fallout of particulate nitrogen forms.

4. Few data are available for historical comparisons, but available

data suggest that the mean concentration of inorganic nitrogen forms in wet-only precipitation has increased about three-fold in Florida over the past 20 years.

5. In comparison with critical nitrogen loading rates for lake eutrophication, the annual deposition of total N at all 24 collection sites were below the values associated with eutrophic conditions (assuming nitrogen ~~were~~ <sup>was</sup> the limiting nutrient). The statewide average deposition rate was about 75% of the "permissible" loading rate for shallow lakes suggested by Vollenweider (1968); deposition rates for several agricultural locations slightly exceeded the permissible criterion but none approached the eutrophic loading criterion.

6. Bulk precipitation has significant levels of total phosphate; the statewide annual average was 38  $\mu\text{g/L}$ , and the mean deposition rate was 50  $\text{mg P/m}^2\text{-yr}$ . On a concentration basis, summer rains had about 1.5 times as much phosphate as winter rains. Land use had an important effect on atmospheric deposition rates for total phosphorus. Rural (non-agricultural) and coastal sites had the lowest rates (27 and 31  $\text{mg P/m}^2\text{-yr}$ , respectively), and agricultural sites had the highest rates (66  $\text{mg/m}^2\text{-yr}$ ).

7. Whereas most of the total atmospheric deposition of inorganic nitrogen comes down in rainfall rather than dry fallout of particulate matter, the opposite is true for phosphorus. At four sites with separate wet-fall/dry-fall collectors, wet deposition accounted for an average of 63 percent of the deposition of total nitrogen, but it accounted for only 20% of the deposition of total phosphorus. Thus, most of the phosphorus in bulk precipitation is dry fallout, presumably of wind-blown particles of dust and soil. These particles probably are large, are not transported large distances ~~and~~ <sup>and</sup> thus do not

represent a source of new phosphorus for terrestrial ecosystems.

8. The statewide bulk deposition of total phosphorus is only one half the permissible loading rate for the lakes that are most vulnerable to eutrophication (shallow lakes with long hydraulic residence times). In most areas of Florida, bulk precipitation supplies only about 12-16% of the loading required to induce eutrophic conditions.

9. Sodium and chloride concentrations are highly correlated in Florida rainfall and occur at Cl/Na ratios near that for seawater (1.8). Concentration isopleths for both ions follow the outline of the peninsula, with values increasing toward the coast. Seasalt is the major (and likely the only significant) source of these ions in Florida rainfall.

10. Average sulfate concentrations in rainfall ranged from about 0.4 to 1.2 mg/L (as S), and about two thirds of the total deposition of sulfate was by rainfall. Deposition rates ranged from 7 to 11 kg S/ha-yr, indicating that the atmosphere serves as a significant source of sulfur to soils in Florida.

#### ACIDITY OF PRECIPITATION

1. Rainfall throughout Florida is acidic, with average values for all but a few stations in south Florida being less than geochemical neutrality (pH ~5.7). Single rainfall events as low as pH 3.9 have been measured at Gainesville, and the lowest pH of a bulk precipitation sample (collected weekly or biweekly) was 3.73 (at Jay in the western panhandle during August of 1978).

2. A definite geographic pattern exists for acid deposition in the state; mean annual pH values (volume-weighted) for 1978-79 were around 4.6-4.7 throughout the panhandle and northern two-thirds of the peninsula. Mean

annual values south of Lake Okeechobee were around 5.0 or above.

3. Neutralization of bulk precipitation was found for coastal sites, but wet-only precipitation collected near both the Gulf and Atlantic coasts was approximately as acidic as inland stations of comparable latitude. Partial neutralization of acidity in coastal rain apparently results from dry deposition of alkaline particles containing calcium carbonate of local (terrestrial) origin. Analysis of the ionic composition of coastal bulk precipitation indicates that sea spray is not the agent of neutralization. Sea-salt sulfate levels were only modestly elevated compared to inland bulk precipitation, and the calculated amount of sea-salt calcium carbonate is too low to account for the neutralization.

4. A seasonal pattern was found in precipitation acidity throughout the state, with summertime pH values averaging 0.2-0.3 units lower than wintertime values. Possible reasons for the differences include (1) increased summertime emissions of  $\text{SO}_2$  and  $\text{NO}_x$  (caused in part by seasonal demands for air conditioning), (2) greater thunderstorm activity in summer, resulting in greater fixation of  $\text{NO}_x$  by lightning, (3) enhanced scavenging efficiency of summer convective showers compared to winter frontal storms, and (4) differences in the frequency and size of individual rain events between summer and winter. Further studies are needed to evaluate the importance of some of these factors.

5. Granat-type analysis indicates that about 70% of the rainfall acidity in Florida is derived from sulfuric acid and 30% from nitric acid. A multiple regression equation involving  $[\text{H}^+]$  as the dependent variable and  $[\text{SO}_4^{2-}]_{\text{xs}}$  and  $[\text{Ca}^{2+}]_{\text{xs}}$  as independent variables explained about 75% of the variance in hydrogen ion concentration over the statewide network. The sub-

script xs refers to the fraction of the ions of non-marine origin. Thus the pH of rainfall in Florida primarily reflects the degree to which sulfuric acid has been titrated by terrestrial calcium carbonate.

6. Bulk precipitation throughout northern and central Florida deposited 250-500 equiv  $H^+$ /ha-yr during 1978-79. This represents about one third to one half of the annual deposition of  $H^+$  in the heavily impacted northeastern United States. Comparable values for excess sulfate are 7-11 kg/ha-yr in Florida and ~13 kg/ha-yr in the northeastern U.S. (10 year average for Hubbard Brook, N.H.). Thus Florida ecosystems receive 50-90% of the excess sulfate from the atmosphere as their northern counterparts.

7. Although historical data are lacking on the pH of Florida rainfall, calculated values for rainfall pH during the mid-1950s indicate wet-only precipitation was not acidic then. Moreover, present values of sulfate deposition in northern Florida are up to four times higher than values for the early 1950s. Scattered information for the pH of rainfall at Gainesville are available from 1973 to the present, and no long-term trends are apparent in this record.

8. In spite of the north-south gradient of decreasing rainfall acidity, long-range (interstate) transport of acid precursors is not a wholly satisfactory explanation for acid precipitation in Florida. A substantial portion of the  $H_2SO_4$  and  $HNO_3$  must be derived from in-state emissions of  $SO_2$  and  $NO_x$ , which are widespread and substantial. These conclusions are supported by several lines of evidence, including the fact that summer rainfall throughout the entire state is more acidic than winter rainfall. From a meteorological viewpoint, peninsular Florida is isolated from the rest of the United States during summer. Large-scale weather patterns for the peninsula come from the southeast (Caribbean) or southwest (Gulf of Mexico)



during summer, and cold fronts from the north rarely penetrate the state during this period.

#### EFFECTS OF ACID PRECIPITATION ON FLORIDA LAKES

1. A large number of soft-water lakes occur in the sand-hill highlands region of peninsular Florida. Based on comparison of historical and current data on a group of 12 such lakes in northern Florida and a group of 8 soft-water lakes in south central Florida, pH has decreased by up to about 0.5 units in many of the northern soft-water lakes, whereas no temporal trends could be discerned for the southern group. The northern (Trail Ridge) lakes lie about 40-50 km east of Gainesville in a region receiving rainfall with a (volume-weighted) average annual pH of 4.5-4.7. The southern (Highlands Ridge) lakes lie northwest of Lake Okeechobee, near the current southern terminus of pronounced rainfall acidity. Corresponding decreases in alkalinity and increases in sulfate concentration were observed in the northern lakes.

2. The 20 survey lakes had annual average pH levels ranging from 4.72 to 6.80, but otherwise had generally similar characteristics (soft water, oligotrophic to mesotrophic nutritional conditions). The group thus served as a good data base to evaluate the effects of acid precipitation on vulnerable aquatic ecosystems in Florida.

3. A general trend of increasing aluminum with decreasing pH was found in the 20 Florida lakes. However, maximum values (100-150 µg/L) were below the levels associated with fish toxicity and may explain the occurrence of largemouth bass and several other common game fish species in lakes with pH values below 5.0.

4. A general trend of increasing chlorophyll a concentration with in-

creasing pH was found. However, total phosphate concentration also tended to rise with pH. The trend of greater oligotrophic conditions in more acidic lakes may be caused by lower rates of nutrient cycling at lower pH, or it may reflect watershed nutrient loading factors that just happened to correlate with lake pH. Further studies are needed on this point.

5. The number of phytoplankton species and their abundance in a lake decreased with increasing acidity, but much scatter occurred for both parameters. Although the data are fairly limited, a trend of increasing phytoplankton abundance with increasing pH was found for a series of lakes with similar levels of phosphate. The lake survey also indicated that species composition varied along a pH gradient, with green algae replacing blue-greens at low pH. In lakes with pH values of 4.5-5.0, 60% of the algae were green (Chlorophyta), and 25% were blue-green (Cyanophyta). Corresponding values for lakes in the pH range 6.5-7.0 were 31% green algae, 63% blue-green algae.

6. Similar trends were found in the zooplankton, i.e. a significant decrease with pH; the trend exhibited considerable scatter. In general, the number of zooplankton species found at a given pH was greater than the number found in temperate lakes of comparable pH. Six species of zooplankton were dominant at all pH levels, and five other species were always present but never dominant. Two types of multivariate analysis (principal component and cluster analysis) showed that the zooplankton populations could be grouped along pH gradients, but the population differences with pH are relatively subtle. Rare species showed greater differences with pH than did common species.

7. No clear trends were seen in either the diversity or the abundance of benthic invertebrates with pH, and the differences that were found among the lakes may reflect differences in trophic conditions more than direct effects of pH.

8. Limited information has been obtained on fish population<sup>s</sup> in acidic Florida lakes. No species replacement or disappearance trends were found. Condition factors relating weight and length indicated that the fish in acidic lakes are in poorer condition than those in less acidic lakes, possibly reflecting decreased availability of food in acidic lakes. Breeding populations are still being maintained in the most acidic lakes. No evidence of gill necrosis was found in any fish, reflecting the relatively low concentrations of aluminum in the lakes.

## CHAPTER 2. RECOMMENDATIONS

This project has resulted in a thorough characterization of the role of atmospheric precipitation as a source of nutrients and minerals. The assembled data base will be useful as a benchmark for future conditions and as input to local and regional-scale nutrient budgets. A few questions remain unresolved with regard to atmospheric sources of nutrients, and further work should be done to address these.

This size distribution of atmospheric phosphate particles should be determined, and work should be done to characterize the chemical form of phosphate in these particles. This information will be useful to clarify questions regarding the atmospheric residence time of suspended phosphate and the distance that such particles travel in the air. Such information is necessary to determine whether the enhanced collection of phosphate in bulk precipitation (compared to wet-only precipitation) represents a new (external) source of phosphate for a given site or merely is part of an internal cycle of wind-induced suspension and particle deposition in the immediate vicinity of a bulk precipitation collector.

Regarding atmospheric deposition of nitrogen, further studies should focus on rates of gaseous deposition (i.e.  $\text{NH}_3$  and  $\text{NO}_2$  uptake by plant, soil and water surfaces). These processes were found to make large contributions to a mass balance model of nitrogen in peninsular Florida (Messer and Brezonik 1980 a,b), but these models calculated gaseous deposition using literature values for deposition velocities and measured levels of these gases in the atmosphere of Florida. Direct measurements of  $\text{NH}_3$  and  $\text{NO}_2$  deposition need to be done under a variety of meteorological conditions and

for a variety of land use and vegetation types. Such work is difficult and time-consuming, but it is necessary to evaluate the model calculations. Further measurements of ambient  $\text{NH}_3$  and  $\text{NO}_2$  concentrations in rural and coastal areas also are needed to refine model calculations.

The acidity of rainfall in Florida has been well documented by this project (e.g. Brezonik et al. 1980). Continued monitoring of pH and associated parameters in rainfall should be undertaken on a network of sampling stations around the state. Such information is needed to determine temporal changes in the severity of the problem at a given site and to determine changes in geographic distribution (e.g. the spread further southward of rainfall acidity). Because Florida's population is still increasing at a rapid rate, demands for electric power and fossil fuel consumption are increasing more rapidly than in most other states. The shift to coal-fired power plants that is occurring in Florida (as in the rest of the United States) is further reason for continued careful monitoring of rainfall. The source of acidity in Florida precipitation has not been resolved completely, although evidence presented in this report indicates that emissions of  $\text{SO}_2$  and  $\text{NO}_x$  within the state are largely responsible. Large-scale modeling and field-measurement studies on acid precursors will be needed to refine estimates of long-distance transport into the state.

The lake studies conducted as part of this project have described the effects of increased acidity on community structure in softwater lakes. Further studies should emphasize the effects of pH changes on metabolic processes--nutrient cycling and productivity in these lakes. The effects of acidification on fish populations need to be quantified. Reasons for the relatively low concentrations of aluminum in acidic Florida lakes should



be determined. Virtually nothing is known about the effects of acid rainfall on the sandy, poorly-buffered soils commonly occurring in Florida. Studies should be undertaken on the effects of acid rainfall on soil chemistry and soil microbiology. Studies on effects of acid precipitation on agricultural crops in Florida (e.g. citrus, pine forest, vegetables, sugar cane) should be conducted. These studies would focus on direct effects of air-borne acid impacting upon the foliage and fruit of such vegetation during various pahses of their growth cycle and indirect effects which could occur with soil acidification. Finally, holistic watershed-level studies need to be undertaken to determine the relationship between acidic inputs to the poorly buffered soils of Florida and the movement of acidity related substances into ~~Lake~~<sup>L</sup> and streams.

### CHAPTER 3 INTRODUCTION

The chemistry of rainfall has been studied for over a century, but many questions remain about its importance in biogeochemical cycles and in transport of pollutants from the atmosphere to terrestrial and aquatic ecosystems. Because the nitrogen cycle involves several volatile or gaseous compounds, the importance of atmospheric reactions and transfers in this cycle has been recognized for a long time. Measurements of the inorganic nitrogen content of rainfall date back to the late 19th century. Much less information is available on levels of organic nitrogen and other "rock-bound" nutrients (e.g. phosphorus) in rainfall. Moreover, information in the literature exhibits a wide variation in concentrations of nutrients both spatially and temporally in rainfall. Causes for this variability are not explained in the literature.

The role of rainfall as a transport mechanism for various pollutants such as heavy metals and acidity has been recognized in recent years, and a considerable volume of data has been assembled on the pH of rainfall in Scandinavia and the northeastern United States. The deleterious effects of acid rainfall on aquatic systems in temperate climates also has been documented. Analysis of geographic and long-term temporal trends in acid precipitation indicates that acid precipitation is a potentially very serious environmental problem of international magnitude. Previous acid rainfall studies in the United States have been skewed geographically to the Northeast, where the problem apparently is most severe. Little information is available on the extent of the problem in other areas, such as the Southeast. Edaphic conditions in their region, and especially in Florida, suggest a high susceptibility

for deleterious ecological effects, and demographic patterns suggest that this region may experience increasingly acidic precipitation in the future.

Information on the role of other atmospheric deposition processes, namely particulate and gas deposition, in nutrient and pollutant transport is much less-definitive. The project that this report summarizes was undertaken to evaluate the role of atmospheric deposition processes in the transport of nutrients, minerals, and certain pollutants (primarily acidity) to the earth's surface.

Most of the results presented in this report are based on two large scale field studies. The first, a statewide sampling network for bulk and wet-only precipitation, was used to evaluate the importance of rainfall and dry fallout as sources of nutrients, minerals, and acidity to Florida ecosystems. The network was established to allow analysis of the influence of surrounding land-use patterns on deposition rates of these substances; samplers were located in urban, agricultural, forested, coastal, and pristine areas. Transects were established to evaluate north-south and east-west (coastal-inland) gradients in deposition patterns. Details of the sampling procedures and results are presented in Chapters 4 and 5. The network provided valuable information on nutrient and mineral deposition patterns (Chapter 4), and yielded the first comprehensive analysis of the acid rainfall problem in the state of Florida (Chapter 5).

The second field effort involved a sampling program on 20 softwater lakes in north-central and south-central Florida. Routine limnological measurements, complete chemical analysis, and analysis of the biota were done on each lake to evaluate the effects of acidification on Florida lakes. Phytoplankton, zooplankton and benthic invertebrate communities were analyzed for species diversity and abundance; results of the lake studies are presented in Chapter 6.

Two other aspects of atmospheric deposition processes were studied during

this project but are not presented in this report. The importance of gas ( $\text{NH}_3$  and  $\text{NO}_2$ ) deposition in the cycling of nitrogen was evaluated by means of a mass balance model of nitrogen in peninsular Florida. The results of this model are presented elsewhere (Messer and Brezonik 1980 a,b), and they indicate that these processes may be major sources of nitrogen to terrestrial and aquatic ecosystems in Florida. Field studies are underway to verify the deposition fluxes calculated in the mass balance model.

The trace heavy metal content of bulk precipitation and within-storm variability on the heavy metal content of rainfall also were determined during this project. In a related project, deposition patterns were determined for various heavy metals in sediments of ten lakes sampled as part of the survey on acidification effects. Results of the trace metal studies are still being assembled for a thesis and will be published separately.

## CHAPTER 4. NUTRIENT AND MINERAL DEPOSITION BY RAINFALL

The primary purpose of this phase of the study was to evaluate the role of precipitation as a source of nutrients to aquatic and terrestrial ecosystems in Florida. Emphasis was placed on nitrogen and phosphorus forms, but all major minerals were measured in rainfall, and results are presented here for deposition of mineral ions, as well. A number of studies have reported on the chemical composition of precipitation in Florida; however, most of the studies had limited objectives and involved only a few parameters, a few sampling locations, or short sampling periods. Comprehensive data on the chemical composition of rainfall in Florida thus are lacking. The most important previous studies are described below.

### HISTORICAL NUTRIENT DATA

Junge (1958) and Junge and Werby (1958) reported on the major ion content (including  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) of wet-only rainfall collected during 1955-56 at four Florida locations (Tallahassee, Tampa, West Palm Beach, and Jacksonville), as part of a nationwide study of precipitation chemistry. A second national sampling network (Lodge et al. 1969) existed from 1960 to 1966 and reported data on major ions, inorganic N, and trace metals in wet-only precipitation for a station in Tampa.

The nutrient content (i.e. nitrogen and phosphorus forms) of Florida rainfall has been measured by a number of investigators in various Florida locations over the past decade, primarily in relation to efforts to determine nutrient budgets for lakes in eutrophication studies. Brezonik et al. (1969) measured inorganic and organic N and P in bulk precipitation collected during 1968 at a rural site 40 km east of Gainesville and computed atmospheric loadings to several isolated, pristine lakes in that area. Nutrient budget studies (Joyner 1971) on Lake Okeechobee, the largest lake in Florida, yielded



data on bulk precipitation collected near the lake during 1969.

Nutrient budget and mineral cycling studies on a mixed hardwood forest (Ewel et al. 1976) and cypress wetlands (Bourne 1976; Hendry 1977) included nutrient measurements on rainfall in the north central Florida area. Gaggiani and Lamonds (1978) and Burton et al. (1978) studied the effects of highway construction on nutrient inputs to lakes in Orlando and Tallahassee, and both studies included nutrient measurements on rainfall. Lamonds and Merritt (1976) determined the nutrient content of bulk precipitation at two sites along the proposed cross-Florida Barge Canal (central Florida) during 1975. Mattraw and Sherwood (1977) conducted urban runoff studies in the Fort Lauderdale area and reported nutrient analyses of rainfall collected in that area. Finally, rainwater samples were collected over South Florida during the 1973 Florida Area Cumulus Experiment (Wisniewski and Cotton (1978)). These samples were collected both at the ground surface and by aircraft at the cloud-base level (600m). The historical data on nutrients in Florida precipitation are summarized in Table 4-1; in general, the various studies show large variability. Because of the large number of different locations and short sampling periods involved in these studies, it is difficult to infer trends. However, recent data for wet-only precipitation indicate that there has been a substantial (three-fold) increase in inorganic nitrogen levels compared to those found 25 years ago (Junge 1958).

#### SAMPLING PROCEDURES AND ANALYTICAL METHODS

##### A. Precipitation Monitoring Network.

In order to assess the regional variations in atmospheric fluxes of nutrients to lakes and soils, a statewide precipitation monitoring network was established in fall of 1977. The network consisted of 24 collection stations from Jay in the panhandle near Pensacola, to Bahia Honda in the lower Keys. The locations of the sampling sites in the Florida Atmospheric Deposition

*united!*

Reference	Collection Period	Location(s)	Sampler Type <sup>1</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	TIN	TON	TN	Ortho P	Total P
Junge (1958)	1955-56	Tallahassee W. Palm Beach Jacksonville	W	40	50	90				
Lodge et. al. (1968)	1960-66	Tampa	W			80				
Brezonik et. al. (1969)	1968	rural north- central Fla.	B	80	120	200	180	380	12	29
Joyner (1971)	1969	Moore Haven	B	260	120	380	310	690	23	40
Schneider et. al. (1969)	1969	Winter Garden	B	180	180		160	430		59
Ewel et. al. (1976)	1971-73	rural north- central Fla.	B							100
Wisniewski and Cotton (1978)	1973	rural south Fla.	B	150	150	300				
		south Fla.	C	230	180	410				
		Miami	B	280	260	540				
Gaggiani and Lamonds (1978)	1972-74	Orlando	B	640	340	980	560	1540	100	140
Bourne (1976)	1974	Gainesville	B	200	100	300	250	550	50	150
Mattraw and Sherwood (1977)	1974-75	Fort Lauderdale	B	120	270	390	130	520	17	26
Burton et. al. (1978)	1974-75	Tallahassee	B	170	290	460			17	37
			W	110	190	300			5	29

Table 4-1. (Continued)

Reference	Collection Period	Location(s)	Sampler Type <sup>1</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	TIN	TON	TN	Ortho P	Total P
Lamonds and Merrit (1976)	1975	Central Fla.	B	310	210	520	390	910	35	50
Hendry and Brezonik (1980)	1977-79	Gainesville	B	120	230	350	470	820	24	85
			W	100	190	290	410	700	19	34
Ranges			B	80- 640	90- 340	200- 980	160- 560	380- 1540	12- 100	29- 140
			W	40- 110	50- 190	80- 300			5- 19	29- 34

<sup>1</sup> B = Bulk; W = Wet-only; C = Cloud.

Study (FADS) are shown in Figure 4-1. Table 4-2 gives the county in which each station is located, its coordinates and starting date of operation.

The large number of collection sites permit interpretation of the rainfall data in terms of various demographic, land-use, and geographic parameters. Urban and semi-urban sites are represented by Miami, Gainesville, Tallahassee, Jacksonville, and Fort Myers. Rural sites in predominantly forested areas include Bronson, Lake Placid, Corkscrew Swamp, and Waldo. A number of sites are in areas of intensive agriculture: Hastings (potato farms); Lake Alfred, Lake Apopka (citrus); Bradenton (vegetables); Belle Glade, Clewiston (sugar cane); Chipley (chicken farm); and McArthur Farms (dairy cattle). Coastal stations include Cedar Key, Marineland, Stuart, and Bahia Honda Key. Three collection transects were organized within the state so that the distribution and trends in rainfall chemistry could be intensively studied. One transect extends the length of the peninsula from Jasper, near the Georgia border, to Belle Glade, south of Lake Okeechobee. A second transect was established east-west across the northern part of the state (Marineland to Cedar Key), and a third transect consists of a series of collectors (east-west) across south Florida (Stuart to Ft. Myers), with a clustering of sites around Lake Okeechobee. Many of the FADS stations are located at and operated in conjunction with University of Florida agricultural research station that collect climatological data. Twenty stations have collectors designed for bulk precipitation (Likens 1972), and four sites were equipped with automatic Aerochem Metrics Model 101 wet/dry collectors that collect the wet and dry fractions separately. Samples were collected bi-weekly at 20 of the sites either by us or by technicians at the research stations, who measured the rainfall amount over the collection period and mailed the samples to our lab for analysis. Samples at three stations (Jay, Jacksonville, and Miami) were collected weekly, and samples at Gainesville were collected on an event

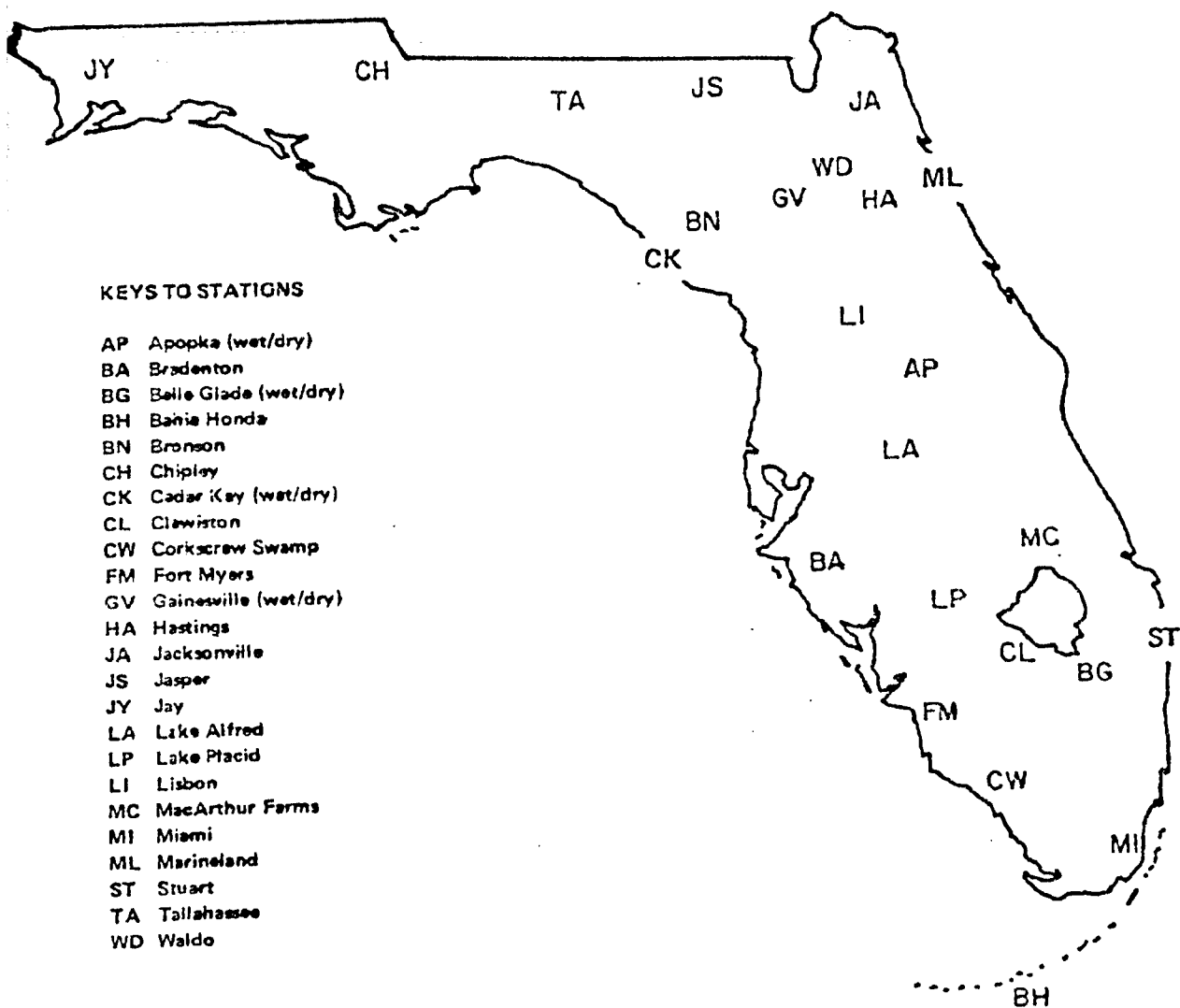


Figure 4-1. Location of sampling stations in the Florida Atmospheric Deposition Study Network.

Table 4-2. Location of Stations in the Florida Atmospheric Deposition Study Network.

Station	County	Coordinates		Starting Date of Operation*
		W	N	
Apopka	Orange	81°30'	28°40'	7/77
Bradenton	Manatee	82°30'	27°30'	3/78
Belle Glade	Palm Beach	80°40'	26°45'	12/77
Bahia Honda	Monroe	81°10'	24°40'	11/77
Bronson	Levy	82°45'	29°30'	12/77
Chipley	Washington	85°30'	30°50'	4/78
Cedar Key	Levy	83°0'	29°10'	12/77
Clewiston	Hendry	81°0'	26°45'	12/77
Corkscrew	Collier	81°40'	26°30'	1/78
Fort Myers	Lee	81°50'	26°45'	11/77
Gainesville	Alachua	82°20'	29°30'	7/76
Hastings	St. Johns	81°30'	29°45'	11/77
Jacksonville	Duval	81°45'	30°30'	8/78
Jasper	Hamilton	82°50'	30°30'	4/78
Jay	Santa Rosa	87°10'	30°45'	4/78
Lake Alfred	Polk	81°50'	28°10'	1/78
Lake Placid	Highlands	81°30'	27°10'	12/77
Lisbon	Lake	81°45'	28°50'	3/77
MacArthur	Okeechobee	80°40'	27°20'	1/78
Miami	Dade	80°15'	25°50'	11/77
Marineland	Flagler	81°10'	29°40'	11/77
Stuart	Martin	80°15'	27°10'	4/78
Tallahassee	Leon	84°15'	30°30'	1/78
Waldo	Alachua	82°15'	29°40'	4/78

\* All stations were sampled until fall of 1979. A modified network consisting of 16 stations sampled weekly is still in operation during 1980.

basis. Dryfall samples were collected by adding 300 <sup>ml</sup> of deionized water to the bucket and scrubbing the bucket with a clean plastic glove to dislodge particulates. Analyses were then run on the rinsings.

## B. Analytical Methods.

Analytical methods for chemical determinations of the precipitation and dryfall samples are summarized in Appendix 1. In general, analyses were performed according to Standard Methods (APHA 1976) and/or the EPA water analysis manual (U.S. EPA 1976). Inorganic nitrogen forms ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) were determined by automated methods on a Technican AutoAnalyzer; soluble reactive phosphate (SRP) (roughly equivalent to orthophosphate) was determined manually with a Beckman Model DBG spectrophotometer and 4-cm cell, using the single reagent colorimetric method. Total Kjeldahl nitrogen and total phosphate were determined by manual (semi-micro) digestion in test tubes, followed by colorimetric analysis for ammonium ion (AutoAnalyzer) and orthophosphate (manually) on the neutralized digestate. Cation analyses were done by flame atomic absorption spectrophotometry following procedures recommended in the instrument manual (Varian, 1973).

## RESULTS AND DISCUSSION

### A. Introduction.

Solute concentrations generally are inversely related to the quantity of rainwater falling during a storm. Computing volume-weighted averaged concentrations tends to equalize the importance of light rains, having relatively high concentrations and heavy rains, in which constituents are more dilute. Volume-weighted concentrations are calculated by:

$$\frac{\sum_{i=1}^n C_i V_i}{\sum_{i=1}^n V_i}$$

where  $C_i$  = constituent concentration (mg/L), and

$V_i$  = rainfall amount (cm).

Summary results of statewide volume-weighted mean concentrations and loadings for major ions and nutrients in bulk precipitation are presented in Table 4-3. Volume-weighted mean concentrations of all parameters at each site and annual depositions are given in Appendix 2. Annual loading rates were calculated by multiplying the volume-weighted concentration for each constituent by the total rainfall over the given time period.

The period, May 1978 through April 1979, represents the first full year during which the entire sampling network was in existence; thus this period was selected for detailed discussion in this report. As shown by Table 4-3, the values of mean concentrations and loadings for this period are close to those found over the entire 2 year study. The month of May also represents the beginning of the summer (rainy) season in Florida, and consequently May is a convenient starting point for an annual study.

## B. NUTRIENTS

The results and discussion of atmospheric deposition of nutrients is divided into six sections: (1) geographical variation of atmospheric fluxes of nitrogen and phosphorus; (2) speciation of the N and P forms in precipitation; (3) seasonal variations in the nutrient content of rain; (4) relative importance of dry fallout and wet deposition as sources of nutrients; (5) comparisons of present concentrations and fluxes with historical data; and (6) examination of the significance of atmospheric nutrient deposition relative to critical loading rates for lake eutrophication.

### 1. GEOGRAPHICAL VARIATION OF NUTRIENT DEPOSITION

#### NITROGEN

Deposition of nitrogen by bulk precipitation at the 24 sites during the period ranged from 0.32 g N/m<sup>2</sup> - yr at Bahia Honda Key to 1.13 g N/m<sup>2</sup> - yr



Table 4-3. Statewide Mean Concentrations and Loadings by Bulk Precipitation for Various Periods during the Two Year Study.

Study Period	<u>5/78-4/79</u>		<u>Calendar 1978</u>		<u>Calendar 1979</u>		<u>Total Study 1978 + 1979</u>	
Number of Samples	595		531		603		1,134	
Number of Bulk Sites	22		21		22		21	
Parameter	Conc. <sup>1</sup>	Loading <sup>2</sup>	Conc.	Loading	Conc.	Loading	Conc.	Loading <sup>3</sup>
Na	1.18	1.49	1.06	1.17	1.37	1.99	1.19	1.58
K	0.21	0.28	0.22	0.27	0.18	0.25	0.18	0.26
Mg	0.16	0.20	0.15	0.17	0.19	0.27	0.16	0.22
Ca	0.65	0.86	0.59	0.72	0.62	0.87	0.58	0.80
SO <sub>4</sub> <sup>2-</sup>	1.81	2.45	1.90	2.43	1.69	2.54	1.75	2.49
CL <sup>-</sup>	2.21	2.80	2.05	2.27	2.55	3.71	2.27	2.99
NH <sub>4</sub> <sup>+</sup> -N	0.18	0.24	0.21	0.27	0.14	0.22	0.17	0.25
NO <sub>3</sub> <sup>-</sup> -N	0.20	0.27	0.23	0.29	0.18	0.27	0.20	0.28
TON	0.17	0.23	0.18	0.23	0.14	0.21	0.16	0.22
SRP	.026	.034	.030	.038	.016	.022	.021	.030
TP	.038	.050	.045	.057	.029	.042	.036	.050

<sup>1</sup> Volume-weighted Mean Concentration; all Values are mg/L.

<sup>2</sup> Loading rates are g/m<sup>2</sup>-yr

<sup>3</sup> Average Annual Loading over the two year period.

at Belle Glade (Figure 4-2A). The Bahia Honda site represents an almost completely maritime regime, while the Belle Glade site is located in the Everglades Agricultural District, a large area of sugar cane plantations and vegetable farms. Mean deposition of nitrogen over all 24 sites was  $0.76 \text{ g N/m}^2\text{-yr}$ .

Brezonik (1976) concluded that bulk precipitation deposits from 1.0 to  $2.0 \text{ g/m}^2\text{-yr}$  of total nitrogen over large areas of the United States, and that deposition rates outside the range of 0.5 to  $3.0 \text{ g/m}^2\text{-yr}$  are likely to occur only under unusual circumstances. Deposition rates across Florida fall in this range (Figure 4-2), except at two pristine sites, Bahia Honda Key as discussed above, and Corkscrew Swamp ( $0.45 \text{ g/m}^2\text{-yr}$ ), a remote Audubon sanctuary, located in the Big Cypress Swamp in south Florida.

Table 4-4 summarizes the mean deposition of TN at the stations grouped according to the dominant land use in the immediate area. Deposition rates were lowest at coastal and non-agricultural rural locations, and highest loadings occurred at sites in dominantly agricultural regions. The latter sites received about 50% more loading of nitrogen than did the coastal sites.

#### PHOSPHORUS

Deposition of total phosphorus by bulk precipitation in Florida (Figure 4-2B) ranged from 17 (Bahia Honda Key) to  $111 \text{ mg P/m}^2\text{-yr}$  (Jasper), with  $51 \text{ mg P/m}^2\text{-yr}$  as the mean for all sites. The site at Jasper is in an area of phosphate mining, and the observed high deposition rate likely reflects the mining activities. In general, highest deposition rates were recorded at agricultural locations, and lowest rates occurred at rural and coastal sites (Table 4-4). Atmospheric deposition of total phosphorus at the former sites was more than double that at the latter sites. According to Chapin and Uttormark (20), atmospheric phosphorus fluxes usually range from 0.1 to  $1.0 \text{ kg/ha-yr}$  (10 to  $100 \text{ mg/m}^2\text{-yr}$ ); the results in Figure 4-2B fall in this range.

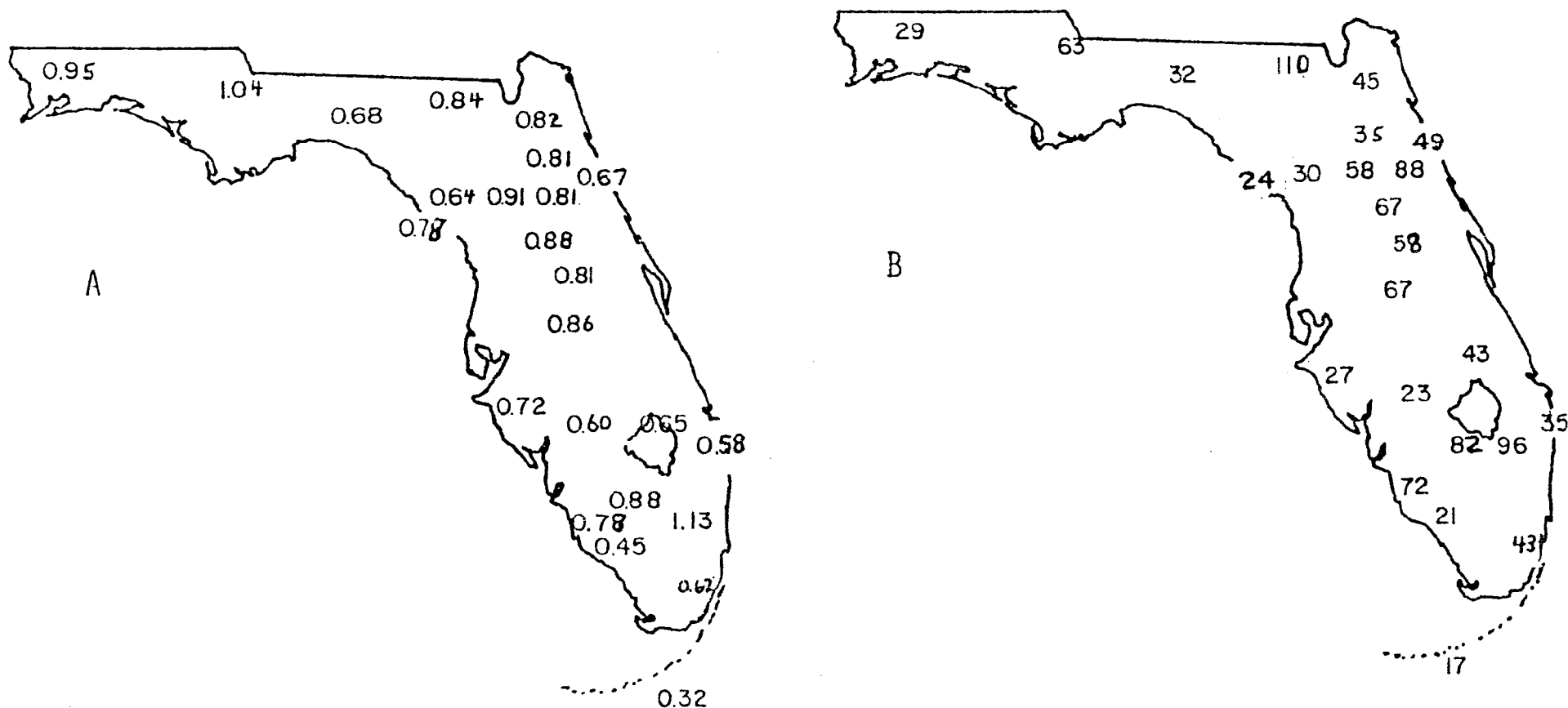


Figure 4-2. (A) Total nitrogen deposition (gN/m<sup>2</sup>-yr) and (B) Total phosphorus deposition (mg P/m<sup>2</sup>-yr) in bulk precipitation across Florida, May, 1978 to April, 1979. At sites equipped with wet/dry collectors the sum of the wet and dry deposition is shown.

Table 4-4 Deposition of total nitrogen and total phosphorus at stations grouped according to dominant land use in the area.

	TN g/m <sup>2</sup> -yr	TP mg/m <sup>2</sup> -yr
Coastal	0.58	31
Urban	0.76	50
Rural (non-agricultural)	0.62	27
Rural (agricultural)	0.88	66
State	0.75	51

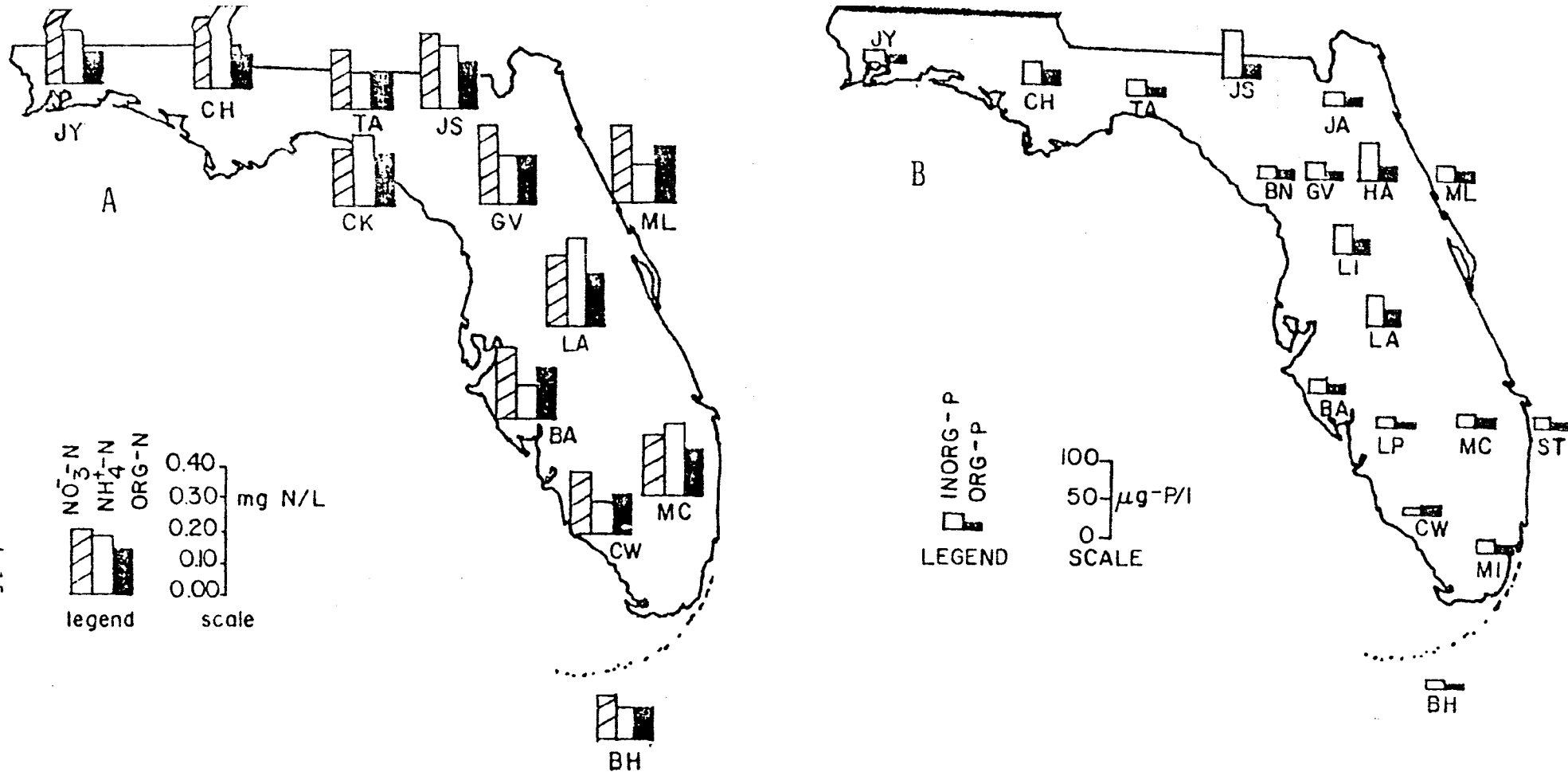


Figure 4-3. (A) Volume-weighted average concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and organic nitrogen and (B) Volume-weighted average concentrations of inorganic and organic phosphorus in bulk precipitation. For clarity, not all sites are shown.

### 3. SEASONAL VARIATIONS IN THE NUTRIENT CONTENT OF PRECIPITATION

#### NITROGEN

Rainfall in Florida generally follows a bimodal seasonal pattern, with most of the rain occurring in the summer and winter months. Summer rainstorms are convective events; winter rains generally are associated with cold fronts moving down the peninsula. Spring and fall generally are dry seasons, and thus it is convenient to compare Florida rainfall chemistry on a summer/winter basis. The summer values are for the months May to October, while the winter values are for November to April. As shown in Table 4-5, concentrations of both inorganic and organic nitrogen are greater in summer (convective) rain storms than in winter (frontal) events. Averaged over all sites, ammonium and TON concentrations in summer rains were almost double the winter levels, and  $\text{NO}_3^-$  and TN were 40 and 70% higher, respectively. The greater concentrations in summer rain may have resulted from three factors: increased biogenic emission of gaseous nitrogen compounds due to higher summer soil temperature; nitrogen fixation by lightning, which frequently is associated with summer storms; and/or more efficient washout of substances in the highly turbulent convective storms.

Plots of monthly (volume-weighted) average concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in bulk precipitation do not show such pronounced seasonal trends as might be expected from the summary data in Table 4-5. Figure 4-4 shows monthly variations in these ions and monthly amounts of rainfall at three sites distributed across the state: Jay (in the northwest corner), Gainesville (in the north central part of the peninsula), and Miami (in southeast Florida). Although concentrations at Jay (Figure 4-4A, and Gainesville (Figure 4-4B) were higher during the summer months than the winter months, highest concentrations occurred in a few samples collected during spring and fall, when there was little rain. These high values likely reflect

Table 4-5. Statewide annual and summer/winter (volume-weighted) mean concentrations of nitrogen and phosphorus in bulk precipitation. All values in  $\mu\text{g/l}$ .

	Annual	Summer	Winter	Ratio: $\frac{\text{Summer}}{\text{Winter}}$
$\text{NH}_4^+-\text{N}$	180	230	120	1.9
$\text{NO}_3^--\text{N}$	200	230	160	1.4
ORG N	170	210	110	1.9
TN	550	670	390	1.7
SRP	26	32	20	1.6
Org P	12	15	10	1.5
TP	38	47	30	1.6

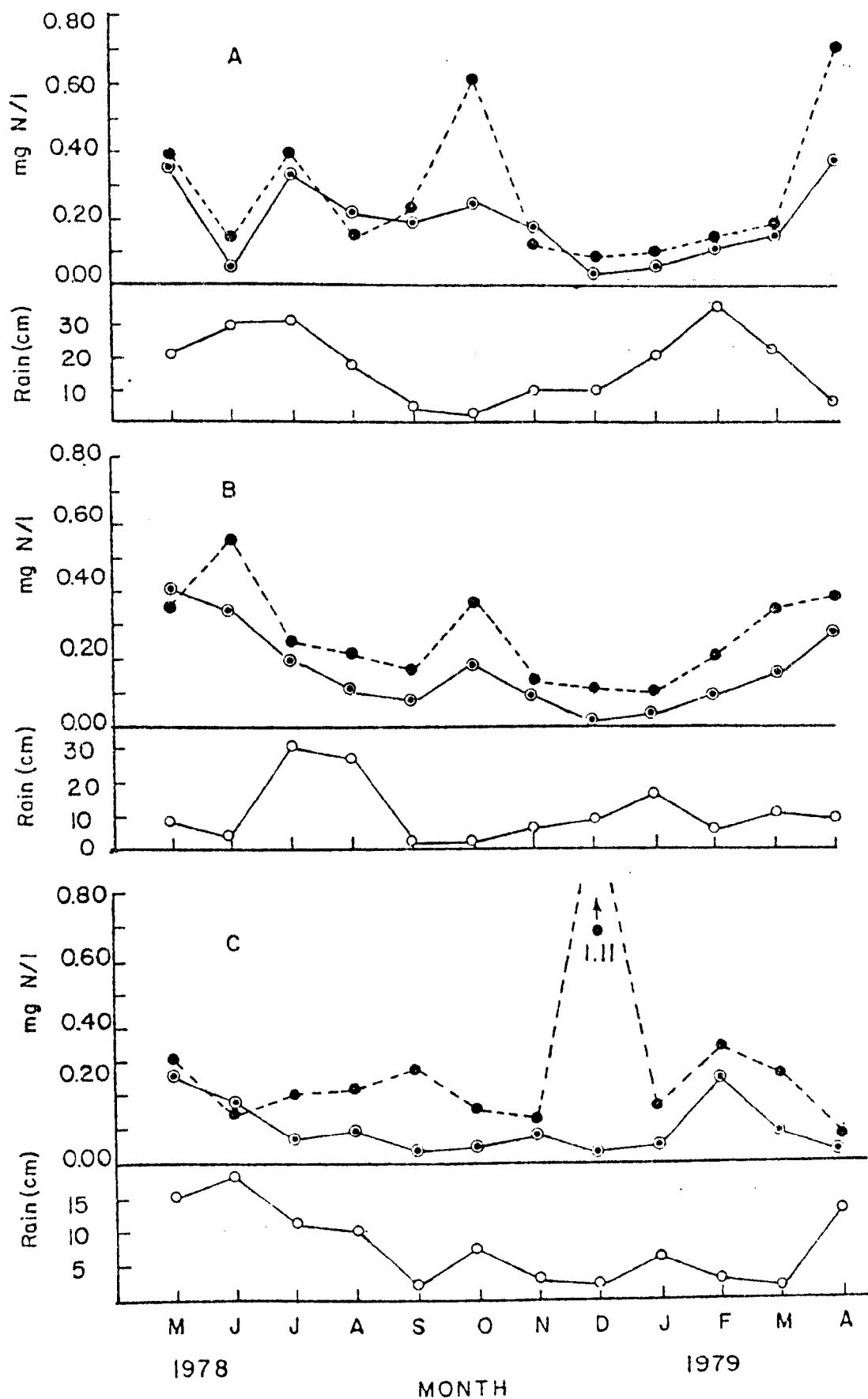


Figure 4-4. Monthly volume-weighted mean concentrations of  $\text{NH}_4^+$  (Solid Line),  $\text{NO}_3^-$  (Dashed Line), and rainfall at Jay (A), Gainesville (B), and Miami (C) from May, 1978 to April, 1979.



atmospheric buildup of contaminants during these dry periods. A seasonal (summer/winter) pattern is not discernable at subtropical Miami (Figure 4-4C), with highest concentrations occurring during the drier months.

#### PHOSPHORUS

As shown in Table 4-5, volume-weighted average concentrations for SRP and ORG-P are 60 and 70% higher, respectively in the summer months compared to the winter months. Monthly plots of SRP and TP for Jay and Gainesville (Figure 4-5A and B) show a pronounced decline in monthly mean values during the winter months (Dec., Jan., Feb.) for both SRP and TP. However, the levels of SRP and TP at Miami (Figure 4-5C) were greatest during these months. As was true for the nitrogen species, the driest months generally had the highest concentrations of both SRP and TP.

#### 4. COMPARISON OF WET VS. DRY DEPOSITION OF NUTRIENTS

##### NITROGEN

Wet/dry collectors yield information concerning the mechanism of deposition for nutrients. Table 4-6 summarizes results for the wet and dry deposition of total nitrogen at the four sites with wet/dry collectors. Mean deposition of TN by wet-only input over all four sites was approximately double the average dryfall input. The highest total deposition occurred at Belle Glade, while the coastal site at Cedar Key had the lowest TN deposition of the four wet/dry sites. The dryfall collector at Belle Glade generally collected the largest amounts of particulate matter among the four sites, especially during fall and winter, when the sugarcane fields were burned prior to harvesting. At these times, the dryfall collector had noticeable amounts of black soot.

The manner in which the forms of nitrogen are partitioned between wet and dry fallout is illustrated in Table 4-7. Deposition of ammonium and ni-

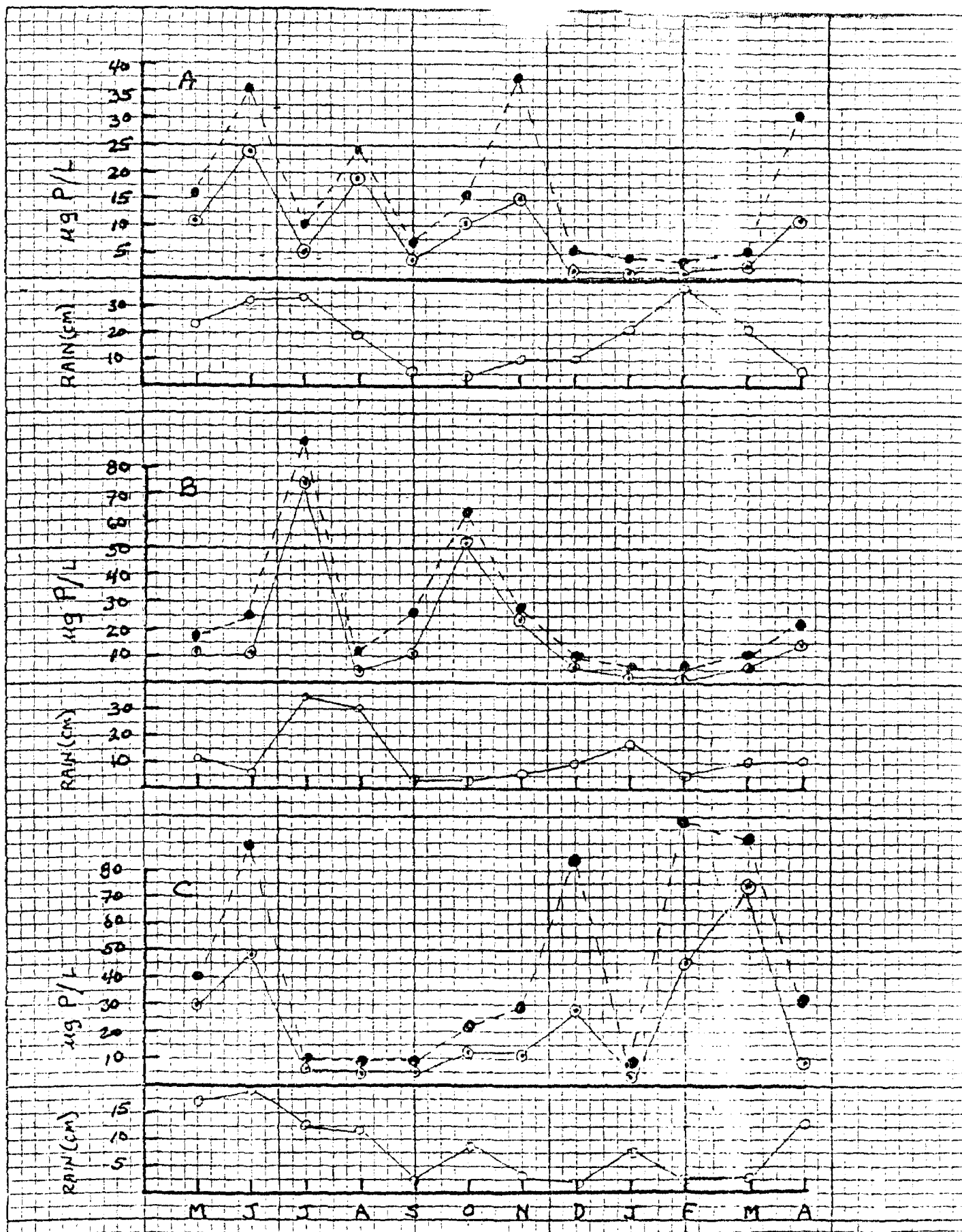


Figure 4-5. Monthly volume-weighted mean concentrations of SRP and TP at Jay (A), Gainesville (B) and Miami (C) from May, 1978 to April, 1979.

Table 4-6. Wet and dry deposition of total nitrogen and phosphorus at sites with wet/dry collectors.

Site	Total Nitrogen (g/m <sup>2</sup> -yr)			Total Phosphorus (mg/m <sup>2</sup> -yr)		
	Wet	Dry	Total	Wet	Dry	Total
Gainesville	0.63	0.28	0.91	16	42	58
Cedar Key	0.52	0.25	0.77	6	18	24
Apopka	0.47	0.34	0.81	9	48	57
Belle Glade	0.64	0.49	1.13	12	84	96
mean	0.57	0.34	0.91	11	48	59

Table 4-7. Relative deposition of nitrogen and phosphorus forms by wet versus total (wet plus dry) deposition at the four wet/dry collection sites.\*

Location	$\text{NH}_4^+$	$\text{NO}_3^-$	TIN	Org N	TN	SRP	Org P	TP
Gainesville (urban)	88	70	74	59	69	40	19	28
Cedar Key (Coastal)	82	62	69	61	68	33	20	25
Apopka (agric.)	70	74	72	33	58	20	11	16
Belle Glade (Agric.)	83	67	72	38	57	15	9	13
Average	81	68	72	48	63	27	15	20

\*Values are % deposition by "wet-only" precipitation = (100 x loading from wet collector)/total loading (wet plus from dry).

trate by wet-only input averaged 81 and 68%, respectively, of the total deposition (wet + dry). Thus for these two substances, rainfall was the predominant deposition mechanism. Atmospheric precursors of ammonium and nitrate in rainwater are gases ( $\text{NH}_3$  and  $\text{NO}_x$ ) and secondary aerosols (particulates formed by gaseous reactions, e.g.  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{HSO}_4$ ). These aerosols are very small ( $<1 \mu\text{m}$ ) and thus do not settle from the atmosphere as dryfall. They are hygroscopic, however, and as a result they are important as condensation nuclei for rain drop formation.

While wet-only input is the major mechanism for inorganic nitrogen deposition, it is less important for the input of organic nitrogen; only 47% of the average atmospheric input of organic nitrogen was from wet deposition. At Gainesville and Cedar Key, ca. 60% of the TON deposition was by wet input, while at Apopka and Belle Glade, TON deposition via wet input was only about 35%. As discussed above, the Apopka and Belle Glade sites are located in areas of intensive agriculture, and atmospheric deposition in these areas seems to reflect activities such as plowing and harvesting that introduce relatively large (hence rapidly settling) particles into the atmosphere. Dryfall of soil-derived particles thus appears to be an important mechanism for organic nitrogen input, while rainfall is more important for inorganic nitrogen deposition.

#### PHOSPHORUS

Data summarizing the wet and dry deposition of phosphorus at the four wet/dry sites are presented in Tables 4-6 and 4-7. The Belle Glade collector recorded the highest (wet plus dry) deposition of total P ( $96 \text{ mg/m}^2\text{-yr}$ ), while the coastal Cedar Key collector measured the least deposition ( $24 \text{ mg/m}^2\text{-yr}$ ). The mean (wet plus dry) deposition of total P for the four collectors was  $59 \text{ mg/m}^2\text{-yr}$  (Table 4-6).

Dryfall input of phosphorus was more important than wet precipitation, accounting for 80% of the total deposition averaged over the four sites (Table 4-7). The reverse was true for nitrogen (see above discussion). Only 15% of the organic phosphorus (operationally defined here as total phosphate minus soluble reactive phosphate [SRP]) was deposited via rainfall, while 27% of the SRP was from rainfall. Total phosphorus deposition at the agricultural Belle Glade site was 87% via dryfall and only 13% by rain (Table 4-7). Since phosphorus is a nonvolatile element, its cycle generally is limited to rock-soil-water phases. Atmospheric deposition of phosphorus, therefore, occurs primarily by gravitational settling of particles that enter the atmosphere by various activities (e.g. agriculture, mining, fires). The high dryfall deposition of phosphorus (relative to wet input) at the agricultural Apopka and Belle Glade locations demonstrates the importance of land-use activities on atmospheric deposition of terrigenous substances.

##### 5. HISTORICAL COMPARISON

Historical data are available for the wet-only deposition of inorganic nitrogen to compare with the present data. Chapin and Uttormark (1976) constructed an isopleth map of inorganic nitrogen flux using Junge's (1958) data for ammonia and nitrate in wet-only precipitation. The map shows a flux of inorganic nitrogen of 0.10 to 0.15 g/m<sup>2</sup>-yr across the southeastern U.S., including Florida. Inorganic nitrogen fluxes via wet-only precipitation measured in this study range from 0.32 to 0.44 g/m<sup>2</sup>-yr, with a mean of 0.39 g/m<sup>2</sup>-yr. The annual mean concentration of TIN in 1955-56 averaged over the four Florida sites in Junge's study was 0.09 mg/L, while Lodge et al. (1968) found a volume-weighted mean TIN concentration of 0.08 mg N/L in wet-only precipitation at Tampa during the period 1960-66. Although there have been numerous studies of bulk precipitation across Florida since the Lodge et al.

study, only two wet-only investigations have been reported (Table 4-1). Burton et al. (1978) found 0.30 mg/L TIN in wet-only precipitation collected during 1974-75 at Tallahassee, while Hendry and Brezonik (1980) reported 0.29 mg/L TIN in Gainesville wet-only precipitation (1976-77). Averaged over the 4 wet-only collection sites in this study, the TIN concentration was similar to the above values (0.28 mg N/L); thus the mean concentration of inorganic nitrogen in wet-only precipitation and corresponding flux have increased about three-fold in Florida over the last two decades.

In bulk precipitation TIN averaged 0.38 mg/L over all the sites, ranging from 0.28 (Corkscrew) to 0.59 (Chipley) mg/L. Historical data (Table 4-1) for TIN in bulk precipitation in Florida ranged from 0.20 to 0.98 mg/L. With such large variability due to a number of different sampling locations, no historical trends can be inferred concerning the levels of TIN in bulk precipitation. Fewer data are available for TON levels in Florida precipitation (Table 4-1) and the values again show a large range, 0.16 to 0.56 mg/L. The state-wide mean (all sites) for TON in this study was 0.17 mg/L which is near the low value of the above range.

Average total phosphorus (TP) concentration was 38  $\mu$ g/L for all the bulk precipitation sites, with a range of 29 to 59  $\mu$ g/L for individual sites. Previous studies (Table 4-1) have reported a large range (29-140  $\mu$ g/L) of TP values at various locations over the last ten years. As mentioned earlier, this large variation likely is due to different locations and short (< 1 yr) sampling periods.

## 6. SIGNIFICANCE OF N AND P LOADINGS RELATIVE TO LAKE EUTROPHICATION

The atmospheric loading rates of total nitrogen and phosphorus found at each bulk precipitation site can be examined in the context of critical nutrient loading rates for lake eutrophication. Figure 4-6 illustrates the relationship between the bulk loading rates of N and P at each site and the

## NITROGEN

## PHOSPHORUS

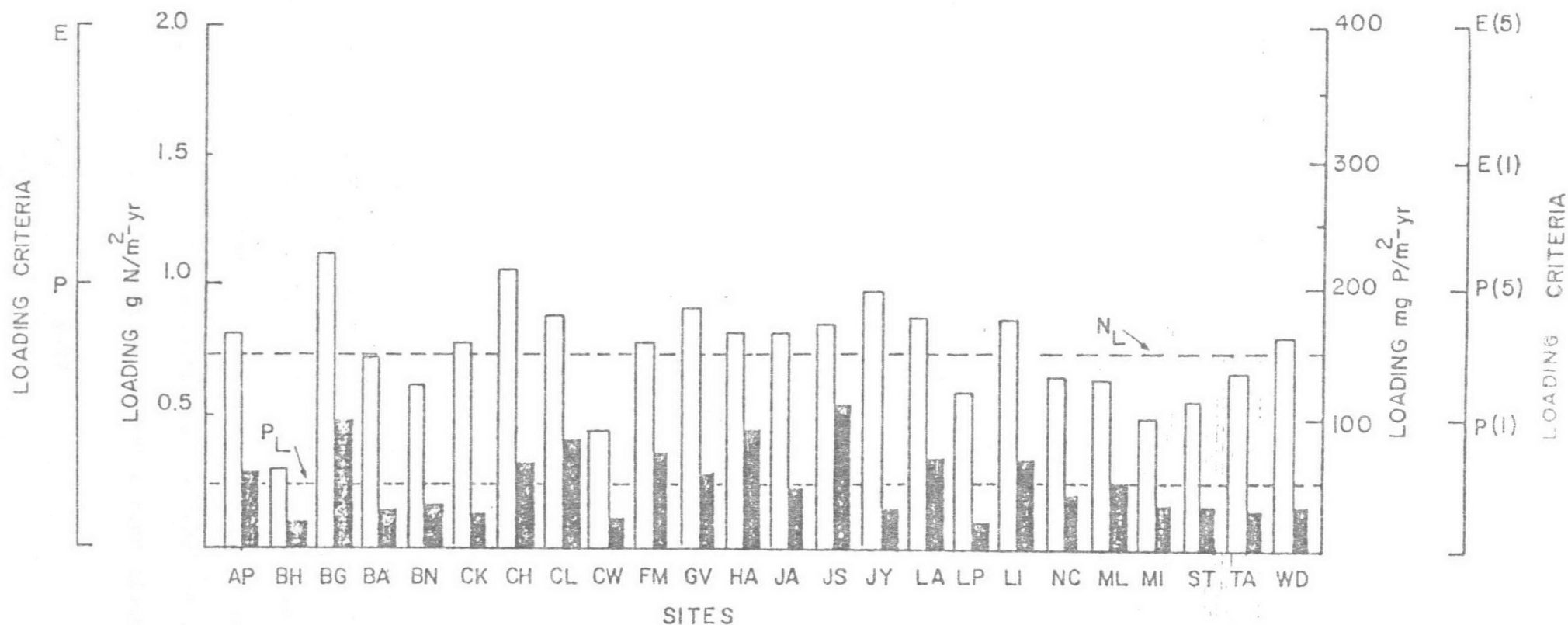


Figure 4-6. Loadings of nitrogen (open bars) and phosphorus (closed bars) by bulk precipitation at each sampling site. Statewide average loadings shown by dashed lines. Permissible (P) and Excessive (E) loading criteria for nitrogen are for lakes with mean depth < 5 m (Vollenweider 1968). Loading criteria for nitrogen are for two values of areal water loading ( $q_s = 1$  and  $5 \text{ m/yr}$ ) as given by Vollenweider (1975).



critical loading rates developed by Vollenweider (1968, 1975). The state-wide mean (averaged over all the sites) deposition rate is also shown in the figure. For both nitrogen and phosphorus, the statewide mean rates are below the "permissible" values defined by Vollenweider. However, the rates at several predominantly agricultural sites did exceed the "permissible" levels. While atmospheric inputs of N and P by themselves would not produce the water quality problems generally associated with lake eutrophication, the higher deposition rates may support substantial standing crops of phytoplankton. Moreover, the mean loading rate for nitrogen from bulk precipitation is about 75% of the total "permissible" loading and about 37% of the nitrogen loading rate associated with the onset of eutrophic conditions.

Thus even rather low contributions of nitrogen from surface water sources may be sufficient either to make nitrogen non-limiting or to induce eutrophic conditions, assuming nitrogen were the limiting nutrient. The above calculations also do not consider the atmospheric nitrogen inputs from gaseous absorption or from rainfall that reaches a lake via runoff in the watershed; for further discussion of these aspects see Messer and Brezonik (1980b). The high rates of nitrogen deposition from the atmosphere, coupled with the relative mobility of nitrogen (compared to phosphorus) in terrestrial systems, help to explain why nitrogen seldom is observed to be the limiting nutrient in lakes.

For phosphorus the situation is somewhat different. The statewide mean loading is half the permissible rate for lakes that have  $q_s$  (areal water loading rate) = 1 m/yr, and only one fourth of the permissible loading for lakes with  $q_s$  = 5 m/yr. Most Florida lakes have  $q_s$  values < 5 m/yr. Figure 4-6 suggests that atmospheric deposition alone supplies only about 12 to 16% of the loading required to cause eutrophic conditions in Florida lakes.

## C. MAJOR MINERALS

### 1. SODIUM, CHLORIDE AND SULFATE

Volume-weighted average concentrations of sodium and chloride concentrations are plotted in Figure 4-7A and 4-8A. The concentration isopleths for both  $\text{Na}^+$  and  $\text{Cl}^-$ , roughly follow the outline of the peninsula. This is not surprising since the source of the  $\text{NaCl}$  in rain and dryfall across Florida is the Atlantic Ocean and Gulf of Mexico. In fact, the  $\text{Cl}^-/\text{Na}^+$  ratios in bulk precipitation (Figure 4-7B) across the state are close to the ratio of these ions in seawater (1.8). Sites with precipitation ratios less than 1.8 indicate  $\text{Na}^+$  enrichment, while ratios greater than 1.8 indicate  $\text{Cl}^-$  enrichment relative to sea salt. The mean ratio for the state (22 sites) is 1.83. The concentrations isopleths (Figure 4-7A and 4-8A) are more closely spaced on the west than east coast of the state, indicating a sharper concentration gradient. The east coast (Atlantic) is a high-energy coastline and salt particles are carried farther inland than is the case along the west coast and panhandle.

The input of  $\text{NaCl}$  appears rather constant over time. Junge and Werby (1958) reported  $\text{Na}^+$  concentrations at Jacksonville and Tampa of 0.96 and 0.63 mg/L, respectively for 1955-56. Sodium concentrations at sites (Jacksonville and Bradenton) in this study near the earlier sampling locations were 1.08 and 0.51 mg/L, respectively.

Sulfate ( $\text{SO}_4^{2-}$  - S) concentrations in bulk precipitation (Figure 4-8B) ranged from 1.18 (Marineland) to 0.38 mg/L (Corkscrew Swamp). Sulfate in rainfall originates from three sources; (1) marine-derived sulfate from sea-salt aerosols, (2) biogenic emission to the atmosphere and subsequent oxidation of reduced sulfur compounds ( $\text{H}_2\text{S}$ , dimethyl sulfide, dimethyl disulfide), and (3) anthropogenic emission of sulfur compounds ( $\text{SO}_2$ , particulate  $\text{SO}_4$ ). Sulfate deposition was principally by wet processes (average of about

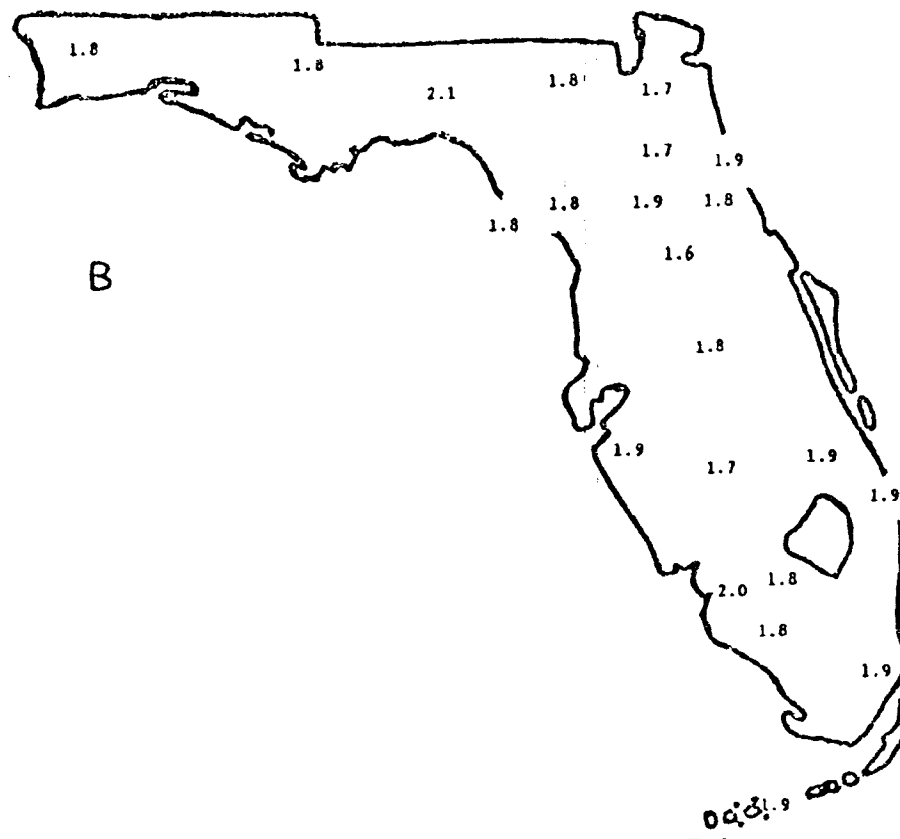
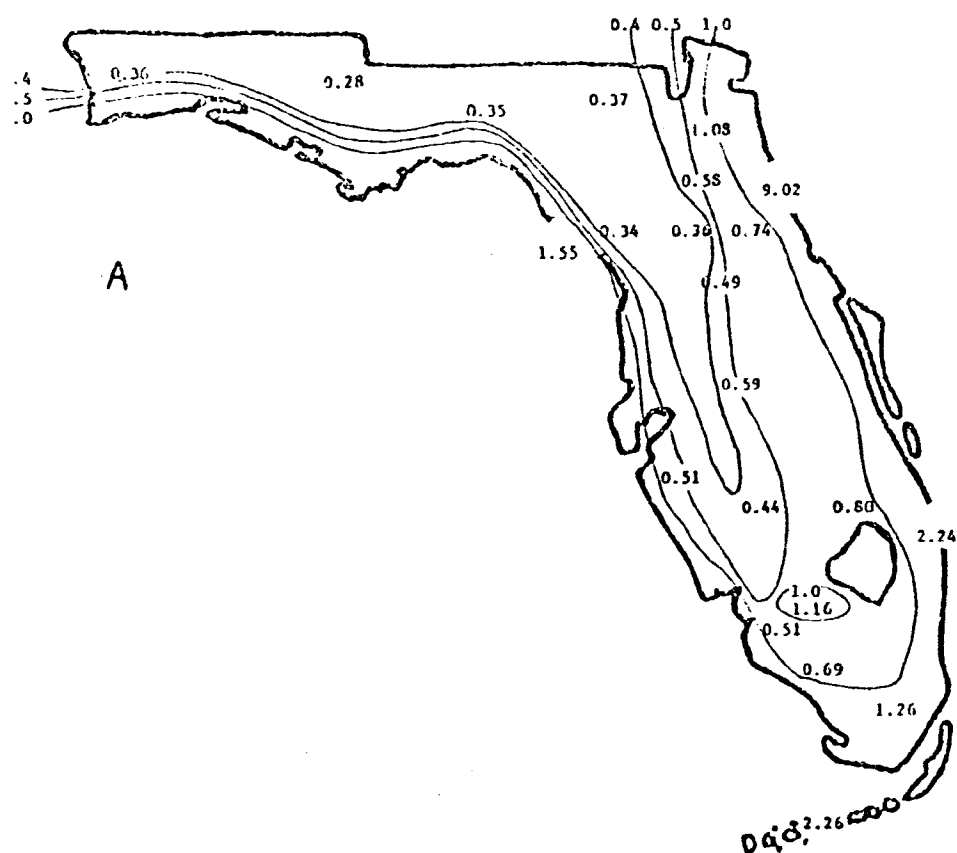


Figure 4-7. (A) Volume-weighted mean concentrations of sodium (mg/l) in bulk precipitation and (B) Cl/Na wt/wt concentration ratios (Volume-weighted values) in bulk precipitation in Florida, May 1978-April 1979.

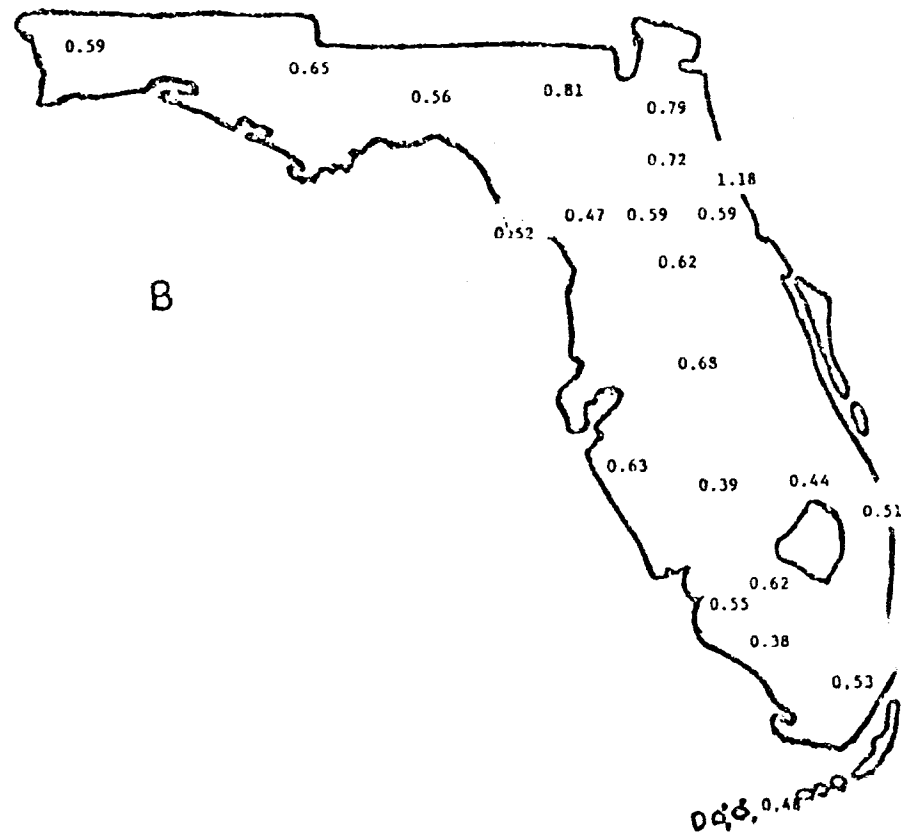
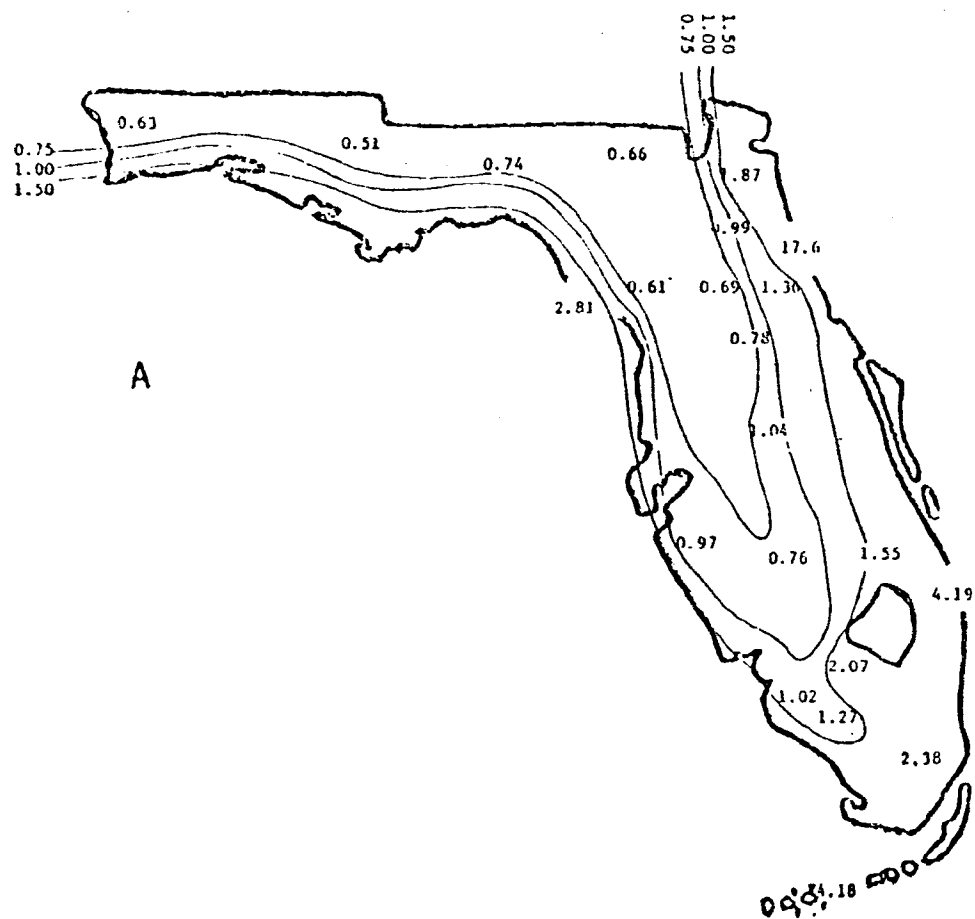


Figure 4-8. Volume-weighted mean concentrations of (A) chloride and (B) sulfate (as sulfur) in bulk precipitation in Florida, May, 1978 - April, 1979. All concentrations in mg/l.

75% of the total deposition (Table 4-8), with dry deposition rates higher during the winter months than the summer months (Table 4-9). The importance of wet versus dry deposition for sulfate, the relative importance of the above sources for sulfate in Florida precipitation, and the relationship of sulfate to rainfall acidity are discussed in greater detail in Chapter 5.

## 2. CALCIUM, MAGNESIUM AND POTASSIUM

Highest levels of calcium generally were recorded in the southern half of the state (Figure 4-9A). Calcareous deposits (limestones) in this area are located just a few feet below the surface of the top soil, and they outcrop in some areas south of Lake Okeechobee. Mining of these deposits for use in concrete manufacturing is extensive in south Florida.

Calcium in rainwater arises from terrestrial sources; i.e. the ocean provides only small amounts of  $\text{Ca}^{2+}$  to the atmosphere; this matter is discussed further in Chapter 5 relative to the factors affecting rainfall acidity in Florida. As a result of this terrigenous origin, isopleth patterns for Ca are not similar to those for  $\text{Na}^+$  and  $\text{Cl}^-$ . Although the highest volume-weighted average concentration of  $\text{Ca}^{2+}$  in bulk precipitation occurred at Marineland on the Atlantic coast (Figure 4-9A), calcium derived from sea-salt particles accounted for only about 0.34 mg/L of the total  $\text{Ca}^{2+}$  concentration; i.e. 1.30 mg/L is "excess" calcium. The high level of  $\text{Ca}^{2+}$  in the rain at this site is likely due to combination of wave-action on the outcroppings of coquina (limestone) rock along the coast and wind-driven suspension of calcareous particles in coastal soils. The historic buildings in St. Augustine (16 km north of Marineland) are constructed in large part of naturally-occurring coquina. A high "excess"  $\text{Ca}^{2+}$  (0.72 mg/L) also was recorded at the entirely maritime site, Bahia Honda in the lower Keys (Figure 4-9). This excess Ca undoubtedly arises from the limestone rock which forms the archipelago known as the Florida Keys. Calcium and the associated carbonate-bicarbonate

Table 4-8. Wet and dry deposition of minerals at the wet/dry collection sites. Values are in  $\text{g/m}^2\text{-yr}$ .

	Gainesville			Cedar Key			Apopka			Belle Glade		
	Wet	Dry	% by wet	Wet	Dry	% by wet	Wet	Dry	% by wet	Wet	Dry	% by wet
Sodium	0.35	0.24	59%	1.96	0.48	80%	0.40	0.33	55%	0.59	0.47	56%
Chloride	0.67	0.46	59%	3.63	0.82	82%	0.77	0.53	59%	1.22	0.99	55%
Calcium	0.38	0.67	36%	0.47	0.40	54%	0.32	0.31	51%	0.70	1.71	29%
Magnesium	0.06	0.07	46%	0.25	0.08	76%	0.06	0.06	50%	0.08	0.15	35%
Potassium	0.12	0.06	67%	0.14	0.06	70%	0.10	0.15	40%	0.15	0.20	43%
Sulfate(s)	0.65	0.25	72%	0.72	0.13	85%	0.66	0.16	80%	0.51	0.25	67%

Table 4-9. Dry Deposition of Minerals on a (Summer/Winter) Seasonal Basis. All Values are  $\text{g/m}^2\text{-yr}$ .

Location	Deposition Rate ( $\text{g/m}^2\text{-yr}$ )					
	$\text{Na}^+$	$\text{Cl}^-$	$\text{Ca}^{+2}$	$\text{Mg}^{+2}$	$\text{K}^+$	$\text{SO}_4^{2-}\text{-S}$
Gainesville						
Winter	0.27	0.51	0.69	0.07	0.06	0.25
Summer	0.19	0.40	0.57	0.09	0.06	0.25
Cedar Key						
Winter	0.57	1.00	0.41	0.09	0.06	0.14
Summer	0.25	0.65	0.32	0.06	0.06	0.12
Apopka						
Winter	0.37	0.58	0.39	0.07	0.13	0.19
Summer	0.33	0.53	0.21	0.05	0.11	0.14
Belle Glade						
Winter	0.56	1.18	1.95	0.18	0.23	0.31
Summer	0.33	0.71	1.53	0.10	0.14	0.18

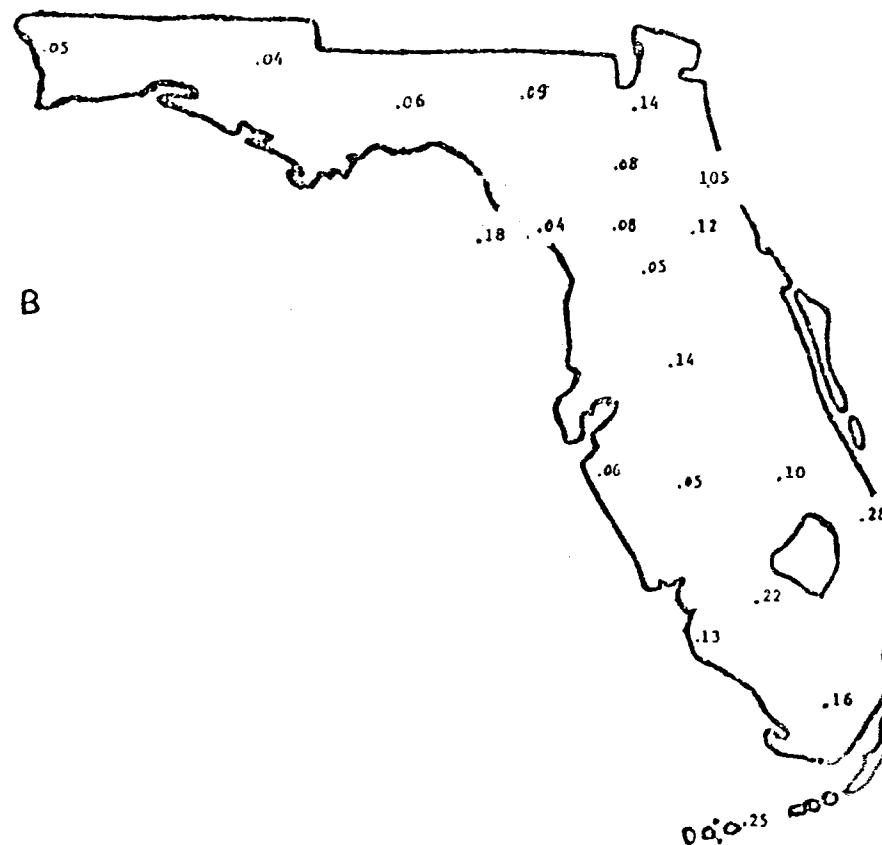
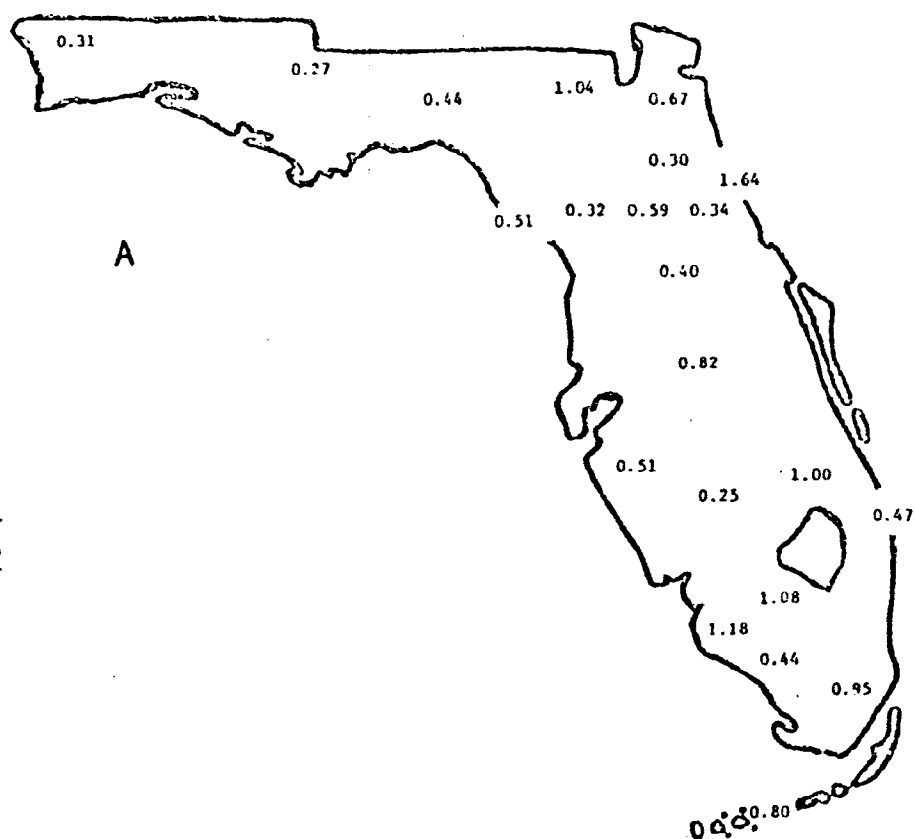


Figure 4-9. Volume-weighted mean concentrations of (A) calcium and (B) magnesium in bulk precipitation in Florida, May 1978-April 1979. All concentrations in mg/l.



species are important parameters controlling the acidity (pH) of precipitation in south Florida. The pH of Florida rainwater results from complex interactions of atmospheric acids ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) with terrestrially-derived bases (e.g.  $\text{CaCO}_3$ ); see chapter 5 for a detailed discussion of Florida rainfall acidity and elements controlling the pH of Florida precipitation.

In general, magnesium levels in bulk precipitation (Figure 4-9B) correlate with calcium concentrations (Figure 4-9A). Highest  $\text{Mg}^{2+}$  levels were found at the southern sites, and high values also were measured for coastal locations. Seasalt supplies a substantial proportion of the  $\text{Mg}^{2+}$  in coastal precipitation at coastal location. In fact all of the magnesium in rain at the four coastal sites (Cedar Key, Bahia Honda, Stuart, and Marineland), is derived from seasalt ( $\frac{\text{Mg}}{\text{Na}}$  in seawater is 0.12).

Potassium arises in rainfall principally from soil-derived particles. Concentrations of  $\text{K}^+$  were highly variable over the bulk precipitation sites (Figure 4-10), and they seem to reflect nearby land use activities. Lowest average concentrations were found at the two most pristine locations (Lake Placid and Corkscrew Sanctuary), while somewhat higher levels were recorded at agricultural locations (Clewiston, Hastings).

### 3. WET AND DRY DEPOSITION OF MINERALS

The relative importance of wet vs. dry input of minerals is summarized in Table 4-8. Sodium and chloride deposition at all four wet/dry sites occurred primarily by wet-only input. Atmospheric sea-salt particles are highly hygroscopic and thus are important as condensation nuclei for rain drop formation. No simple trend in deposition mechanism can be seen for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , and either wet or dry processes dominated depending on the site. For example, at the highly-agricultural Belle Glade site, total deposition of all three metals was largely by dry fall (Table 4-8), but at Apopka and Cedar Key, wet and dry deposition of  $\text{Ca}^{2+}$  was about equal. A strong seasonal-dependence

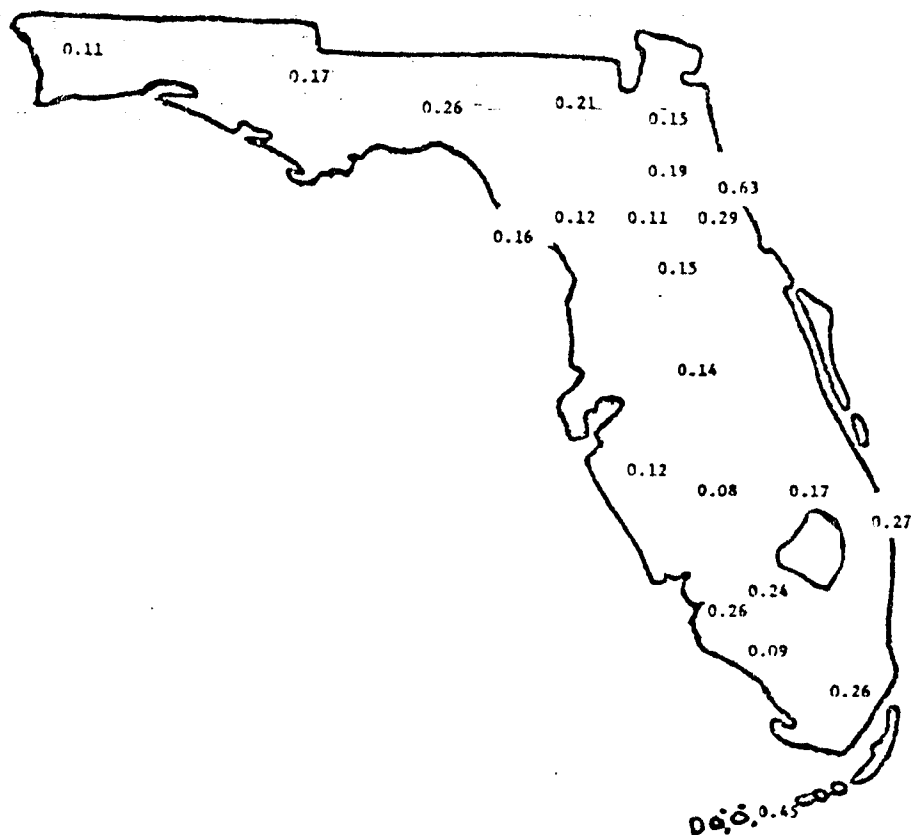


Figure 4-10. Volume-weighted concentrations of potassium in bulk precipitation across Florida (May 78-May 79). All values are mg/l.

was found in the dry deposition of the five minerals (Table 4-9), with dry-fall input during the winter months being greater than that in the summer. This trend likely reflects a lower frequency of rain events during that season compared to the summer rainy season.

#### 4. Comparison of Wet + Dry and Bulk Deposition Rates for Major Minerals.

Two different types of collectors (i.e. wet/dry and bulk) were employed in the precipitation network, and it is of interest to determine whether the wet plus dry deposition rates (from the wet/dry collectors) correspond to the bulk deposition rates for various species. Assuming that wet deposition did not vary with collector type, two questions are raised regarding dry deposition. The first involves collector height; bulk collectors in the network were located 2 m above ground, a concentration gradient exists between 1 and 2 m, then there may be a corresponding deposition gradient between the two collectors.

The second question involves shape: bulk collectors are conical, while the wet/dry collectors are cylindrical. The flow of air around the two collectors is different, and thus the rate of turbulent deposition also may differ. This problem is not completely distinct from that of reference height, because wind speed and eddy diffusivity are functions of height. However, the intent here is simply to point out the gross differences between collectors and then to determine whether these differences might be responsible for inconsistent deposition rates.

Adequate data are available at two sites (Gainesville and Orlando) to compare adjacent wet/dry and bulk collectors, and deposition of major cations and anions in the two types of collectors are summarized in Table 4-10. Generally, the agreement between wet/dry and bulk collectors is acceptable. Deposition of sulfate and nitrate, which both originate as gases or sub-micron particles, was the same in both types of collectors at

Table 4-0. Comparison of loading rates of major ionic species as determined by wet/dry and bulk precipitation collectors.

	Annual Deposition (kg/ha)								
Location	H <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup>	excess SO <sub>4</sub>	Cl <sup>-</sup>
Gainesville									
Wet + Dry	0.24	5.79	1.65	10.0	1.43	1.85	3.55	24.5	11.3
Bulk	0.27	5.25	1.58	8.5	1.15	2.33	3.44	24.4	10.0
<u>Wet + Dry</u> x 100 Bulk	89	110	104	118	124	80	103	100	113
Orlando									
Wet + Dry	0.19	7.43	2.00	6.18	1.20	1.52	3.16	23.7	13.3
Bulk	0.22	6.71	2.07	5.49	0.71	1.97	3.18	23.8	10.1
<u>Wet + Dry</u> x 100 Bulk	86	111	97	113	169	77	99	100	132

the two sites. Deposition of hydrogen ion and ammonium was lower in both wet/dry collectors than in the nearby bulk collectors. The difference in  $H^+$  deposition reflects large cation excesses (hence by inference, alkalinity) in the dry bucket. The wet deposition of  $H^+$  alone was higher in both cases than the bulk deposition. In the calculation of total loading from wet/dry collectors, the alkalinity was assumed to titrate a stoichiometric amount of  $H^+$ . The ammonium discrepancy is unexplained, but may signify either a positive gradient in the vertical direction or simply differences in  $NH_3$  interaction with the two collector surfaces.

$Ca^{+2}$  and  $Mg^{+2}$  deposition rates are consistently higher for the wet/dry collectors than the bulk collectors. This may reflect the difference in collector heights and suggests the presence of a concentration gradient of suspended soil species near the ground. Assuming that most of the  $Ca^{+2}$  and  $Mg^{+2}$  deposited in the collectors is associated with carbonate, the excess of these ions in the wet/dry collectors, relative to the bulk collectors, explains the observed underestimate of  $H^+$  deposition in the wet/dry system.

Sea-salt ( $Na^+$  and  $Cl^-$ ) deposition was also higher in the wet/dry collector. Although this could be due to association of NaCl with soil particles, this explanation seems unlikely since it would necessitate a relatively high percentage of  $Na^+$  and  $Cl^-$  in soil dust. This is unlikely due to the differential solubilities (leaching rates) of terrestrially-derived and oceanic species. The fact that deposition of most particulate species was higher in the wet/dry collectors suggests that the shape and height of the bulk sampler may contribute to turbulent scouring of the funnel and thus to low deposition rates.

Despite the aforementioned differences between the wet/dry and bulk deposition rates, the results are generally comparable. Most species were deposited to the two collectors with less than 20% difference, and for several species differences were only a few percent. Unless sampling requirements are very stringent, it seems that either collector will yield an adequate description of atmospheric deposition. Furthermore, deposition patterns are reflected in the consistent manner by the collectors. Both collection systems indicate that  $H^+$  deposition at Gainesville was higher than that at Orlando, while  $Na^+$ ,  $Cl^-$  and  $K^+$  deposition was higher at Orlando than Gainesville. The problems associated with deposition of particulate species may be overcome, or at least diminished, by adjustment of collector height and by careful selection of sampling location.

##### 5. Comparison of Bulk Precipitation and Throughfall.

Bulk precipitation at the Waldo site, 10 km NE of Gainesville, was collected atop a 20 m (65 ft) steel tower which extended through the top of the forest canopy. Concurrent with these collections, throughfall also was collected at the base of the tower, below the tree canopy. As shown in Table 4-11, distinct chemical differences were found between the bulk precipitation and throughfall. On an annual, volume-weighted average basis, throughfall contained elevated concentrations of all chemical species except  $H^+$  and  $NH_4^+ - N$ . On a seasonal basis, summer (May 1978 - Oct. 1978) differences in concentration between the two types of samples were relatively small, and nutrient concentrations were approximately the same in the two sample types. Concentrations found in the winter months (Oct. 78 - Apr. 78), however, were much higher in throughfall than in bulk precipitation (except for  $H^+$ ). This likely reflects the fact that the leaves on the trees (primarily cypress, Taxodium distichum) die in the late fall and minerals are more easily leached

Table 4-17. Comparison of Major ions, conductivity, and nutrients in bulk precipitation and throughfall on an annual and a summer/winter basis at the Waldo site.

		Annual		Summer		Winter	
		Bulk	Throughfall	Bulk	Throughfall	Bulk	Throughfall
H <sup>+</sup>	mg/L	24 (pH 4.62)	19 (pH 4.73)	32 (pH 4.49)	18 (pH 4.74)	16 (pH 4.80)	19 (pH 4.72)
Specific Conductance	MS/cm @ 25°C	18.1	29.9	20.7	19.7	15.4	42.3
Na	mg/L	0.59	1.57	0.51	0.71	0.67	2.60
K	mg/L	0.20	0.59	0.30	0.52	0.09	0.67
Mg	mg/L	0.08	0.33	0.06	0.19	0.09	0.50
Ca	mg/L	0.30	1.34	0.31	0.83	0.28	1.96
SO <sub>4</sub> <sup>2-</sup>	mg/L	2.15	3.18	2.31	2.88	1.99	3.55
CL <sup>-</sup>	mg/L	0.99	3.24	0.69	1.02	1.31	5.94
NH <sub>4</sub> <sup>+</sup> N	mg/L	.144	.121	.094	.054	.197	.2
NO <sub>3</sub> <sup>-</sup> N	mg/L	.202	.219	.231	.232	.170	.203
TON	mg/L	0.24	0.34	0.30	0.32	0.17	0.37
SRP	mg/L	.014	.017	.021	.019	.007	.015
<del>TP</del>	mg/L	.025	.030	.041	.039	.009	.019

from the leaf tissue. Ewel et al. (1976) found increased mineral levels (Ca, Mg, K, and P) in both throughfall and stemflow compared to bulk precipitation collected in a north Florida mixed hardwoods forest, and they attributed the higher levels to leaching of the plant tissue. Ewel et al. also reported higher levels of the four minerals in throughfall collected in the winter than summer.

Hendry (1977) found higher levels of major ions including hydrogen and N and P forms in throughfall than in bulk precipitation collected during 1976-1977 in a cypress dome north of Gainesville. The higher concentration of hydrogen ion (lower pH) may have been due to leached organic acids, since the TOC levels in throughfall were approximately double those of bulk precipitation. Cronan and Schofield (1979) recently reported higher  $H^+$  levels in throughfall than in bulk precipitation collected on Mount Moosilauke, New Hampshire. The lowered pH corresponded to increased concentrations of organic anions in the throughfall.

The throughfall samples collected in this study generally contained visibly colored organic materials; thus some leaching was occurring, but the extent of this, relative to simple washing of accumulated particulates and absorbed gases from the canopy, is unknown.

#### D. MINOR MINERALS

##### 1. SILICA

Volume-weighted mean silica ( $SiO_2$ ) concentrations in bulk precipitation (Figure 4-11) ranged from 14 (Lisbon) to 63  $\mu g/l$  (Ft. Myers). Silica levels for most of the sites (coastal, northern and central) were about 20 to 30  $\mu g/l$ , and highest values were recorded for three south Florida sites, Ft. Myers, Clewiston and Miami. This pattern is similar to calcium (Figure 4-9A) and it indicates input of terrigenous substances.



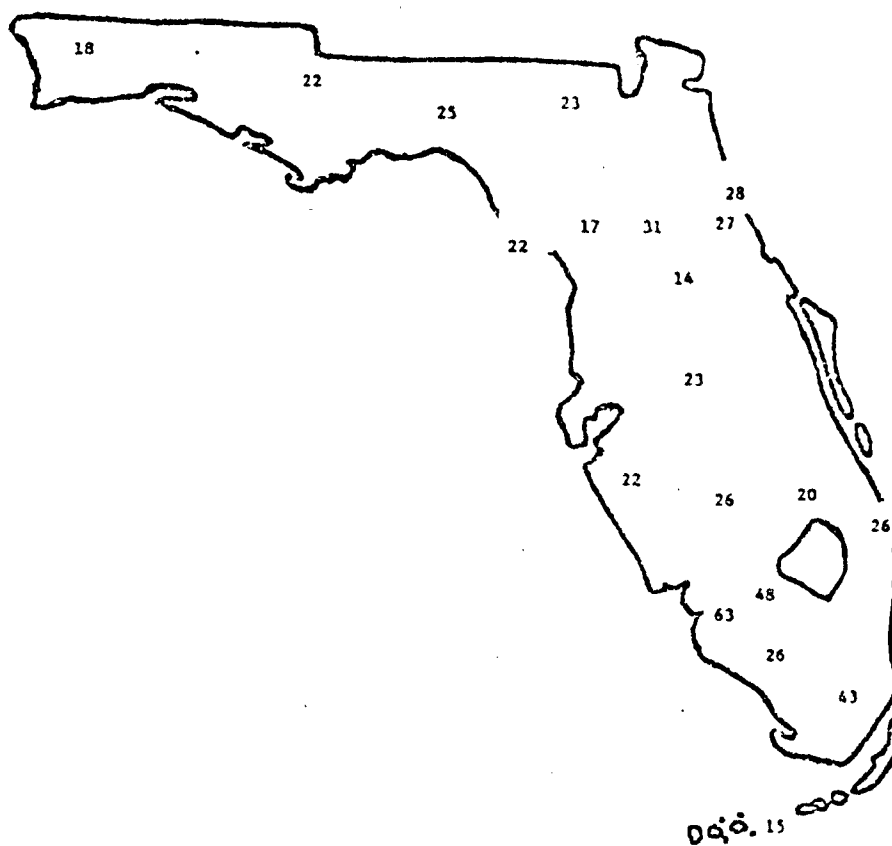


Figure 4-11. Volume-weighted mean concentrations of  $S_2O_3$  in bulk precipitation in Florida May 1978 - April 1979.

## 2. Fluoride

Detectable levels ( $> 20 \mu\text{g/l}$ ) of fluoride were found in rainfall samples from only 4 sites: Bradenton ( $28 \mu\text{g/l}$ ), Lake Placid ( $29 \mu\text{g/l}$ ), Lake Alfred ( $82 \mu\text{g/l}$ ), and Jasper ( $55 \mu\text{g/l}$ ). All four sites are located in or near areas of phosphate mining and the processing of phosphate into phosphoric acid for use in fertilizers. This processing involves the addition of acid to apatite rock ( $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ ;  $\text{X} = \text{OH}$  or  $\text{F}$ ) with the resultant release of fluoride as gaseous hydrogen fluoride ( $\text{HF}$ ). Tatera (1970) estimated the annual emission of fluoride to the atmosphere at  $10^3$  tons by this process. No estimates, however, are available for particulate (dust) emissions from the mining and processing of fluoroapatite.

## Chapter 5.

### The Acidity of Rainfall in Florida

The atmosphere has long been known as an important pathway in the cycling of nutrients and minerals (Junge 1958; Lodge et. al. 1968). Numerous recent studies also have shown that many pollutants have significant atmospheric pathways. Acid precipitation is perhaps the most widely known example of this phenomenon, and its occurrence throughout the northeastern United States has been reported widely (e.g. Cogbill & Likens 1974). The geographic progression of acid rainfall southward and westward has been described elsewhere (Likens, 1976; Likens et. al., 1979). However, relatively little information is available on the geographic and temporal distribution of acid precipitation in Florida. Two recent studies demonstrated the occurrence of acid rain at Tallahassee (Burton et. al. 1978) and Gainesville (Hendry & Brezonik 1980); rainfall at these locations is about 25 to 30% as acidic as the rain in severely affected areas of the Northeast. Nevertheless, published data do not delineate the areas of acid precipitation in Florida; nor do they indicate the relative importance of oceanic aerosols and biogenically produced sulfur to Florida rainfall chemistry.

This chapter summarizes results on rainfall acidity (and related parameters) obtained from the statewide precipitation chemistry network described in Chapter 4. This chapter describes spatial and temporal trends of rainfall acidity in the State of Florida, delineates the southeastern boundary of acid rain in the United States, and discusses the origin and composition of substances affecting the acidity of Florida precipitation.

#### EXPERIMENTAL METHODS

The Florida Atmospheric Deposition Network (FADN) had 24 precipitation collectors (20 bulk, 4 wet/dry) located primarily at state agricultural and

NOAA climatological stations, extending from the western panhandle of the state to the southern Keys (see Figure 4-1). Precipitation samples and rainfall data were gathered at these stations and sent to the University of Florida for analysis. Sample collection was performed on an event basis at Gainesville, weekly at the vertices of the state (Jay, Jacksonville, Miami), and biweekly at all other locations. Routine chemical analyses relevant to this chapter include major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ), major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), pH, and specific conductivity.

Chemical analyses of rainfall samples were done according to accepted methods (see Appendix 1 for details) using either standard methods (APHA 1976) or EPA (1976). The pH of rainfall samples was determined as soon as samples were received in the laboratory, using an Orion Model 801 pH meter equipped with a Corning #476002 reference electrode and Corning #476024 pH electrode calibrated at pH 4.00 and 7.00 with Fisher certified buffer solutions. Major anions were analyzed by automated (AutoAnalyzer) procedures: sulfate by the methylthymol blue method, chloride by ferric thiocyanate, and nitrate by the copperized-cadmium wire reduction method. Ammonium ion also was measured by an AutoAnalyzer, using the indophenol method; and other cations (Na, K, Mg, Ca) were determined by atomic absorption spectrophotometry, using a Varian Model 1200 spectrophotometer and instrument settings and procedures recommended by the manufacturer (Varian 1973).

## SPATIAL TRENDS IN ACIDITY AND RELATED PARAMETERS

Concentrations and depositions of the various acid-mediating species in Florida rainfall, for a number of time periods (i.e. calendars 1978 and 1979, 1978 through 1979, and the intensive year), are summarized in Table 5-1. Tabulated values represent averages for all bulk collectors operative during the time period of interest. The following discussion will be limited to the intensive study year (May 1978 - April 1979), during which all 24 monitoring sites were in operation.

A. Spatial Distribution of Acidity. Results for the sampling year (May 1978 - April 1979) show that precipitation is distinctly acidic over most of Florida (Figure 5-1). With few exceptions, sites north of Lake Okeechobee had annual (volume-weighted) pH values in the range of 4.6 to 4.8, while those south of the lake had acidities approaching geochemical neutrality.

Episodes of acid precipitation ( $\text{pH} < 5.0$ ) were observed at all sites except Bahia Honda, McArthur Farms, Clewiston and Fort Myers (Figure 5-1). The first of these sites, far into the Florida Keys, is separated from major point sources of sulfur and nitrogen oxides by at least 100 km and, in spite of seasonally variable local automobile traffic, probably approximates background conditions for the eastern United States.

The high pH values in bulk precipitation at Fort Myers and McArthur Farms probably reflect local effects of cement mining (elevated  $\text{Ca}^{+2}$  and  $\text{SO}_4^{2-}$ ) and cattle ranching (elevated  $\text{NH}_4^+$ ), respectively. High sodium and calcium concentrations in Clewiston rainfall indicate probable contamination by lake-spray from eutrophic Lake Okeechobee ( $\text{pH} > 8.0$ ). These three sites thus show evidence of locally-neutralized rainfall acidity.

Precipitation collected at Lake Placid and Corkscrew Swamp is probably more representative of that occurring over most of South Florida. Both

Table 5-1 Summary of concentrations and depositions of  $H^+$  and acid-mediating species in rainfall during various study periods.

Time	Interval	Species									
		$H^+$		$NH_4^+$		$Ca^{2+}$		excess- $SO_4^{2-}$		$NO_3^-$	
Time	Interval	C*	D**	C	D	C	D	C	D	C	D
Calendar	1978	11.6 (4.94)	161.	15.0	192.	29.6	360.	34.2	446.	16.3	209.
Calendar	1979	13.5 (4.87)	215.	10.2	154.	31.0	437.	27.9	424.	12.6	189.
Calendar	1978-79	12.4 (4.91)	362.	12.4	339.	28.9	759.	30.2	840.	14.1	387.
Intensive year (May 1978 - April 1979)		11.9 (4.92)	170.	12.7	173.	32.6	430.	31.7	433.	14.1	191.

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\* Concentrations (C) are averages for all operative sites, units are meq/L.

\*\* Depositions (D) are averaged over all sites, units are EQ/HA.

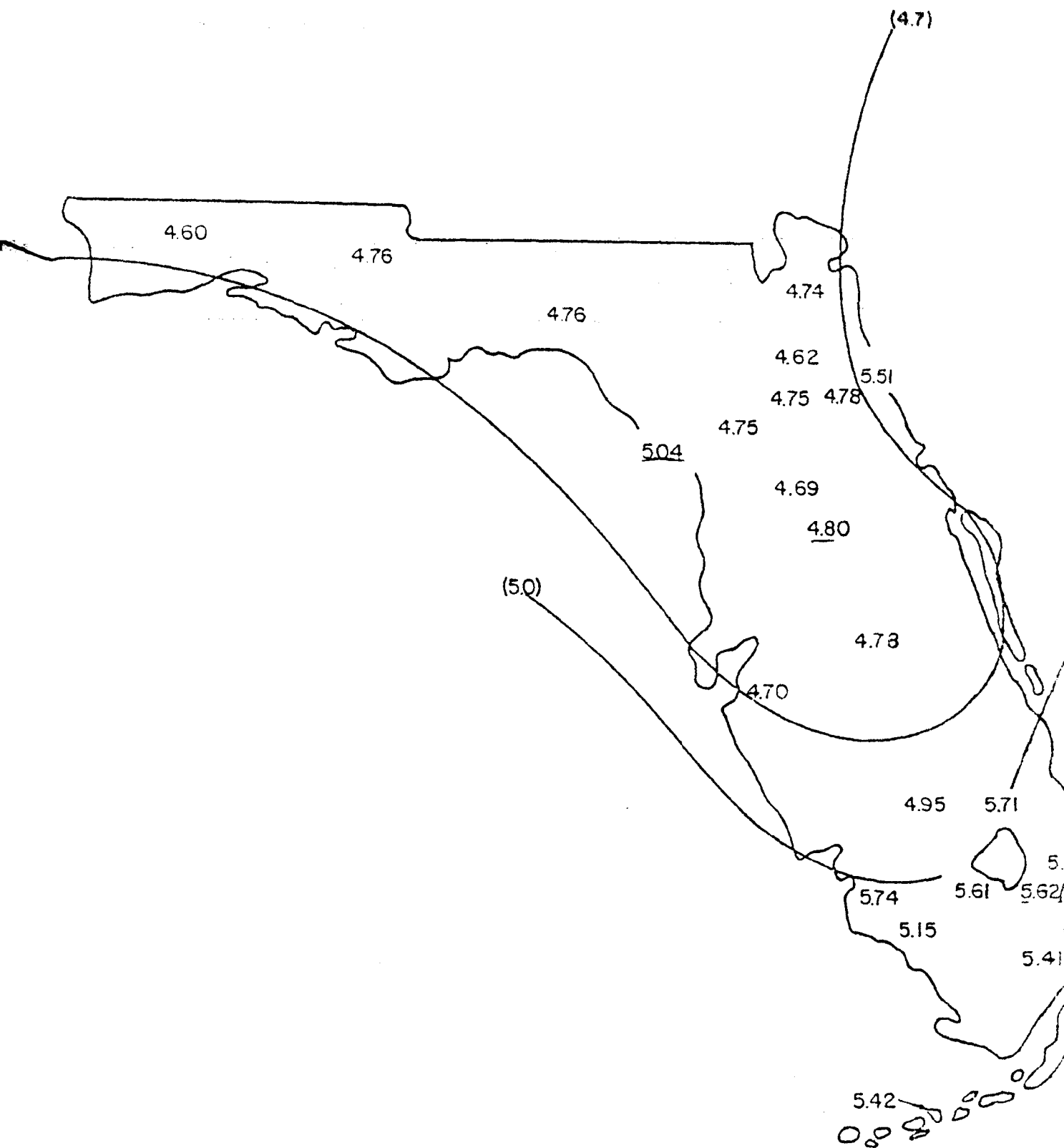


Figure 5-1. Volume-weighted mean pH of precipitation throughout Florida, May 1978-April 1979.

sites are pristine, at least 50 km from point sources of  $\text{SO}_2$  and  $\text{NO}_x$ , and well protected from surface disturbances associated with agriculture and transportation. Bulk precipitation pH values for the study year were 4.95 at Lake Placid and 5.15 at Corkscrew Swamp. In all likelihood, the area receives even higher levels of acidity in rainfall. Based on three months of wet-only rainfall data from Corkscrew Swamp. The volume-weighted mean pH of rainfall probably is less than 5.0 at least this far south in Florida.

Highly acidic events ( $\text{pH} < 4.0$ ) occurred at several northern sites during the study period. The most acidic event ( $\text{pH} 3.76$ ) occurred at Jay in August, 1978. Storms with  $\text{pH} 3.93$  were collected at Gainesville in September, 1978 and February, 1979. These events were brief and intense, and because of low rainfall amounts, they correspond to average, or even small hydrogen ion loadings.

In northern Florida, a strong pH gradient is apparent near coastal areas. Bulk precipitation at Cedar Key (on the Gulf Coast, 100 km SE of Gainesville) was only half as acidic as that at Bronson (50 km inland); and rainfall at Marineland (on the Atlantic coast) had less than one-third the acidity of rainfall at Hastings (15 km inland). There are several possible explanations for the coastal neutralization effect: direct titration with marine aerosols, dilution or displacement of polluted air masses by relatively clean maritime air, and enhanced deposition of terrestrially-derived alkaline particles. The first mechanism is of limited significance, as a simple calculation shows. The volume-weighted average concentration of sodium at Marineland was 9.0 mg/L (more than 4x that of any other site). The amount of sea-salt corresponding to this sodium concentration represents about 2.0  $\mu\text{eq/L}$  of oceanic bicarbonate, or only 30% of the observed difference in  $\text{H}^+$  concentration between Marineland and Hastings. (For the state as a whole,



the direct input of sea-bicarbonate to rainfall amounted to less than 0.25  $\mu\text{eq/L.}$ )

Inspection of Table 5-2 shows that concentrations of excess-sulfate and nitrate were similar at neighboring coastal and inland sites. Coastal rainfall thus is not less acidic than inland rainfall for lack of typically acidic species.

Ammonium and calcium (actually its basic counterions) could be responsible for the reduction in precipitation acidity at coastal sites. Ammonium was present in fairly constant amounts at the two sets of inland-coastal sites in question (Table 5-2), and indeed concentrations of  $\text{NH}_4^+$  varied only slightly on a statewide basis (see Chapter 4). Calcium, on the other hand, was present at significantly higher concentrations at coastal sites than at the adjacent inland sites. If carbonate was the associated counterion, it would have been deposited in sufficient quantities to account for the pH differences between coastal and inland sites.

Thus it appears that the commonly invoked principal of rainfall neutralization by sea salt is not of great significance for Florida precipitation chemistry. Moreover, daily land-breeze wind patterns did not significantly alter the deposition of acidic species at coastal locations; similar levels of nitrate and excess-sulfate occurred at the two inland and two coastal sites (Table 5-2). The distinguishing feature of coastal rainfall in north Florida is elevated calcium concentrations, the counterion of which is presumably responsible for high pH values.

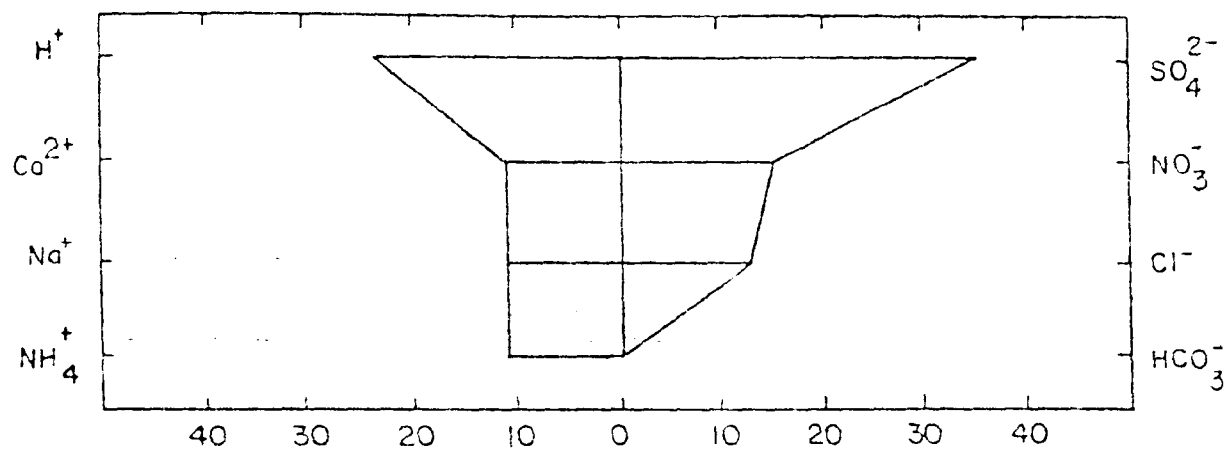
The predominant ionic constituents in Florida precipitation vary considerably from location to location; however, the salient geographic trends are clarified when the sites are organized into northern, southern and coastal groups (see Figure 5-2). The northern group of 12 precipitation collectors includes all inland sites north of Bradenton; and  $\text{H}^+$  and  $\text{SO}_4^{2-}$  dominated

Table 5-2. Comparison of acid-base chemistry of bulk precipitation at two coastal-inland pairs of sites in north Florida.

Site	Concentration (μeq/L)				
	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>+2</sup>	Excess-SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup>
Cedar Key (100 m from Gulf)	9.1	8.2	25.8	24.4	12.1
Bronson (50 km from Gulf)	18.2	10.3	15.8	27.7	10.9
Marineland (100 m from Atlantic)	3.0	7.4	82.0	26.8	17.7
Hastings (25 km from Atlantic)	17.4	7.5	17.0	32.8	11.6

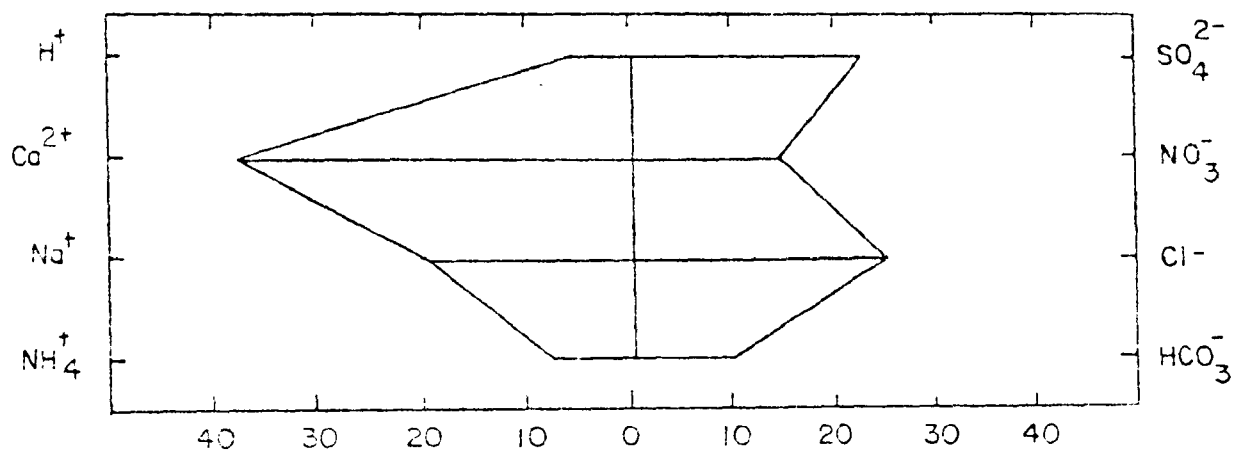
NORTHERN

(n=12)



SOUTHERN

(n=8)



COASTAL

(n=4)

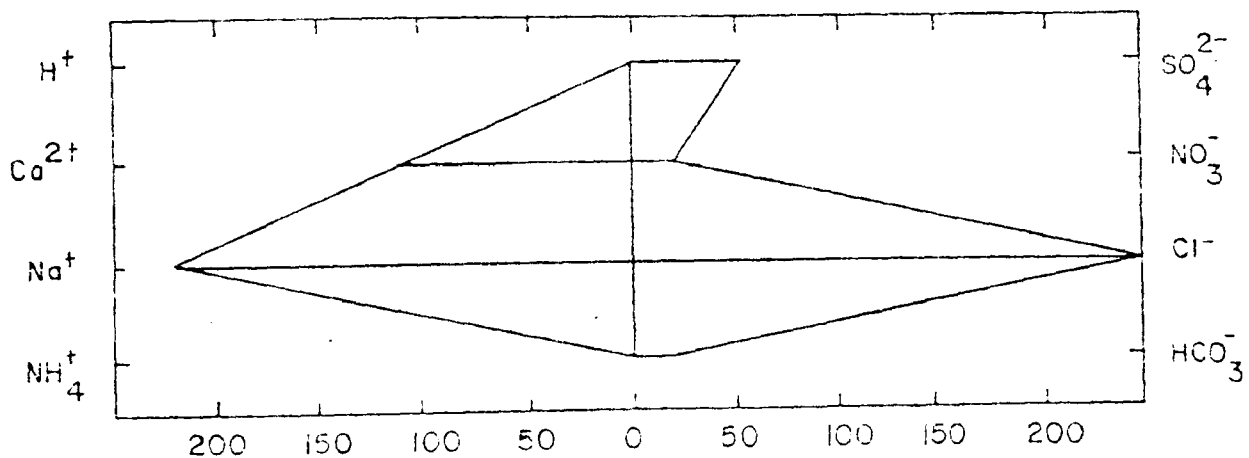


Figure 5-2. Chemistry of precipitation collected at (A) northern, (B) southern and (c) coastal locations. Units are ueq/L.

precipitation chemistry at these sites, representing 43% of the cations and 60% of anions, respectively. Compared to the northern sites, precipitation at southern locations (8 inland sites) exhibited a pronounced decrease in acidity, accompanied by a large increase in calcium and the appearance of substantial amounts of bicarbonate. Marine species ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) contributed significantly to the ionic loading at these sites, indicating the transition from a terrestrial-dominated to a maritime-dominated atmosphere in the southern region of the peninsula. Sulfate levels were about two thirds as high as in northern precipitation, but levels of nitrate (derived from  $\text{NO}_x$  that is emitted somewhat isotropically from mobile sources) and ammonium were similar in the two groups of sites. The north-south differential in  $\text{SO}_4^{2-}$  concentrations would be much larger if the Bradenton site had not been included in the southern group. This site had one of the highest (volume-weighted) mean  $\text{SO}_4^{2-}$  concentrations in the state (1.88 mg/L) and apparently is influenced by large emissions of  $\text{SO}_2$  in the Tampa Bay region.

Only at coastal locations (i.e. sites <5 km from the Atlantic Ocean or Gulf of Mexico) did sea salt constituents dominate the chemical composition of precipitation. Nevertheless, these four sites (two northern: Cedar Key and Marineland, and two southern: Stuart and Bahia Honda) show greater similarity to their inland counterparts than simple ionic balances suggest. Deviation from geological neutrality was minimal at these sites, but the cause of this, as previously mentioned, does not involve marine aerosols directly. Significant excesses of calcium, sulfate, ammonium and nitrate were found at all sites, after subtraction of the sea-salt component.

Ignoring sea-salt species, southern-coastal precipitation resembles southern-inland precipitation. Northern-coastal rainfall, with the exception of calcium and biocarbonate, likewise is similar to northern-inland rainfall. The exposed soils associated with coastal and southern areas apparently

foster entrainment of carbonate species (soil dust, shell fragments, limestone particles) in bulk collectors. Considering wet-only precipitation, there is a high resemblance between northern-inland and northern-coastal precipitation. For example, at Cedar Key wet-only samples were more than twice as acidic as corresponding bulk samples. Similarly, wet-only precipitation collected 100m from the ocean on Cape Canaveral had a pH of 4.56 (B. Madsen, University of Central Florida, pers. comm., 1979), which is very close to our value of 4.60 for Orlando, over 50 km inland.

#### B. Spatial Trends in Deposition of Acidity.

Deposition of acidity via bulk precipitation in Florida (Figure 5-3) ranged from 497 eq/ha at Jay to 21.1 eq/ha at MacArthur Farms, and averaged 182 eq/ha statewide. The extreme deposition at Jay reflects a combination of intensity and volume factors. Jay had the most acid bulk precipitation (weighted mean pH-4.62) in the network, as well as the heaviest precipitation (206 cm), during the study year.

At McArthur Farms, the situation was completely reversed. Rainfall pH was near geochemical neutrality, and rainfall amount, correspondingly, was the lowest in the state.

Loadings of  $H^+$  at the northern locations (n=14) were more than three times those of the southern locations (n=10), 272 eq/ha and 82 eq/ha, respectively. This latter value is only 2.6 times greater than would be contributed by the average annual southern rainfall at a pH of 5.6.

In general, loadings mirror the concentration distribution over the state; however, as in the case of the extremes previously discussed, there is some perturbation due to interaction between the concentration field and the rainfall field. This effect will be explored further in a later section.

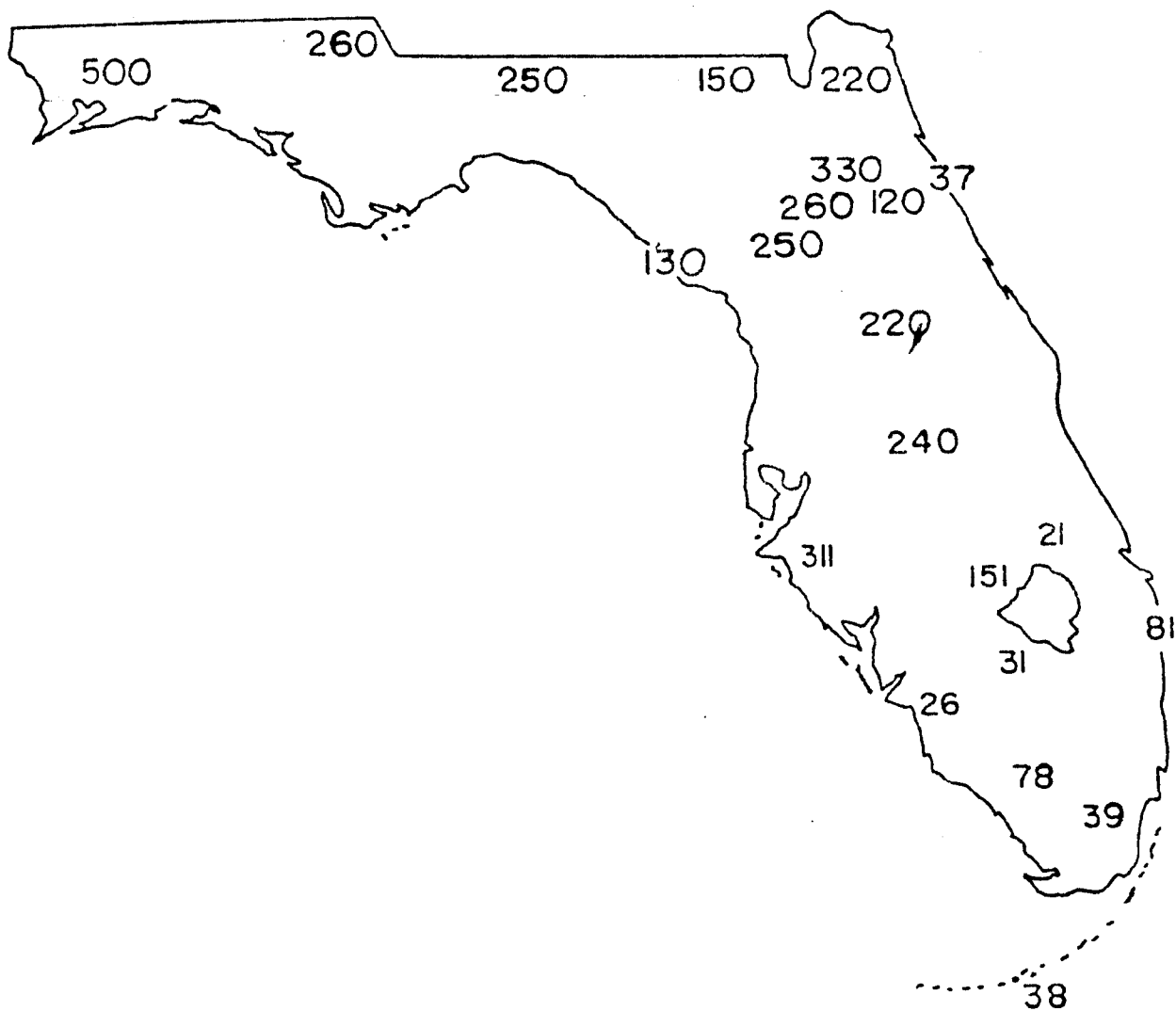


Figure 5-3. Acidity deposition (eq H<sup>+</sup>/ha) throughout Florida, for the period May 1978-April 1979.

### C. Spatial Trends in Sulfate Concentrations.

Sulfur occurs in precipitation almost exclusively as sulfate ion ( $\text{SO}_4^{2-}$ ). This fact is attributable to the high levels of  $\text{SO}_4^{2-}$  aerosols in the atmosphere, relative to other sulfur species, as well as the fact that most other forms of sulfur are rapidly oxidized to  $\text{SO}_4^{2-}$  in aqueous solution.

Sulfate can be partitioned into two classes on the basis of origin: sea -  $\text{SO}_4^{2-}$  and excess -  $\text{SO}_4^{2-}$ . The first of these refers to the sulfate present as a component of sea-salt, and is determined by the following expression:  $(\text{SO}_4^{2-})_{\text{sea}} = 0.25 \times (\text{Na}^+)$ ; where all  $\text{Na}^+$  in precipitation is assumed to be of oceanic origin.

Excess - Sulfate is that sulfate having any source other than the ocean (i.e. total -  $\text{SO}_4^{2-}$  minus sea -  $\text{SO}_4^{2-}$ ). On a global scale, the major precursors of excess -  $\text{SO}_4^{2-}$  are anthropogenic  $\text{SO}_2$  emissions and biogenic emissions, consisting primarily of  $\text{H}_2\text{S}$ , DMS and DMDS. Currently, these two sources of sulfur are thought to contribute about equally to the world sulfur cycle; however, the former is usually dominant in areas of high population density and industrial activity. The relative importance of these two sources on Florida precipitation will be treated in a later section.

A further distinction between excess -  $\text{SO}_4^{2-}$  and sea -  $\text{SO}_4^{2-}$  lies in the fact that only excess -  $\text{SO}_4^{2-}$  is an acidifying species in precipitation. Numerous rainfall studies (Coghill & Likens, 1974; Granat, 1972) have shown that excess -  $\text{SO}_4^{2-}$  is the dominant mineral acid in acid rain ( $\text{pH} < 5.6$ ), Sea -  $\text{SO}_4^{2-}$ , on the other hand, is not associated with  $\text{H}^+$ , due to the high pH of the ocean. Based on the ionic composition of seawater, sea -  $\text{SO}_4^{2-}$  is predominantly associated with  $\text{Na}^+$  and (to a lesser extent)  $\text{Mg}^{2+}$ . The spatial

distribution of excess -  $\text{SO}_4^{2-}$  and sea -  $\text{SO}_4^{2-}$  in Florida precipitation therefore merits separate discussion.

Concentrations of excess - sulfate in the state varied considerably from north to south (Figure 5-4a). In northern Florida, concentrations ranged from 1.17 mg/L (at Cedar Key) to 2.34 mg/L (at Jasper), and averaged 1.72 mg/L. Southern values, except for Bradenton (which is effected by Tampa area emissions), were distinctly lower, averaging only 1.14 mg/L. The three most pristine southern sites, Bahia Honda, Corkscrew Swamp, and Stuart, had concentrations of excess -  $\text{SO}_4^{2-}$  below one mg/L: 0.89, 0.96 and 0.98 mg/L, respectively. Thus, a factor of two differences occurred in the distribution of potentially acidifying excess - sulfate concentrations around the state.

Sea-salt sulfur is a less significant component of Florida rainfall chemistry than might be inferred from the peninsular nature of Florida and its extensive coastline. As shown in Figure 5-4b, sea -  $\text{SO}_4^{2-}$  concentrations were small everywhere in the state, except for the coastal periphery. Concentrations ranged from 0.09 mg/L, at Tallahassee and Jay, to 2.25 mg/L, at Marineland, and averaged 0.27 mg/L (or 18% of excess -  $\text{SO}_4^{2-}$ , statewide).

The average sea -  $\text{SO}_4^{2-}$  concentration for the four coastal sites (Marineland, Bahia Honda, Stuart, Cedar Key) was 0.95 mg/L, and only Marineland, had higher sea -  $\text{SO}_4^{2-}$  than excess -  $\text{SO}_4^{2-}$ . Inland sites, in contrast, averaged 0.11 mg/L sea -  $\text{SO}_4^{2-}$ , or only 7% of excess -  $\text{SO}_4^{2-}$  concentrations. The rapid disappearance of sea -  $\text{SO}_4^{2-}$  in rainfall with distance from the coast implies that oceanic aerosol particles are relatively large. The atmospheric lifetime of such aerosols thus is short, as a result of rapid gravitational settling.



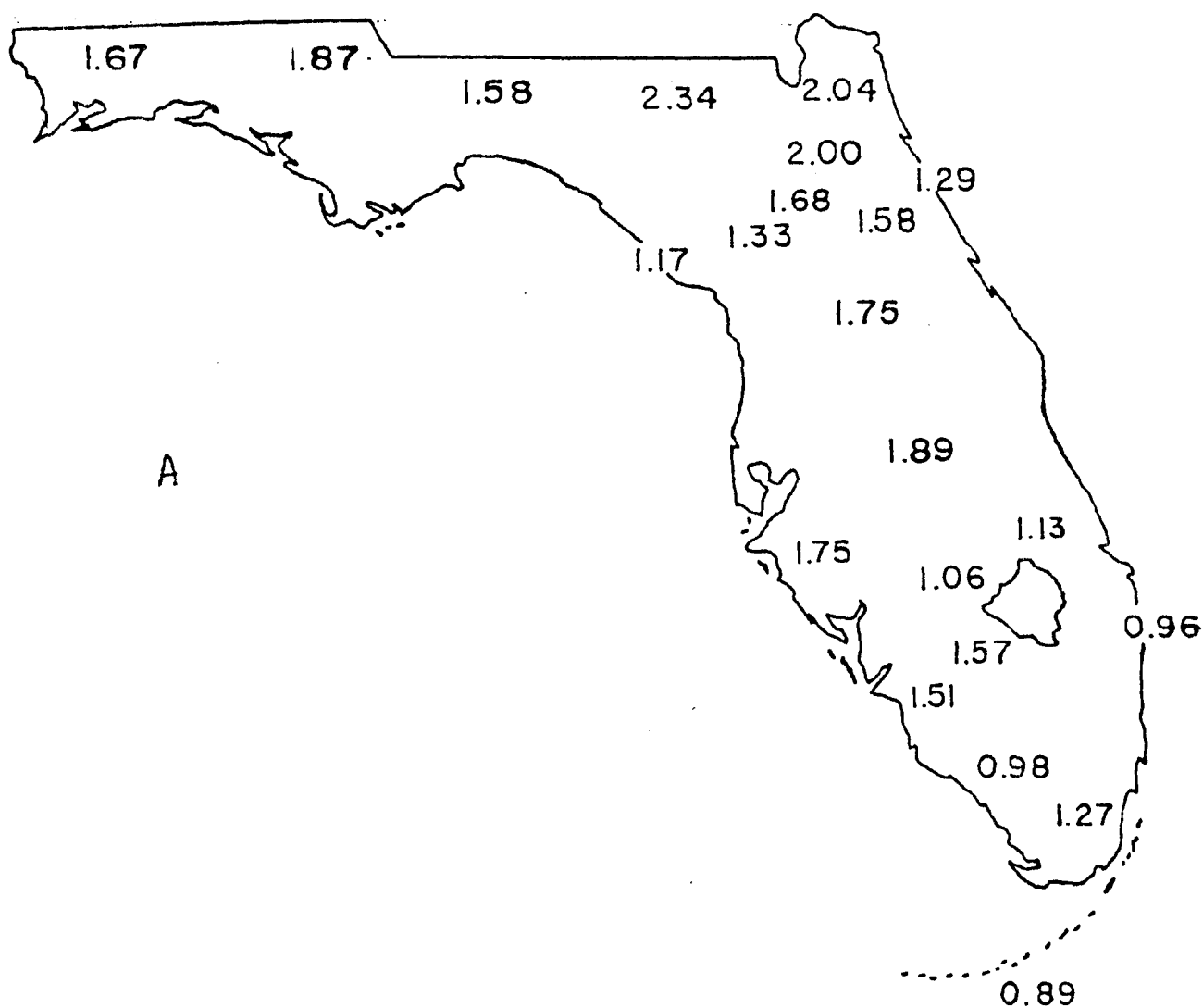


Figure 5-4. Volume-weighted mean concentration of (A) excess- $\text{SO}_4^{2-}$  and (B) sea- $\text{SO}_4^{2-}$ , for the intensive study year. Units are mg/L. (These figures to be reduced and displayed on same page).

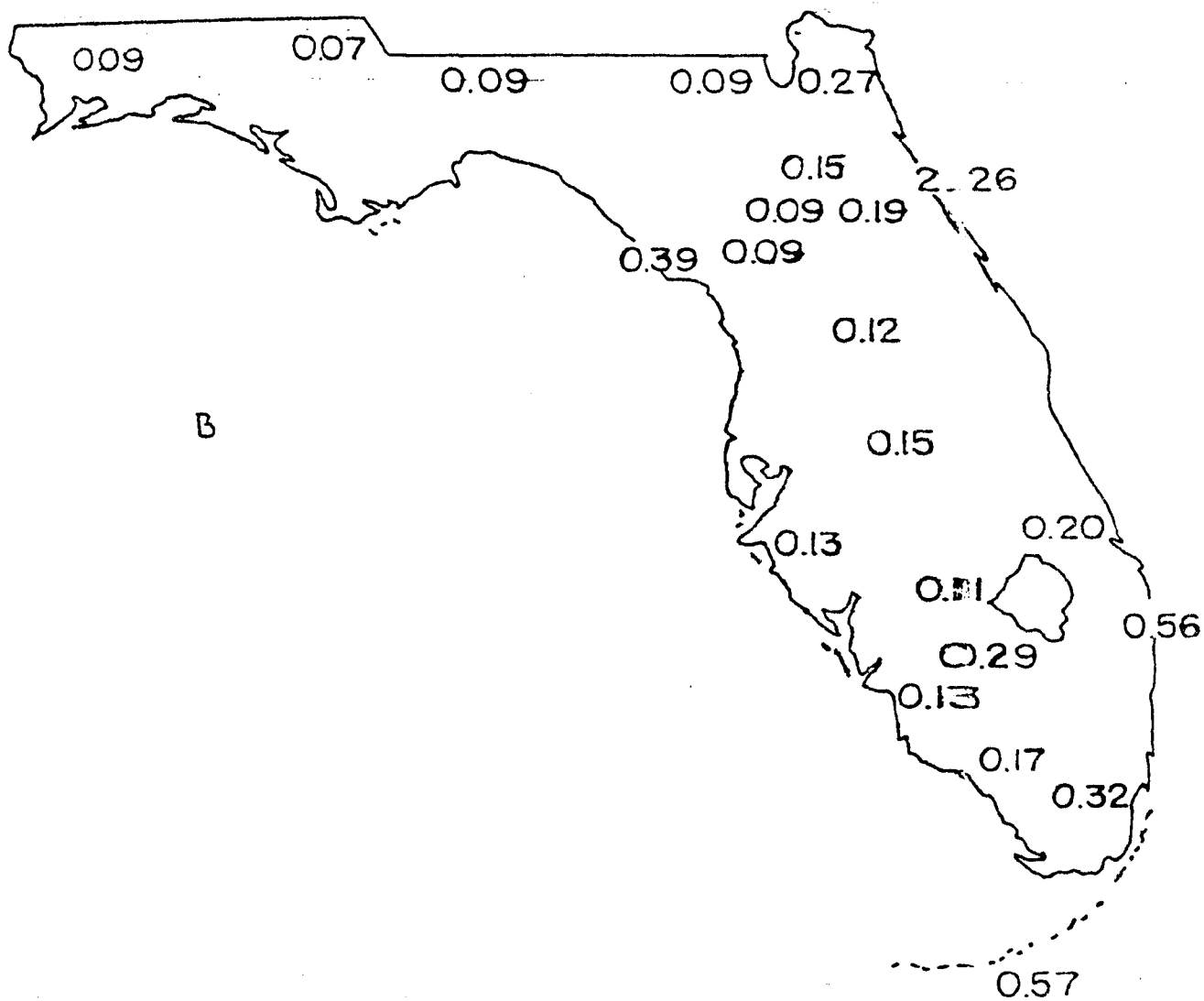


FIG. 5-4 B

#### D. Spatial Trends in Sulfur Deposition.

Deposition of sulfur in bulk precipitation at the 24 sites during the 12-month study period ranged from 12.1 kg/ha at Jay to 4.2 kg/ha at Corkscrew Swamp Sanctuary. As in the previous section on concentrations, it is meaningful to decompose the total-sulfur deposition into its sea-sulfur and excess-sulfur components, and to stratify the sites on the basis of northern, southern, and coastal locations.

Annual deposition of excess-sulfur (Figure 55a) thus was high at northern sites (mean=7.8 kg/ha), intermediate at southern sites (mean=5.2 kg/ha), and lowest at coastal sites (mean=4.4 kg/ha). The order is reversed for sea-sulfur (Figure 55b), where coastal sites, has the highest input, followed by southern, and then northern locations.

Excess-sulfur dominates sulfur deposition at all locations except Marineland, where large quantities of sea-salt are deposited near the turbulent coast. The ratio of excess-sulfur to sea-sulfur deposition at this site was 0.57, whereas that at inland Jay was 18.3. The corresponding ratio for the entire state was 5.8.

Annual deposition of excess-sulfur across the extreme northern portion of the state (Jacksonville, Jasper, Tallahassee, Chipley, Jay) averaged 9.5 kg/ha, which is similar to the value of about 10 kg/ha reported by Whelpdale & Galloway (1980) for the entire eastern United States.

Excess-sulfur deposition is considerably lower only a short distance (~50 km) south, where the Cedar Key-Bronson-Hastings-Marineland transect (See Figure 4-1) exhibited an average annual deposition of 5.8 kg/ha, within a relatively narrow range (5.35-6.41 kg/ha).

Still further south, excess-sulfur deposition rose substantially. At the Bradenton, Lisbon and Lake Alfred sites annual deposition averaged 8.5 kg/ha. This return to a higher rate of sulfur deposition may involve local

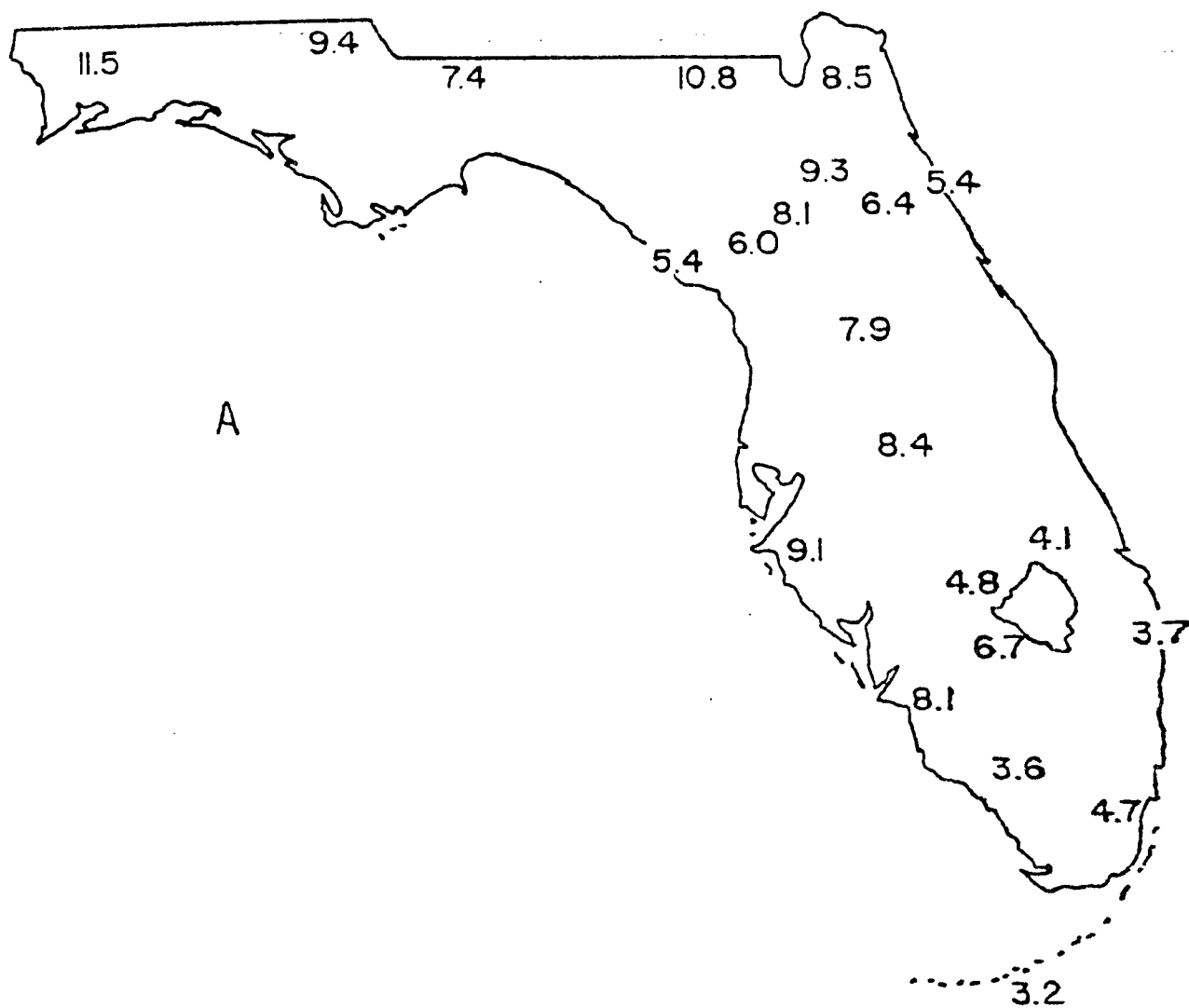


Figure 5-5. Annual deposition (kg/ha) of (A) excess-S and (B) sea-S across Florida. (These figures to be reduced and shown on same page)

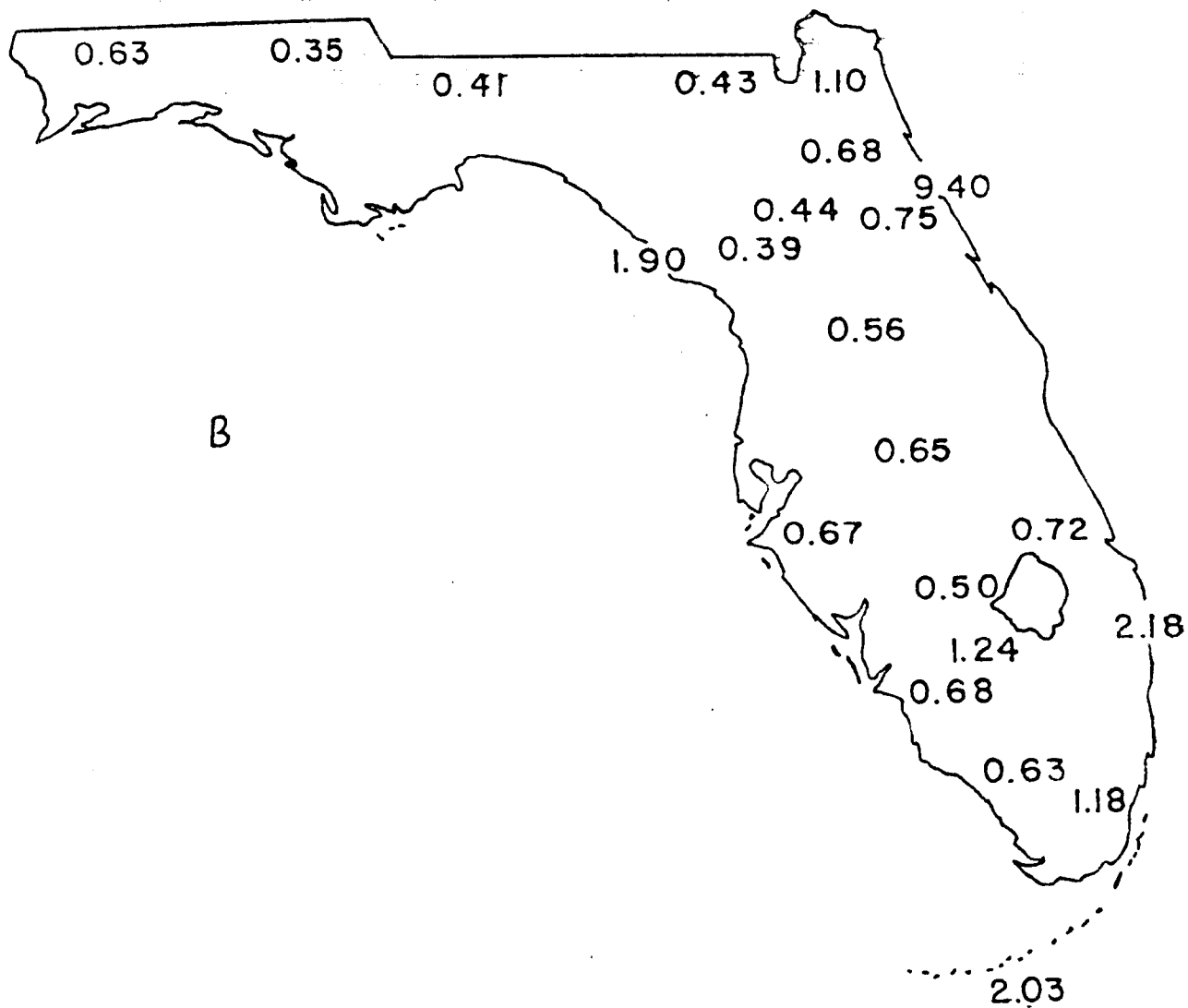


FIG. 5-5B

surface activities. However, a more likely source of the excess - sulfur increment is the Tampa area; where more than 20% of statewide sulfur emissions originates.

The undisturbed sites located south of Bradenton (Lake Placid, MacArthur, Stuart, Miami, Bahia Honda) had much lower annual deposition rates of excess sulfur. The average for this group of sites was only 4.1 kg/ha, and values ranged from 3.2 kg/ha at Bahia Honda to 4.8 kg/ha at Lake Placid.

Considering the state as a whole, analysis of the various groups of monitoring stations suggests a general trend of decreasing excess-sulfate deposition along the north-south axis. Super-imposed on this pattern is a region, within the central portion of the state, which is influenced by Tampa area emissions.

#### E. Acid-Mediating Species in Florida Precipitation.

Ionic balances and Granat-type calculations indicate that sulfuric and nitric acids account for the strong acidity of north Florida rainfall. Sulfate contributes about  $2.0\text{--}2.5 \times \text{H}^+$  as nitrate while chloride is highly associated with sodium and other sea-salt cations and does not influence acidity. Total acidity titrations of Gainesville precipitation (Hendry and Brezonik 1980) demonstrated that samples with ambient pH levels below 5.0 are dominated by strong acid species. The free acidity in such samples averaged about 80% of the total acidity, comparable to values reported for several northeastern locations. As noted by Galloway et al. (1976), weak acids encountered during a titration dissociate well above the initial pH of the rain sample, and thus do not contribute to the observed pH of rainfall.

Regression of  $\text{H}^+$  against excess- $\text{SO}_4^{2-}$  for 52 Gainesville wet-only rain samples collected from May 1978 - April 1979 gave a high  $r^2$  (0.70). A similar analysis using volume-weighted annual mean values for all 24 sites

resulted in a much lower  $r^2$  (0.25). Multiple regressions of  $H^+$  versus excess- $SO_4^{2-}$  and other parameters taken one at a time did not improve the correlation, until  $Ca^{2+}$  was added to the expression. Regression of  $H^+$  against  $xs-SO_4^{2-}$  and  $xs-Ca^{2+}$  yielded the equation:  $H^+ = 6.1 \text{ (to) } 0.54 (xs-SO_4^{2-}) - 0.35 (xs-Ca^{2+})$ ,  $R^2 = 0.75$ . Similar results were obtained earlier for Gainesville wet-only precipitation by Hendry and Brezonik (1980). Ammonium and nitrate do not contribute to the explanation of  $H^+$  levels significantly because they are distributed more or less isotropically in precipitation over the state (see Chapter 4). On the other hand, excess-sulfate and calcium vary considerably from site to site statewide; thus these two species and the degree of neutralization between them determine the pH of Florida precipitation. The endpoint of such an acid-base titration has been attained over most of Florida; i.e. the natural constituents (buffers) tending to resist change in precipitation acidity appear to have been overcome, especially in the northern part of the state.

#### F. The Influence of Rainfall Variability on Network Results.

Up to this point, concentrations and loadings of species have been presented, and geographic trends have been discussed, without reference to the variability of statewide precipitation. Since atmospheric deposition is a function of both concentration and rainfall amount, the examination of loading patterns necessarily requires consideration of rainfall patterns, as well. The purpose of this section is to determine the influence of spatially variable rainfall on the chemistry of the precipitation network, and to investigate the manner in which temporally variable rainfall (i.e. deviation from annual norms) effects precipitation chemistry at individual sites.

The first of these topics can be addressed by considering the amount of rain collected at the 24 monitoring stations during the study period.

As shown in Figure 5b, the 12-month rainfall was uniform over the central portion of the state, relatively high in the Panhandle, and relatively low in the southern extremes. The average rainfall for the 14 northern and 10 southern sites was 140 in and 127 in, respectively. This 9% difference in rainfall between the two groups of sites is small relative to the concentration/deposition differentials observed for many species. Thus, it can be inferred that rainfall amount is not a major factor contributing to the disparate results for northern and southern Florida.

The relationship between statewide deposition values and rainfall amounts was further tested by regression of annual loadings against weighted-mean concentrations and yearly precipitation at all 24 sites. Results of this analysis show that concentration is the dominant variable in the deposition of all major anions and cations (including the various nutrient forms).

The above findings suggest the regional concentration/deposition pattern is real, and not an artifact of rainfall variability; however, there are a number of potential difficulties with the method of spatial averaging. Most important is the possibility that systematic effects are incorporated, rather than eliminated, by such an averaging process. For example, this effect could occur as the result of a significant departure from the average annual rainfall over an entire region (e.g. North Florida vs. South Florida). When only a single year of chemical data is available, this possibility is more serious, because there is no way to smooth results by averaging several yearly values that represent a range in annual precipitation.

Insight into the reasonableness of the data for the individual monitoring sites can be obtained by comparing observed rainfall with long-term annual averages. The ratio of observed to average precipitation can



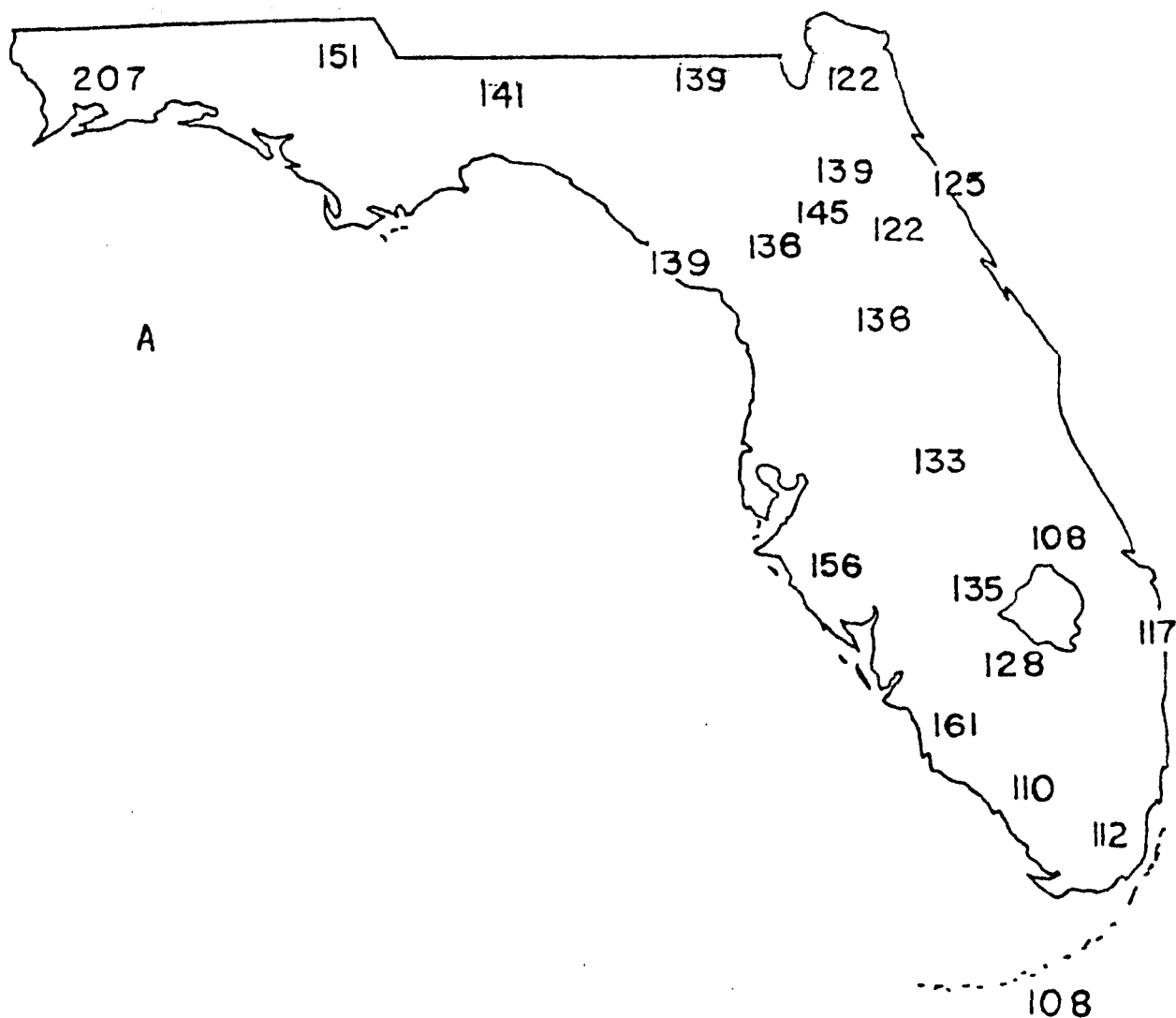
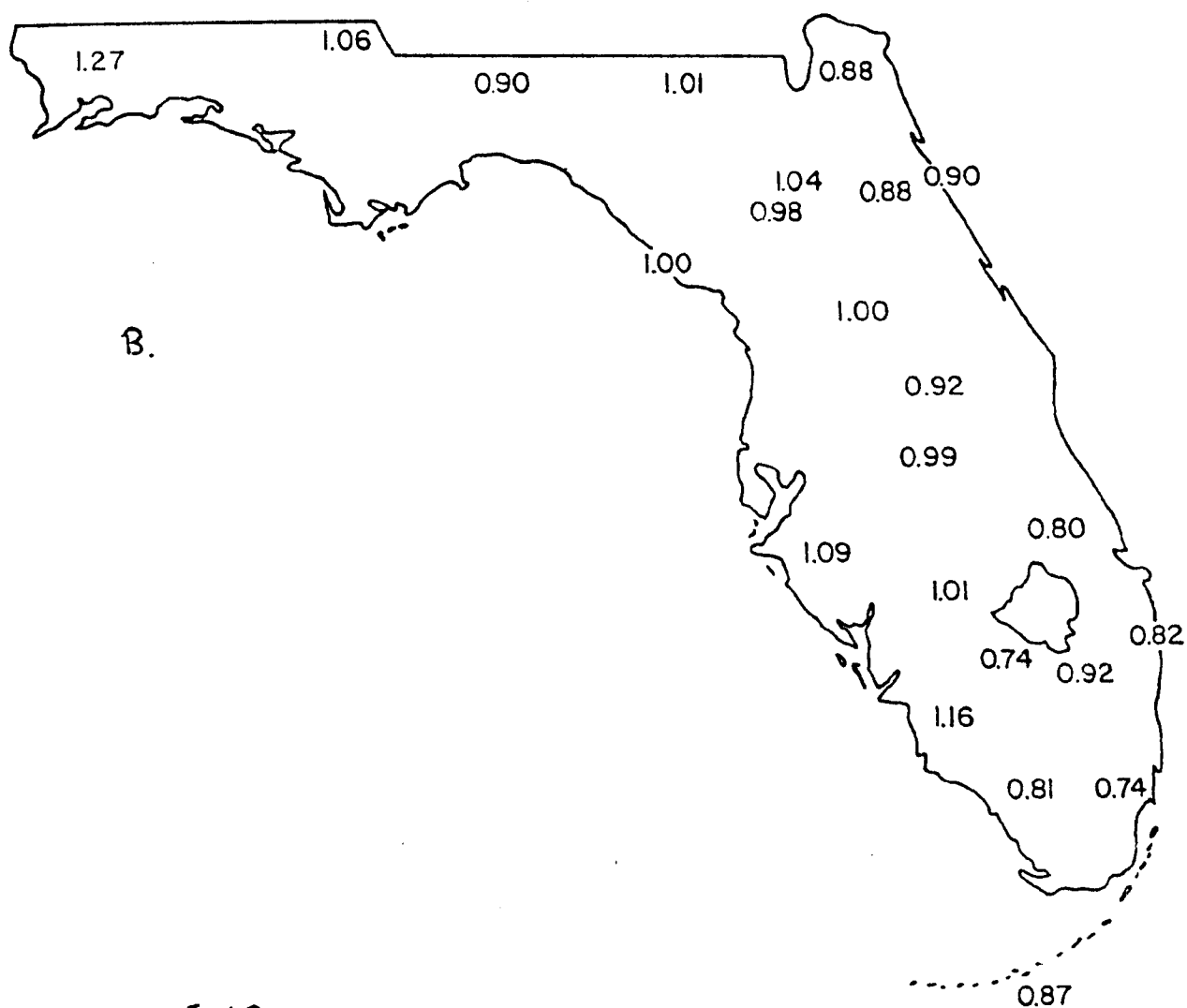


Figure 5-6. A. 12 month rainfall totals (cm) for stations in the Florida Atmospheric Deposition Study, May 1978-June 1979. (These figures to be reduced and shown on same page)  
 B. Above data normalized to 10-year average (1969-1978) rainfall at identical, or nearly, locations.



be used to infer the true (long term) average concentrations and average depositions, assuming that two limiting cases bound the relationship between rainfall chemistry and rainfall amount.

In the first case, abnormal rainfall is considered to be a function of the size of the average event. A wet year would have larger events than usual; hence solute concentrations would tend to be low (compared to the average year). The converse would be true for a dry year. This relationship follows from our experience at Gainesville, where the concentrations of  $H^+$ , excess- $SO_4^{2-}$  and  $NO_3^-$  were found to obey the following expression:

$$[\text{solute}] = a (\text{rain})^b,$$

where rain is the size of an event, and b is in the range  $-0.55$  to  $-0.65$ .

In the other limiting case, high or low annual rainfall can be construed as simply a function of event frequency. For Gainesville precipitation, no apparent relationship has been found between  $H^+$ ,  $SO_4^{2-}$ ,  $NH_4^+$ ,  $NO_3^-$  concentrations and the period of time between events. Rainfall concentrations, then, will be taken as invariant with respect to event frequency.

By combining these limiting assumptions, a range of expected concentration/deposition values can be estimated for the individual sites, as a function of annual precipitation. For years with below average rainfall (i.e.  $R/\bar{R} \leq 1.00$ ), we have:

$1.00 \leq C/\bar{C} \leq (R/\bar{R})^{-0.60}$   $(R/\bar{R})^{0.40} \geq D/\bar{D} \leq (R/\bar{R})^{1.00}$  and for years with above average rainfall (i.e.  $R/\bar{R} > 1.00$ ) we have:

$$(R/\bar{R})^{-0.60} \leq C/\bar{C} \leq 1.00; (R/\bar{R})^{1.00} \geq D/\bar{D} \geq (R/\bar{R})^{0.40}$$

Referring to Figure 6L, it is apparent, on the basis of rainfall alone, that a number of sites may have experienced somewhat unusual rainfall chemistry during the study period. Jay, for example, was extremely wet,

indicating that long-term average concentrations might be higher by as much as 15%, and deposition values lower by 10-20%. For all remaining northern sites, correction factors amount to less than 10%, and so there is little real advantage to their use.

The situation is different for the southern sites, as rainfall was far from average in this part of the state during 1978-1979. Seven of the ten sites received significantly less than average rainfall, while two received somewhat more than average. Clewiston and Miami were the driest sites, with just under 75% of the normal annual rain. For these extreme locations, representative concentration values may be as low as 73% of those reported, while deposition values may be 13-35% higher. Correction factors for the other sites are lower than this, but are still significant in most cases.

The mean northern and southern rainfall amounts were 99% and 89%, respectively, of the long-term average. Since the anomalous value for the southern sites raises the possibility that rainfall was systematically involved in spatial trends, corrected loadings were calculated for all sites, using excess-SO<sub>4</sub><sup>2-</sup> as an example species. Resultant deposition was essentially unchanged for the north Florida group, but deposition may have been up to 13% higher for the south Florida group. Despite these corrections, the excess-SO<sub>4</sub><sup>2-</sup> deposition remained statistically higher ( $p < 0.05$ ) in north Florida than in south Florida, even when the upper-limit deposition correction was applied to the latter area.

The findings presented in this section support two conclusions. First, the spatial variation in rainfall during the study year exerted only a

minor influence on the overall geographic trends in concentration and deposition. Second, the 1978-79 observations deviate in certain instances from expectation; in a general sense, however, they are representative (especially for northern Florida) of what might be observed during a year of normal (average) precipitation.

#### G. Variations in Precipitation Chemistry within the Vicinity of Gainesville.

The statewide precipitation network described above has provided useful information on meso-scale trends in precipitation chemistry, but by itself it does not address the question of local (micro-scale) variability in precipitation chemistry. In addition, the statewide network had no paired stations to compare urban and non-urban rainfall quality for a given area (i.e. a city and its surrounding countryside), although such sites are of interest to obtain information on the geographic extent of urban influence on precipitation chemistry. Consequently, a mini-network of precipitation collectors was established, and sampled on a weekly basis during the period July-September, 1979. This consisted of a line of three bulk rainfall collectors, spaced at approximately 3 km intervals and extending due south from Gainesville to Paynes Prairie, the dry bed of the former and ephemeral Alachua Lake.

With access controlled by the Florida Department of Natural Resources and no inhabitants on the prairie, Paynes Prairie is an ideal setting for the collection of rural precipitation. The collectors were located at least 2 km from the nearest well-traveled road and from any agricultural activity.

The reference collectors for this study were a wet/dry and a bulk sampler at the University of Florida campus in southwest Gainesville,

a semi-urban site with considerable automobile traffic within a few hundred meters in any direction and a small (~50 car) parking lot within 10 m of the collectors. The campus sewage treatment plant is 250 m north of the collectors. The only significant point sources of sulfur oxides in the area are 3 km due east and 15 km northwest of campus. Rainfall sampling at this site was performed on an event basis, as described earlier.

The 10-week volume-weighted mean concentrations of  $H^+$ ,  $NH_4^+$ ,  $Ca^{+2}$ ,  $SO_4^{-2}$  and  $NO_3^-$  for the four sites (Table 5-3) show that the three Paynes Prairie rain collectors yielded similar chemical data. For the rural stations,  $H^+$  exhibited the broadest concentration range (3.9  $\mu eq/L$ ), corresponding to a pH difference of 0.06 units, but this range is only slightly larger than the inherent uncertainty in pH measurements (~0.03 units). Concentrations of the remaining major ions were within their respective analytical uncertainties, with the exception of  $NH_4^+$ , which ranged from 3.7  $\mu eq/L$  at site 2 to 6.3  $\mu eq/L$  at site 1.

There is no evidence of contamination or of local sources for any of the species analyzed at the Paynes Prairie sites. Rainfall amount was the only parameter exhibiting any sort of a trend, (a monotonic decrease with distance from Gainesville), but there was no correlation of this trend with rainfall chemistry.

Comparison of the rural Paynes Prairie results with those for Gainesville (semi-urban) bulk precipitation show that the latter environment appreciably disturbs the bulk deposition of numerous species. This is demonstrated by substantial increased in  $Ca^{2+}$  and  $SO_4^{2-}$  levels, and a reduction of acidity at the Gainesville site. Calcium (actually its counter-ion) is clearly indicated as the neutralizing species of the semi-urban bulk precipitation, i.e. it is the only cation with a sufficient concentration gradient

Table 5-3. Comparison of acidic and basic species in Gainesville and Paynes Prairie precipitation, collected 7/12 - 10/1/79. Numbers in parentheses correspond to distances, in kilometers, from Gainesville site.

Location	Rainfall (cm)	pH	Concentration (meq/L)				
			H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>+2</sup>	SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup>
Gainesville wet	41.9	4.49	32.3	6.7	7.3	25.2	14.4
Gainesville bulk	41.9	4.65	22.4	7.1	17.6	32.7	15.6
Paynes Prairie #1 (4)	39.8	4.57	26.8	6.3	5.0	24.8	11.9
Paynes Prairie #2 (7)	38.3	4.57	26.8	3.7	6.1	26.7	13.1
Paynes Prairie #3 (10)	36.8	4.51	30.7	5.4	5.9	25.6	13.9

between the Gainesville and Paynes Prairie sites. The correlation of high  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in Gainesville bulk precipitation suggests that, in the absence of a strong  $\text{SO}_2$  or particulate sulfate concentration gradient between Gainesville and Paynes Prairie, high bulk precipitation  $\text{SO}_4^{2-}$  values in town may result from scavenging of  $\text{SO}_2$  by locally high levels of particulate  $\text{Ca}^{2+}$ .

The nitrogen species  $\text{NH}_4^+$  and  $\text{NO}_3^-$  appear to be slightly influenced by Gainesville, the former probably by the nearby sewage treatment plant, and the latter perhaps, by automobile traffic in the urban area. However, the magnitude of the differences is small, and their significance is uncertain. For the most part, there is a high degree of similarity between the Gainesville wet-only and the Paynes Prairies bulk precipitation, suggesting that the dryfall component at the rural sites is less significant than that in town.

Gainesville wet-only precipitation did have higher concentrations of several species than the Paynes Prairie sites, however (Table 5-3).  $\text{H}^+$  was significantly higher at the semi-urban site while  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  were marginally higher. These results underscore the fact that wet collectors also are affected by local perturbations of the environment. Comparing the Gainesville wet-only and bulk results, it is clear that the wet/dry collector is capable of filtering out the greater part of local influences.

Two conclusions can be derived from the mini-network. First, the impact of the urban areas on precipitation chemistry is dependent on the type of sampling (wet/dry or bulk) performed. Relative to the University of Florida site, its proximity to Gainesville exerts an important influence on bulk precipitation but only a minor influence on wet-only precipitation. Second, the perturbations of rainfall chemistry caused by Gainesville are of limited spatial extent. At the nearest Paynes Prairie site (4 km from



~~At~~ The Gainesville site), the impact of Gainesville is not discernible from the random variability of the measured parameters. Atmospheric contaminants generated within Gainesville thus blend smoothly into the regional background, either by dispersion or deposition mechanisms, over a scale length of less than 4 km.

## WET, BULK, AND DRY DEPOSITION OF ACIDIC AND BASIC SPECIES

### A. Comparison of Wet and Bulk Precipitation Chemistry.

Wet-only precipitation was more acidic than bulk precipitation throughout the state; pH values of wet rainfall were 0.2-0.4 units lower than those of nearby bulk samples (Figure 5-7).

The relationship of rainfall acidity to rainfall amounts indicates some differences between the two methods of collection. For wet-only samples (Figure 5-7a), hydrogen ion concentration decayed rapidly with rainfall amount, and leveled off, in the vicinity of 10-20  $\mu\text{eq/L}$  for large (>2 cm) events. The plot for bulk events differs in that the vertical limb of the previous relationship is absent and many small storms were almost completely neutralized. Concentrations of  $\text{H}^+$  in bulk precipitation tend to increase with the amount of rain collected up to about 2 cm of rainfall, then level off in the same manner as the wet samples. Apparently, the  $\text{H}^+$  content of the initial rainfall (1-2 cm) is neutralized by an alkaline component of dryfall, most likely carbonate.

Comparison of wet deposition with bulk (wet plus dry) deposition at five sites (Table 5-4) shows that nitrate, sulfate and ammonium are associated with an acidic wet phase, while calcium is predominantly a component of dry deposition. The anion associated with calcium thus neutralizes rainfall in bulk collectors and is largely responsible for differences observed between neighboring wet and bulk samplers (Figure 5-7). At Gainesville, the average precipitation event (2.50 cm of rain) deposited 600 and 450  $\mu\text{eq}$

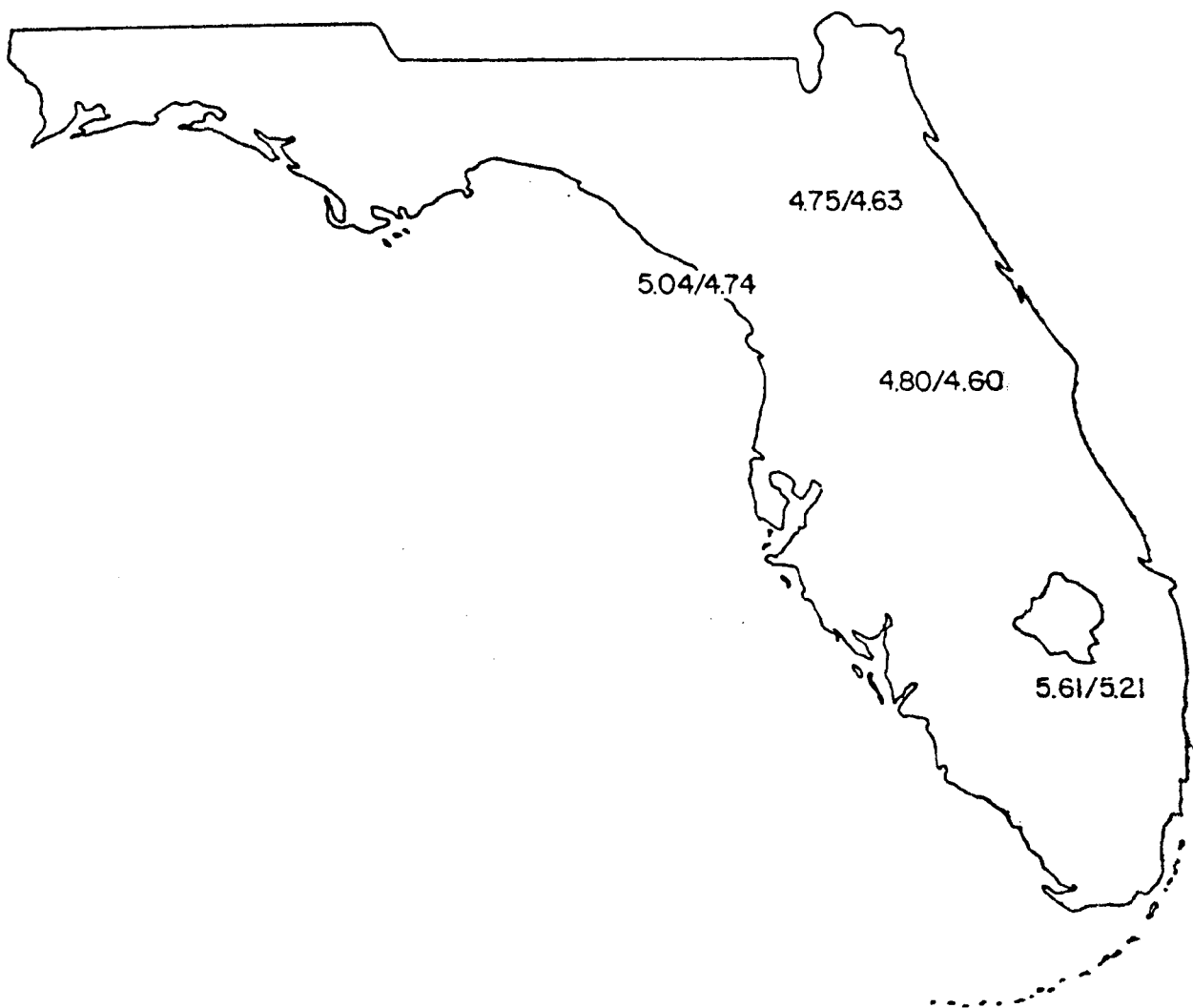


Figure 5-7. Comparison of annual weighted-mean pH of bulk (above slash) and wet-only (below slash) precipitation. Locations are, from north to south: Gainesville, Cedar Key, Apopka, Belle Glade.

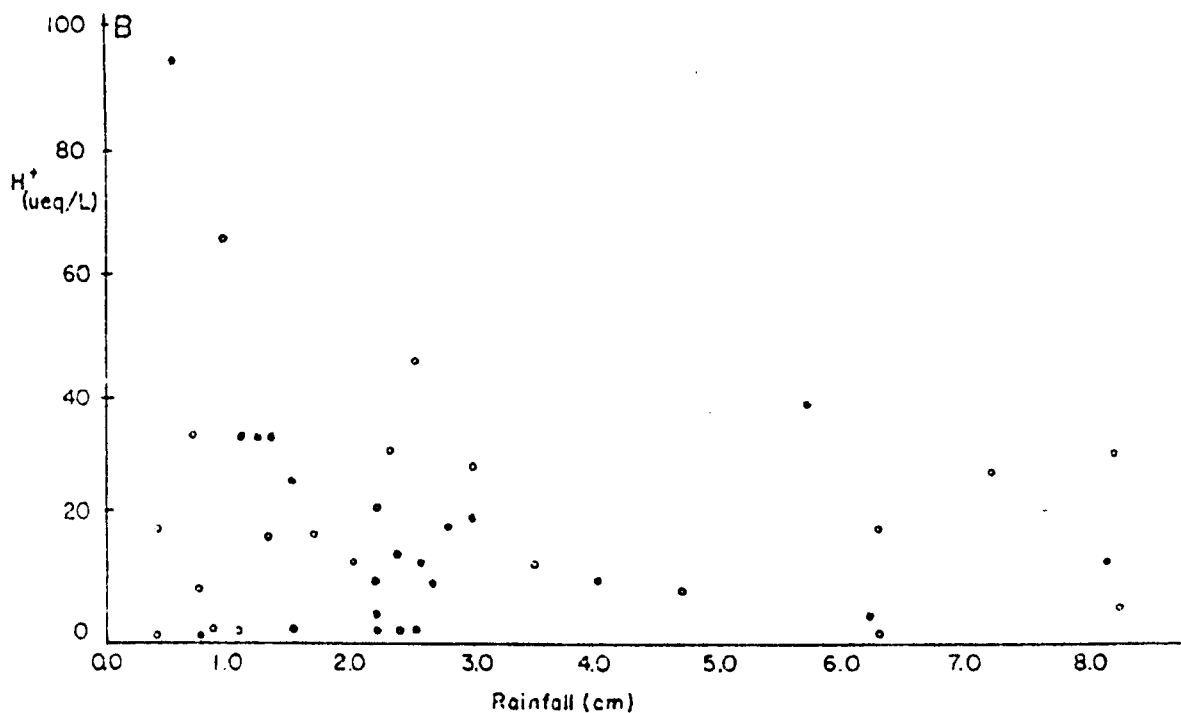
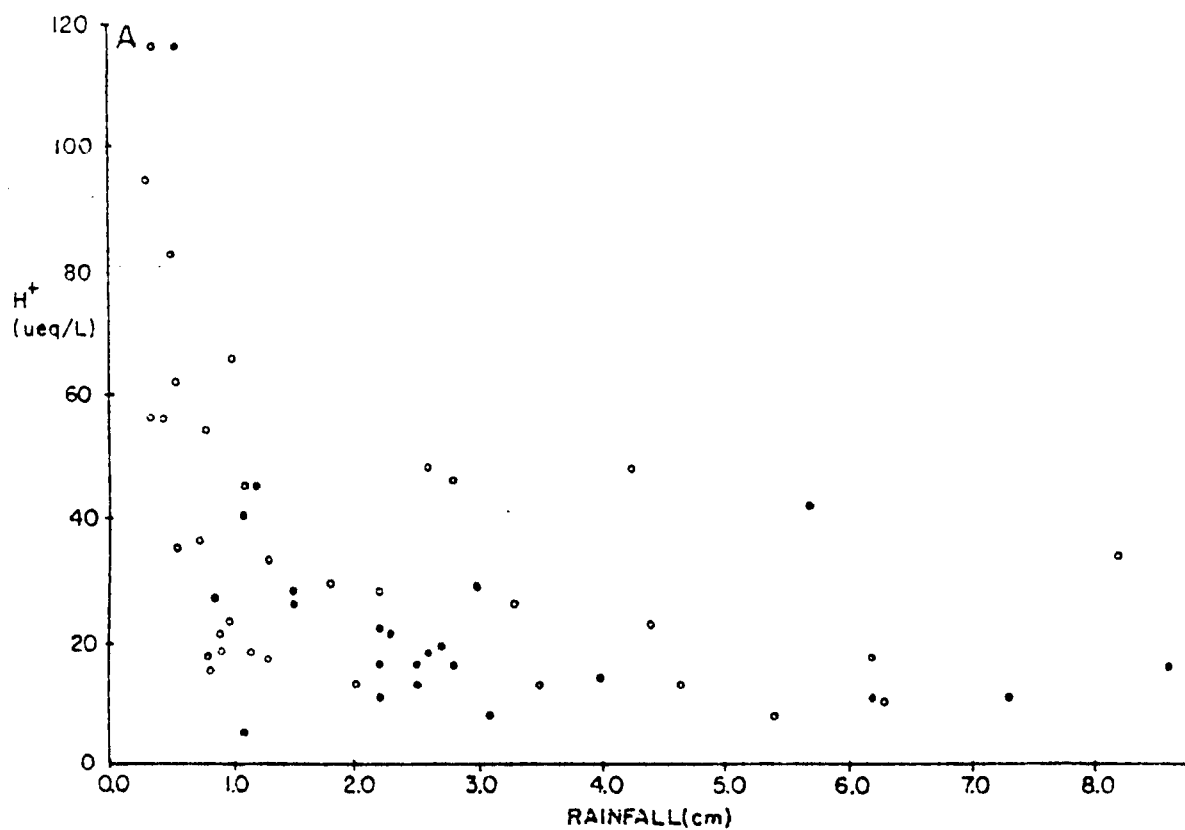


Figure 5-8. Relationship of  $H^+$  concentration to rainfall amount for winter (•) and summer (o) wet-only events (A) and bulk events (B) collected at Gainesville.

Table 5-4. Relative loadings in wet versus total (wet + dry) precipitation. Values correspond to % deposition from wet-only precipitation.

Location	H <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	Excess SO <sub>4</sub> <sup>=</sup>	Cl <sup>-</sup>
Gainesville (semi-urban)	100	59	59	31	40	88	68	74	61
Orlando (Agricultural)	100	57	55	52	45	73	74	77	61
Belle Glade (Agricultural)	100	59	60	40	45	85	72	75	60
Cedar Key (Gulf Coast)	100	81	72	54	69	82	62	88	81
Cape Canaveral (Atlantic Coast)	100	18	18	24	19	71	61	71	17

$H^+/m^2$  in wet and bulk collectors, respectively. The difference is almost exactly balanced by the  $147 \mu eq/m^2$  of bicarbonate deposited (on the basis of cation excess) in statewide dryfall samples between collections.

#### B. Dry Deposition of Acidic and Basic Species.

Dry deposition is well known as an important mechanism of nutrient and mineral input to ecosystems (see Chapter 4). The term 'dry deposition' embraces a variety of interaction mechanisms between surfaces (sinks) of variable resistance to deposition, aerosol particles over a broad size range and gaseous species of widely disparate reactivities. Dry deposition involves two distinct physical processes: eddy and gravitational deposition. The first of these addresses the transport of gases and sub-micron particles to receptor surfaces via turbulent eddies. Gravitational deposition is simply the settling of relatively large ( $> 2\mu m$ ) particles due to gravitational forces that impart high settling velocities to these particles..

The purpose of this section is twofold: 1) to examine the significance of dry deposition versus wet deposition for species related to acid precipitation, and 2) to determine the influence of season on dry deposition rates.

Annual loading rates of alkalinity, excess- $SO_4^{2-}$ ,  $NO_3^-$ ,  $Ca^{2+}$ ,  $NH_4^+$  to dryfall collectors at five locations within the state are summarized in Table 5-5. Alkalinity was inferred by ionic balance and presumably reflects carbonate species. This parameter represents an appreciable fraction of the total dryfall loading at all sites. Deposition rates of  $Ca^{2+}$ , excess- $SO_4^{2-}$ , and alkalinity follow the pattern Belle Glade > Gainesville > Cedar Key = Apopka area, though agricultural activity (sugarcane, winter vegetables), where large quantities of particulate matter are injected into the atmosphere. The Apopka area, though agricultural, is planted largely to citrus, which requires substantially less tillage than do the crops grown at Belle Glade.

Table 5-5. Annual dry deposition of acid-mediating species at 4 Florida sites.

Location	Alkalinity*	<u>Deposition (EQ/HA)</u>			
		Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
Gainesville	173.	315.	19.3	159.	57.1
Orlando	105.	152.	29.1	104.	49.2
Cedar Key	90.	182.	18.5	84.2	72.3
Belle Glade	741.	868.	21.2	153.	87.2

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\* Alkalinity inferred from net excess of analyzed anions. Value for Belle Glade is probably a several-fold over-estimate, due to high deposition of soil organic matter (associated with Ca<sup>2+</sup>) at this site.

Inorganic nitrogen species are relatively minor components of dryfall. Except for Belle Glade,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were deposited more or less uniformly throughout the state, suggesting that the atmospheric sources of  $\text{NH}_3$  and  $\text{NO}_x$  are either quite diffuse or remote from the collection sites.

The relative importance of wet and dry deposition for species that affect rainfall acidity is summarized in Table 5-4. Hydrogen ion, excess- $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are highly associated with an acidic wet phase. Being gases, or sub-micron aerosols, these species have insignificant settling velocities and small dry deposition rates. The nature of the collector buckets also may affect dry deposition of these species; this topic is addressed later.

The terrestrial species  $\text{Ca}^{2+}$  is deposited primarily through dry processes. Apparently  $\text{Ca}^{2+}$  occurs in the atmosphere in supra-micron particles which have significant settling velocities. Furthermore, the dryfall bucket is near (~1 m) to the source of these species (the soil), and it probably is influenced by steep concentration gradients near the surface.

Dry deposition rates for the major inorganic species were generally higher during winter than summer (Table 5-6). The striking exception to this is  $\text{NH}_4^+$ , of which two-thirds is deposited during the summer. This presumably reflects enhanced evolution of  $\text{NH}_3$  from soils during the warm months. The seasonally disparate deposition rates for most species at Belle Glade are the result of local agricultural practices. During the winter and early spring months (primarily January to April), burning of sugarcane fields results in suspension of large amounts of particulate matter in the atmosphere. The deposition rates of soil species are enhanced directly by this process. Crop burning has recently been shown to release most of the sulfur contained in vegetative tissue (J. Ewel, Univ. Fla. pers. comm. 1979), and deposition of

Table 5-6. Comparison of winter (Nov-Apr) and summer (May-Oct) dry deposition of major ionic species.

Location	Seasonal deposition (kg/ha)							
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	SO <sub>4</sub> <sup>=</sup>	Cl <sup>-</sup>
Gainesville								
Winter	1.35	0.27	3.46	0.36	0.09	0.42	3.82	2.53
Summer	0.95	0.27	2.84	0.46	0.18	0.38	3.82	2.01
Orlando								
Winter	1.83	0.64	1.97	0.35	0.21	0.36	2.84	2.91
Summer	1.67	0.53	1.06	0.25	0.19	0.33	2.14	2.64
Cedar Key								
Winter	2.84	0.29	2.04	0.46	0.09	0.53	2.18	5.02
Summer	1.79	0.27	1.59	0.29	0.16	0.48	1.83	3.26
Belle Glade								
Winter	2.80	1.15	9.70	0.91	0.08	0.60	4.68	5.90
Summer	1.65	0.71	7.65	0.49	0.22	0.62	2.67	3.57



$\text{SO}_4^{2-}$  also may be enhanced by this practice, first by the release of  $\text{SO}_2$  and second by the attachment of  $\text{SO}_2$  to, particulates generated in high concentrations by the burning process.

High wintertime deposition rates for  $\text{Ca}^{+2}$ , at the other sites, may be the result of seasonally high winds. For sea-salt species, this seasonal trend results in increased atmospheric injection as well as rapid transport inland (See Chapter 4, Table 4-9). Soil species such as  $\text{Ca}^{2+}$  also should have augmented suspension and deposition rates due to seasonally high surface turbulence.

Frequency of precipitation may also influence dry deposition rates. All other factors being equal, the more often the atmosphere is cleansed by rain, the lower the time-averaged concentration of contaminants. Precipitation events occur approximately once a week during the winter, in Florida, and two to three times a week during the summer. Therefore the levels of various pollutants, particularly those preferentially scavenged by washout processes (eg.  $\text{Ca}^{+2}$ ), should be lower during the summer. Insufficient seasonal data on atmospheric concentrations are available, as yet, to test the validity of this concept.

#### TEMPORAL PATTERNS IN PRECIPITATION ACIDITY

##### A. Seasonal Trends.

Summer rains (May-Oct) are more acidic (by 0.2-0.3 pH units) than winter rains (Nov-Apr) throughout the state (Figure 5-9). In summer, the pH 4.7 isopleth encompasses all of the panhandle and about half of the peninsular portion of the state, and there is no geo-chemically neutral rain ( $\text{pH} > 5.6$ ) anywhere in the state. During the winter, the pH 4.7 isopleth is displaced to the north of the state and is replaced by a pH 5.0 contour. Geochemically neutral rain occurs in large areas of the southern peninsula during this season.

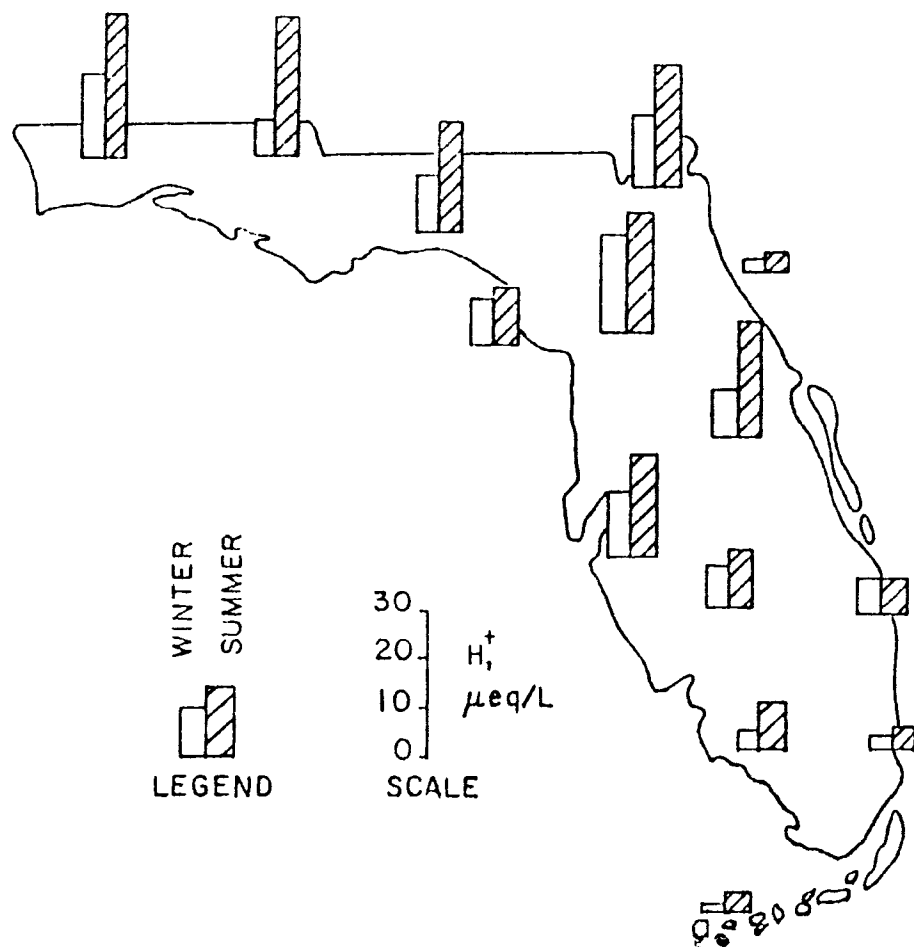


Figure 5-9. Volume-weighted mean  $H^+$  concentration for summer (May-Oct) and winter (Nov-Apr) across Florida. For clarity, not all sites are depicted; statewide means (all sites) are shown in legend.

The seasonal and spatial dichotomies of Florida precipitation are underscored in Figure 5-10, which illustrates monthly volume-weighted mean concentrations of  $H^+$ ,  $xs-SO_4^{2-}$ , and  $NO_3^-$  for the northern (n=14) and southern (n=10) sites during the 1978-79 one-year period. As previously stated,  $H^+$  was higher in northern sites than southern sites, and was highest in the north during the summer months. Southern precipitation varied less in  $H^+$  concentration from month to month, but  $H^+$  was clearly higher in summer than in winter.

In the north, excess  $SO_4^{2-}$  and  $NO_3^-$  exhibited similar seasonal patterns. Excess  $SO_4^{2-}$  levels were consistently high during summer (May-Oct) and low during winter (Nov-Apr). The lowest concentrations occurred, as with  $H^+$ , during the relatively dry months of transition between convective and frontal storm activity (November, December and April).

Nitrate concentrations generally adhered to the pattern of high summer and low winter values. During the dry months of November and April, however, levels of  $NO_3^-$  were elevated rather than reduced. The contrasting behavior of excess- $SO_4^{2-}$  and  $NO_3^-$  during these 2 months reflects the fact that dryfall represents a greater proportion of  $NO_3^-$  deposition (33%) than of excess  $SO_4^{2-}$  deposition (24%).

There were no clearly defined seasonality of excess  $SO_4^{2-}$  and  $NO_3^-$  concentrations in south Florida precipitation. The transition months exhibited the lowest values for these two ions, but the average winter concentration did not differ significantly from the average summer concentrations.

Both excess- $SO_4^{2-}$  and  $NO_3^-$  were as high (or higher) in southern-winter precipitation as in northern-winter precipitation, a reversal of the

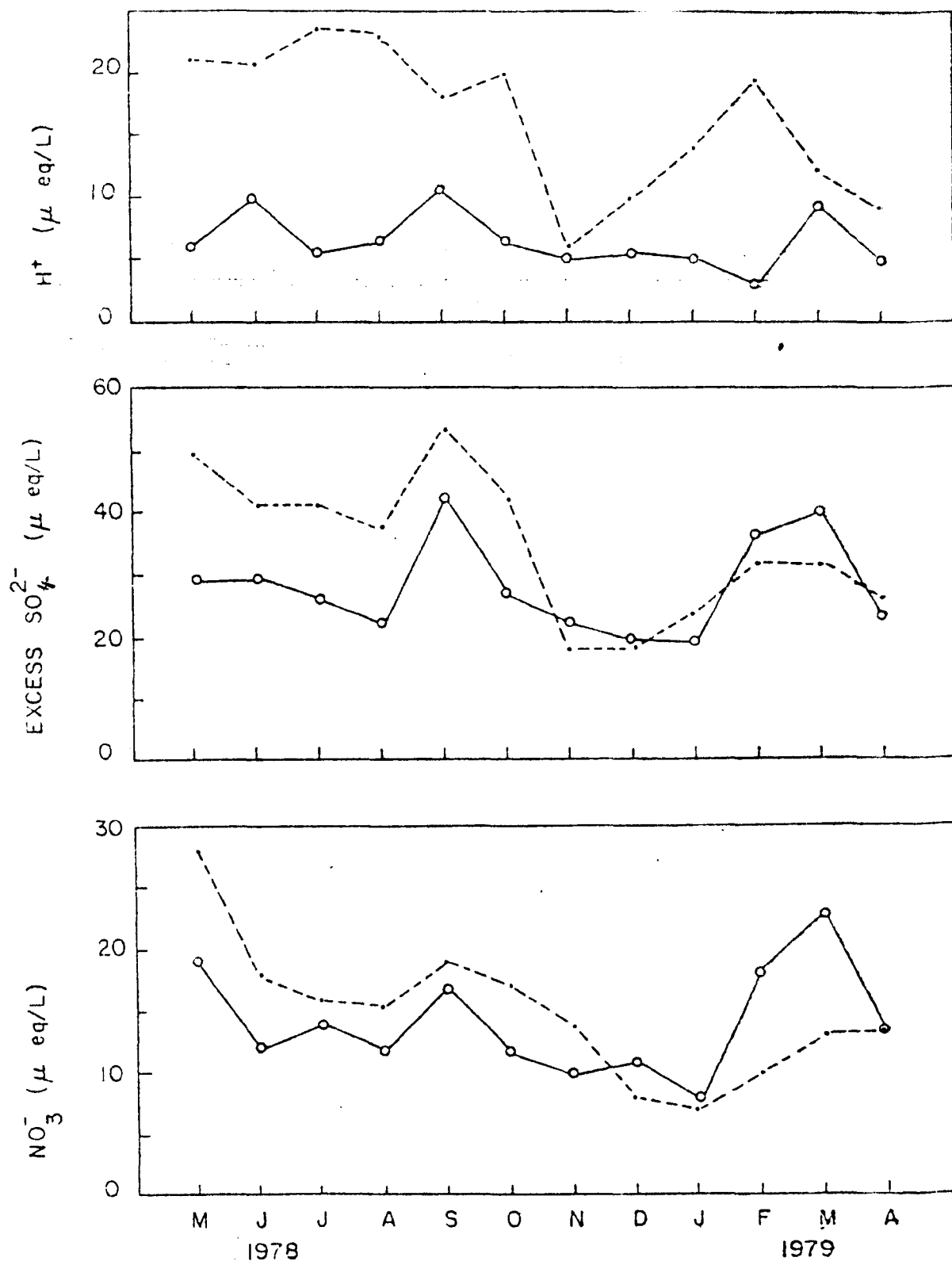


Figure 5-10. Monthly volume-weighted mean concentrations of  $H^+$ , excess- $SO_4^{2-}$  and  $NO_3^-$  for 14 northern (·---·) and 10 southern (o—o) locations.

summer-time relationship between the two groups of sites. Frontal precipitation occurs in Florida approximately once a week during winter, and these widespread systems of rainfall probably confer a degree of homogeneity to winter-time precipitation chemistry. Additionally, southern areas receive less rainfall than northern areas during winter (because the cold fronts weaken as they progress southward).

Despite the seasonal concentration variations described above, the deposition of  $H^+$ , excess- $SO_4^{2-}$  and  $NO_3^-$  was considerably higher at both northern and southern location during summer than winter (Table 5-7). In the north, wintertime depositions of the ions were 29-34% of the annual total, and winter rains accounted for 43% of the yearly rainfall. The inequality of winter/summer deposition thus was a function of both seasonal precipitation and concentration differential at northern sites. In south Florida, winter time deposition of  $H^+$ , excess- $SO_4^{2-}$  and  $NO_3^-$  were 25-32% of the annual total; these values are similar to the seasonal rainfall disparity (winter rainfall was 28% of annual total).

#### B. Sequential Sampling within Rainfall Events.

In an effort to elucidate the infrastructure of winter and summer events, several frontal and convectional storms were sampled sequentially on a wet-only basis by uncovering and rinsing a funnel on the roof of Black Hall immediately prior to the onset of rainfall. Subsamples (25<sub>A</sub>mL), corresponding to 0.05 cm of precipitation, were collected for the first 1.0 cm of each event; thereafter, 50 mL samples were taken until cessation of rainfall. Each fraction was analyzed for  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{+2}$ ,  $Ca^{+2}$ ,  $NH_4^+$ ,  $SO_4^{=}$ ,  $NO_3^-$ ,  $Cl^-$  and conductivity.

Results of the chemical analyses indicate that temporal features of both convectional and frontal events can be complex.  $H^+$  concentration, for example, did not necessarily decrease during the course of an event,

Table 5-7. Seasonal deposition of acidic and basic species in bulk precipitation at northern, southern and coastal Florida locations.

Location	Season	Rainfall (cm)	Deposition (eq/ha)				
			H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>+2</sup>	Excess-SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup>
Northern (n = 12)	Winter	59.9	81	58	161	162	62
	Summer	80.0	187	139	159	361	153
	Annual	140	269	197	320	523	215
Southern (n = 8)	Winter	37.8	17	33	192	88	443
	Summer	88.7	67	105	280	253	133
	Annual	126	84	138	472	341	176
Coastal (n = 4)	Winter	51.5	30	26	281	113	64
	Summer	84.1	40	87	300	198	108
	Annual	136	70	113	581	311	172

as might be expected from the classical "washout curve" exhibited in Figure 5-3a. Rather,  $H^+$  and other ions (generalized in the figure by conductivity) were observed to increase, decrease or oscillate rapidly within events (Figure 5-11). No clear-cut differences between frontal and convective storm types are evident, based on the sampling performed to date.

During most of the events, the major ions ( $H^+$ ,  $NH_4^+$ ,  $Na^+$ ,  $Ca^{+2}$ ,  $SO_4^{=}$ ,  $NO_3^-$ ,  $Cl^-$ ) generally behaved coherently, i.e. concentrations rose and fell in harmony with variations in conductivity. Regression analysis, however, showed that correlations among certain ions consistently were good, while others were poor.  $Na^+$ , excess- $SO_4^{=}$ ,  $NO_3^-$  and  $NH_4^+$ , for example, correlated well with  $H^+$ ; the soil-derived elements ( $Ca^{+2}$ ,  $Mg^{+2}$ ,  $K^+$ ), on the other hand, correlated poorly with  $H^+$ .

The above findings indicate that different processes (i.e. rainout and washout) may affect those species apparently associated with  $H^+$  and those not associated with  $H^+$  during an event.

For example,  $Ca^{2+}$  is derived from the ground in the form of particles with large mass-median diameters, and thus is easily and rapidly scavenged by below-cloud processes (washout). Particulate-sulfate in the Florida atmosphere on the other hand, occupies a range of very small particle sizes (Ahlberg et al. 1978), and is poorly removed via washout.

The above fact may present an important clue to the source of acidic species ( $H_2SO_4$ ,  $HNO_3$ ) in winter (frontal) precipitation. Frontal events that occur in Florida during winter are generated by the collision of a cold dense air mass of arctic or polar origin with a warm, humid air mass of maritime provenance. In the process, the warmer, unstable air is uplifted, causing condensation of moisture and precipitation (Byers 1974). Due to the different source regions of the two air masses, only the uplifted

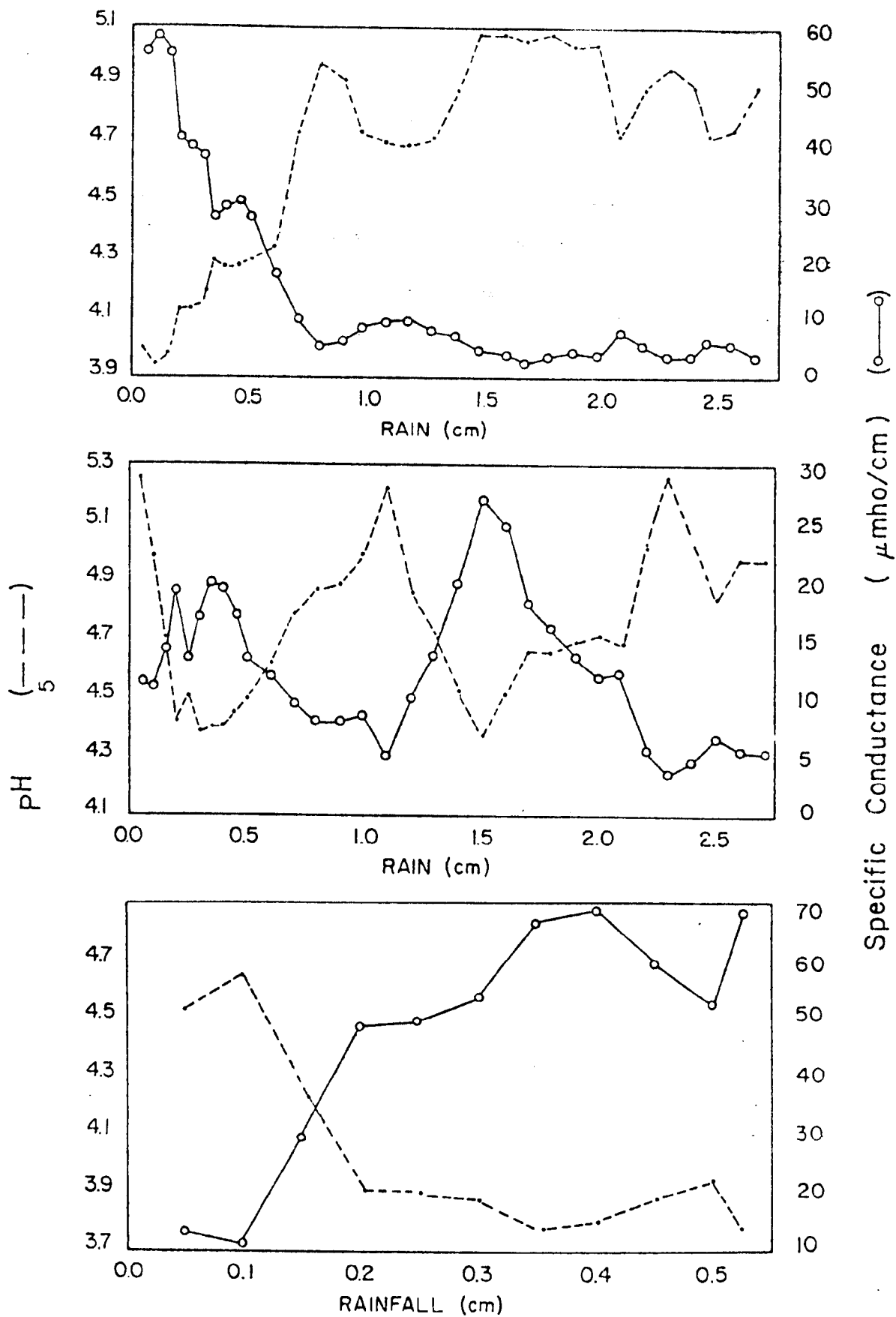


Figure 5-11. Temporal variation of pH and conductivity within 3 events sequentially sampled at Gainesville.



(maritime) air has a significant burden of sea-salt species (e.g.  $\text{Na}^+$  and  $\text{Cl}^-$ ), and thus these are deposited in frontal precipitation only by the process of rainout. Based on the correlation of sea-salt and acidic species, deposition of the latter forms probably follows the same mechanism. The bulk of the  $\text{H}^+$ , excess- $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  in frontal precipitation thus may originate in the southern air, rather than the northern, or midwestern, air; the acid species and their precursors thus appear to be primarily of local origin. Of course, this scheme is an oversimplification because there is mixing between northern and southern air masses when they come into contact. The degree of mixing is of interest in determining the proportion of local vs. imported (northern) pollutants in Florida wintertime precipitation.

#### SOURCES OF ATMOSPHERIC SULFUR IN FLORIDA

Estimates of the global significance of biogenic sulfur emissions are numerous and controversial (Eriksson 1960; Kellogg et al. 1972; Friend, 1974; Granat et al. 1976). Florida has extensive areas of potential importance for biogenic sulfur emissions, and consequently it seems appropriate to attempt an assessment of the contributions of anthropogenic and biogenic sulfur in the Florida atmosphere. Approximately 20% of the state ( $3 \times 10^6$  ha) is occupied by wetlands: fresh and salt water marshes and swamps and poorly-drained soils (Smith et al. 1973; Coultas, 1976; Coultas & Gross 1972; Coultas 1978). The most productive of these areas (tidal flats and mangrove swamps), occur predominantly in southern coastal areas, where conditions of available organic carbon and sea-sulfate, coupled with high year-round temperatures, could give rise to considerable biological sulfate reduction.

Published experimental data on emissions from such areas are scarce, in general, and non-existent for Florida. Emission estimates are further complicated by the fact that a wide variety of experimental designs

has been employed in reported studies. Nevertheless, the available data have been synthesized (Table 5-8) to give a general overview of the potential emissions of biogenic sulfur in Florida, and the results indicate a range of annual biogenic sulfur emissions of about 770-51,800 metric tons, (or 0.05-3.34 kg S/ha) statewide. These figures could be higher if temperature differentials, or other factors, enhance the rates of biogenic sulfur emission in Florida. On the other hand, if slowly-oxidized organic sulfur species (e.g. COS, CS<sub>2</sub>) were the predominant emissions from wetland areas, most of this sulfur would be exported from the state before it could be oxidized to SO<sub>2</sub>.

Another means of generating biogenic emission figures involves the use of areal emission rates developed by various authors to balance global sulfur budgets. These "calculated" emission factors range from about 0.53 kg S/ha-yr (Granat et al., 1976) to about 3.8 kg S/ha-yr. (Friend 1973). Multiplying these factors by the area of the state yields annual emissions of 8,200-60,000 metric tons-S, which agrees fairly well with the previous reckoning.

The above figures are small compared to anthropogenic sulfur emissions within Florida. Statewide sulfur emissions for 1975 were 500,000 metric tons (32.3 kg S/ha). The geographic distribution of these emissions was very uneven; 85% of total emissions occurred in the northern 58% of the state, and county-wide average emissions ranged from 1.2 to 428 kg S/ha-yr (Fig. 5-12).

In comparison, wet and bulk sulfur deposition values for 1978-79 were 83,000 and 100,000 metric tons, respectively. Estimated biogenic emissions amount to no more than 72% and 55% of wet and bulk deposition (and perhaps

Table 5-8. Inventory of Florida wetlands and potential biogenic sulfur emissions.

Wetlands	Area* (m <sup>2</sup> )	Potential # Emission Rate (mg-S/m <sup>2</sup> -yr)	Total Emission (Tons-S/yr)
Freshwater Swamps, Marshes	1.2 x 10 <sup>10</sup>	<10 - 100	120 - 1200
Poorly-drained organic Soils	1.6 x 10 <sup>10</sup>	<10 - 100	160 - 1600
Tidal mudflats	3.0 x 10 <sup>9</sup>	<10 <sup>2</sup> - 10 <sup>4</sup>	300 - 30,000
Mangrove Swamps	1.9 x 10 <sup>9</sup>	<10 <sup>2</sup> - 10 <sup>4</sup>	<u>190 - 19,000</u>
		Total	770 - 52,000

\*Source: Smith et al., 1973; Coultas, 1976; 1978; Coultas & Gross, 1972.  
1975

#Source: Hitchcock, 1972; Maroulis and Bandy, 1976; Jaeschke, 1978; Adams et al., 1979;  
Aneja et al., 1979; Aneja & Aneja, 1979.

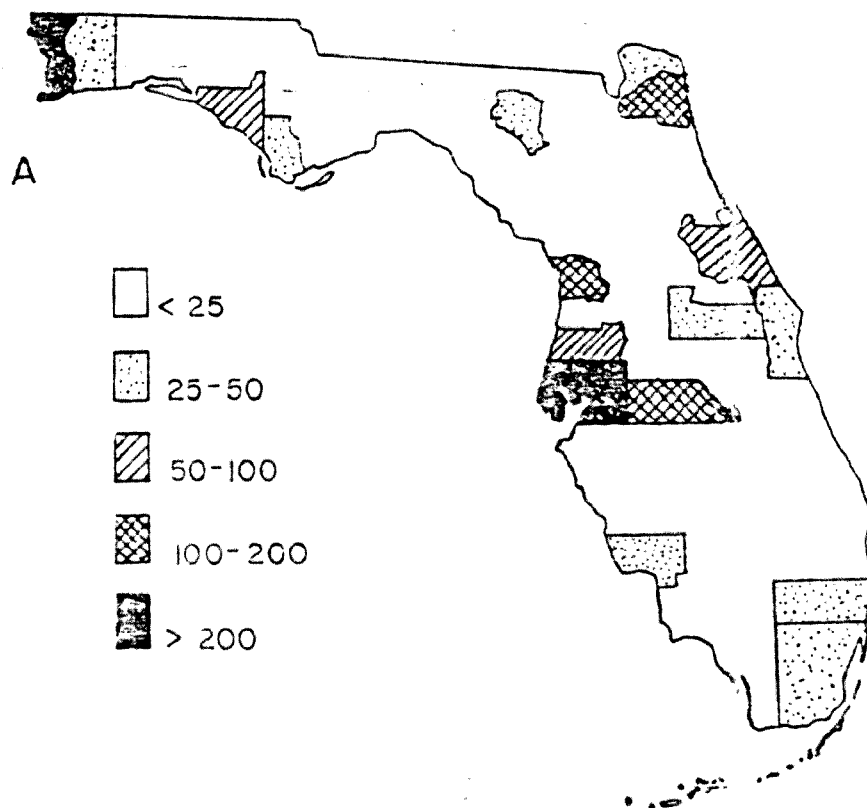


Figure 5-12. County-wide emissions of  $\text{SO}_2$  across Florida for 1978. Units are kg-S/ha-yr. Statewide mean is 32 kg-S/ha-yr; mean of underlined county emissions is 6.2 kg-S/ha-yr.

55-12

much less). Moreover, the geographic distribution of biogenic emission shows little correspondence with the observed pattern of excess- $\text{SO}_4^{2-}$  deposition. Consequently, biogenic sulfur probably plays only a small role in Florida precipitation chemistry.

Anthropogenic emissions, on the other hand, are more than six times wet deposition and five times bulk deposition, and distribution of high emissions correlates roughly with the areas of high rainfall deposition of excess- $\text{SO}_4^{2-}$ .

This is not to say that biogenic sulfur is not a constituent of Florida precipitation; however, if it is the dominant sulfur species in precipitation anywhere in the state, it is only in areas remote from significant point sources (where the presence of strongly acid precipitation (pH 5.0) is yet to be observed).

We also do not imply that sources of sulfur outside the state fail to contribute to sulfur loadings within Florida. Nonetheless, there are several reasons to suspect that such emissions are of limited importance. First, emissions of  $\text{SO}_2$  within Florida are substantial and amount to roughly 40% of emissions in Ohio, which ranks first nationally (EPA, 1976). Second, during summer Florida is isolated meteorologically from large northern  $\text{SO}_2$  sources by the prevailing synoptic weather patterns (southerly air flow). This period corresponds to one of heavy deposition of excess  $\text{SO}_4^{2-}$  and enhanced precipitation acidity throughout the state (see Figure 5-9 and Table 5-7). Unless a mechanism exists for significant diffusion counter to the direction of advective transport, there is little reason to believe that much of the sulfur in summertime precipitation originates in the midwest. Lastly, as mentioned in the sequential sampling section, there is some

evidence that much of the sulfur in winter (frontal) precipitation is also of local origin. Consequently, out-of-state sources probably account for much less than 50% of annual sulfur deposition in Florida.

#### ACID RAINFALL IN FLORIDA: A PERSPECTIVE

##### A. Historical Trends in Florida Precipitation Chemistry

The historical record of precipitation chemistry in Florida unfortunately is incomplete, and there is no exact way to establish the date when acid rain first appeared in the state. However, two rainfall studies conducted in the mid-1950s do yield some insight concerning man's alteration of precipitation during the past quarter century.

Junge's well-known study of U.S. precipitation (Junge & Werby, 1958) included five sites that are comparable to sites in the current Florida network. Although pH was not measured in the former study, the chemical analyses in other respects were complete enough to estimate  $H^+$  concentrations via ionic balances. Comparison of annual volume weighted-mean concentrations of hydrogen ion, excess  $SO_4^{2-}$  and  $NO_3^-$  for 1955-56 and 1978-79 (Table 5-9) indicate that the levels of these species at each site have increased markedly over the 24 year period. A deficiency of measured anionic equivalents compared to measured cationic equivalents was found for each of Junge's Florida sites, suggesting that bicarbonate (an unmeasured species) was present in the rainfall of that period. Consequently, although exact pH values cannot be computed from Junge's data, the results indicate that Florida rainfall was at or about geochemical neutrality ( $pH > 5.6$ ;  $H^+ < 2.5 \mu eq/L$ ). The average increment of excess-sulfate plus nitrate ( $23.5 \mu eq/l$ ) over the period is sufficient to account for the average increase in hydrogen ion ( $15 \mu eq/L$ ). It should be noted that this analysis compares wet-only data (Junge's) with

Table 5-7. Comparison of parameters related to the acidity of Florida rainfall in 1956-56 and 1978-79.

Location	Weighted-Mean Concentration (µeq/L)					
	$H^+$		excess- $SO_4^{2-}$		$NO_3^-$	
	1956	1979	1956	1979	1956	1979
Mobile, AL/Jay	<2.5*	24.0	16.0	34.7	2.6	13.9
Tallahassee	<2.5	17.4	18.8	33.0	2.9	13.9
Jacksonville	<2.5	18.3	27.9	43.5	2.9	16.2
Tampa/Bradenton	<2.5	20.1	28.8	36.4	2.7	14.3
W. Palm Bch./Stuart	<2.5	6.9	13.5	20.1	4.1	12.1
Mean	<2.5	17.3	21.0	33.5	3.1	14.1
1979/1956	>8.4		1.6 <sup>†</sup>		4.5 <sup>†</sup>	

\* Proton concentration inferred via anion/cation balance.

† Present data are for bulk precipitation (rainfall collectors open at all times), whereas 1956 data are for rainfall-only (collectors open to atmosphere only during rain events). Adjacent wet-only (W) and bulk (B) collectors at Gainesville in the study have yielded the following volume-weighted concentrations (in µeq/l): excess sulfate, 35.1 (B) and 26.6 (W), B/W = 1.3; nitrate, 16.9 (B) and 13.6 (W), B/W = 1.24. Thus differences in collector type do not wholly explain the increases in concentrations.

bulk precipitation data (ours). Because concentrations in bulk precipitation are somewhat different than those in wet-only precipitation (cf. Figures 5-8), this leads to a magnification of the current excess of sulfate and nitrate compared to the levels found in 1955-56. In contrast, the 24-year increment of  $H^+$  probably is underestimated, since wet precipitation typically is more acidic than bulk precipitation.

The other historical study, conducted by the USDA (Jordan et al., 1959) to evaluate atmospheric inputs of sulfur to southeastern soils, also had five sites comparable to present ones. Annual loadings (kg S/ha) of sulfate in bulk precipitation for the two studies (Figure 5-13) increased at all five sites between 1952-55 and the present. Atmospheric loadings in the northern part of the state have increased by 3-4 fold, while deposition in southern Florida has increased marginally, and perhaps not significantly. Assuming that sea-sulfur and biogenic sulfur emissions have remained relatively constant over the period, anthropogenic sulfur emissions are the cause of the increased deposition at northern sites.

Wet-only precipitation events have been collected for over three years, in Gainesville. Monthly weighted mean pH values for the period January 1977 - December 1979 (Figure 5-14) fail to indicate any recent trend in precipitation acidity. Annual weighted mean pH values of precipitation for 1977, 1978 and 1979 are 4.51, 4.62 and 4.56, respectively. The uniformity of these results suggests that the current data base can function as a sensitive barometer for gauging future changes in precipitation chemistry.

#### B. Comparison of Florida and Northeastern Precipitation

Comparison of precipitation loadings of  $H^+$  and related parameters for Florida and Hubbard Brook, New Hampshire show that the acid rain phenomenon is considerably more intense in the Northeast. Two factors



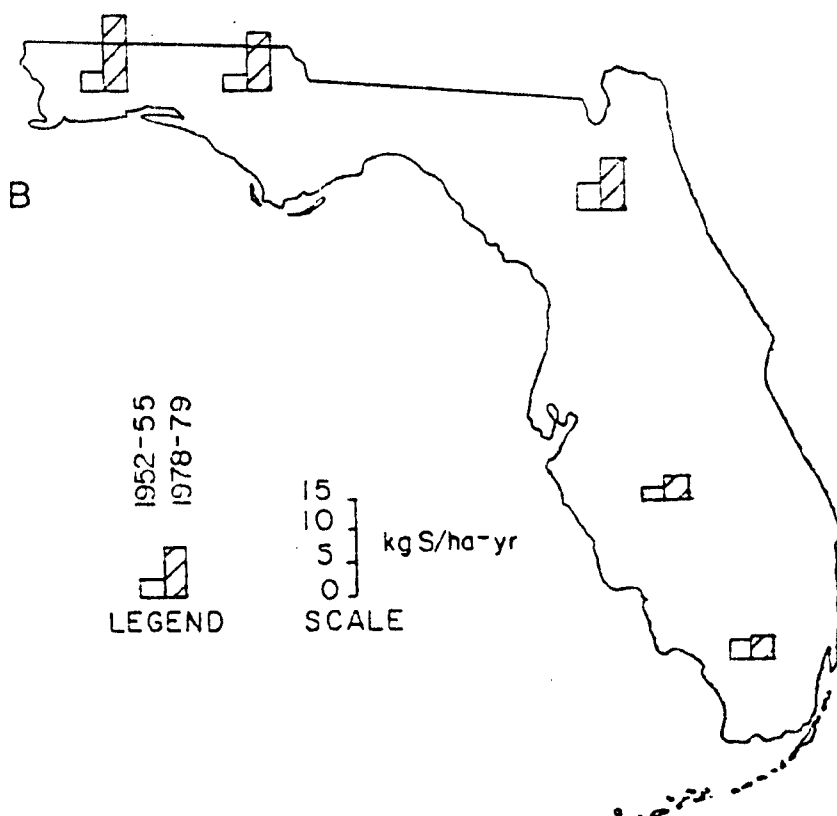


Figure 5-13. Atmospheric sulfur deposition at 5 historical (1952-55) and current (1978-79) precipitation sampling locations. Means for both studies are depicted in legend.

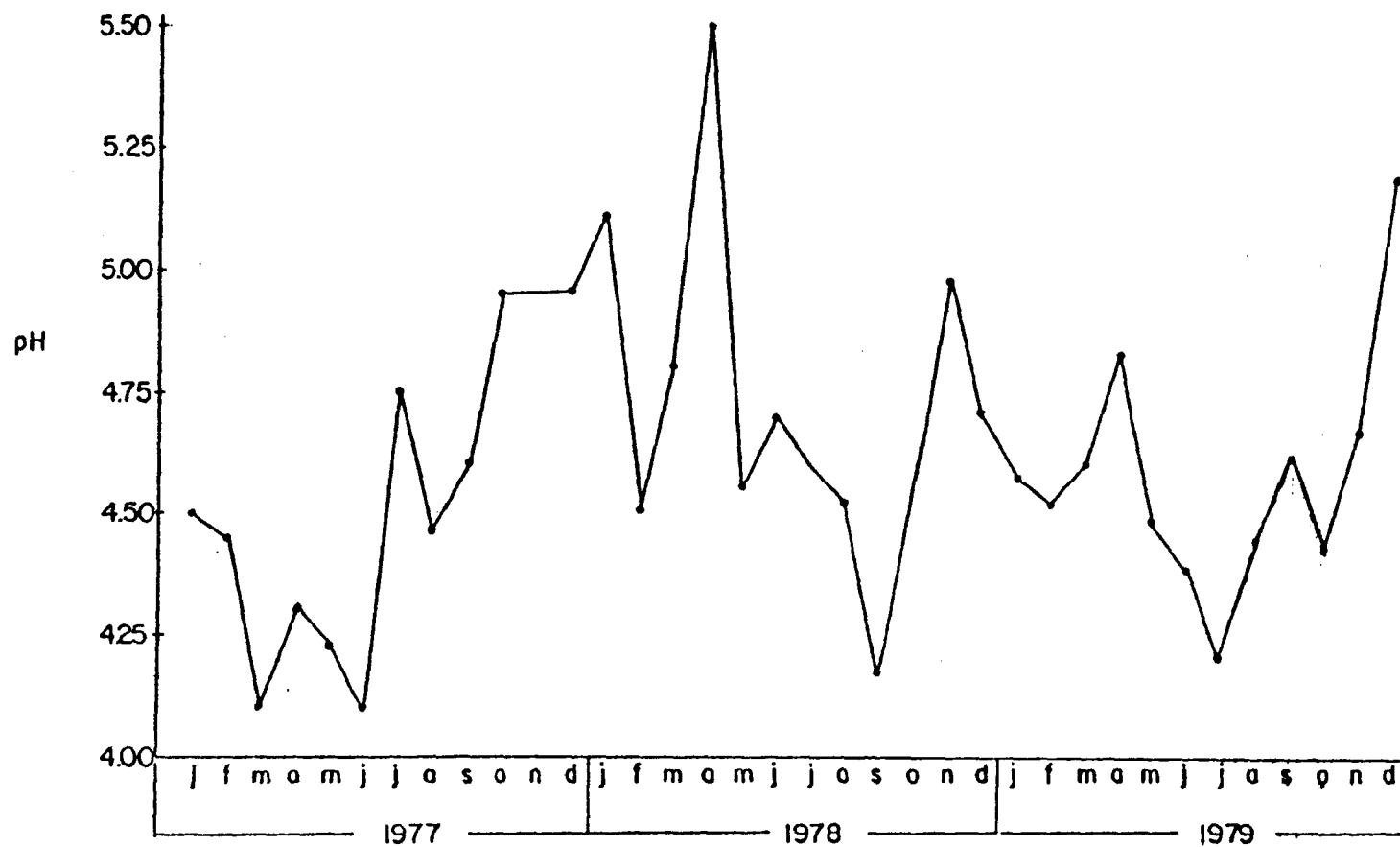


Figure 5-14. Monthly weighted mean pH of Gainesville wet-only precipitation collected from

quantitatively responsible for this difference. First, the levels of acidifying substances (excess-sulfate and nitrate) are somewhat lower in Florida rain. At northern, southern and coastal sites in Florida (Figure 5-2), the sum of these anions is 53, 38, and 43%, respectively of the 10-year average values reported for Hubbard Brook, NH (Likens et al., 1977). Second calcium (and presumably carbonate) occurs at much higher concentrations (3-4 fold) in Florida rainfall.

The effect of these two circumstances is especially apparent at the coastal and southern Florida sites. The rain at these sites typically is only slightly acidic compared to geologically neutral rain (i.e. pH 5.6-5.7). Were it not for the excess of calcium in Florida rain compared to levels in rainfall of the north eastern United States, all of Florida would now be receiving acid precipitation: northern areas would have a pH of about 4.5, and southern sites would exhibit pH levels of about 4.7.

Because Florida generally receives more rainfall than the Northeast, annual deposition of acidity and related species is closer to northeastern values than concentration data alone suggest. The site at Jay, for example, received slightly over 200 cm of rainfall during the study year, resulting in the deposition of 500 eq  $H^+$ /ha and 11.5 kg S/ha. Corresponding values at Lake Apopka, where the rainfall amount was near normal for the state, are: 136 cm, 342 eq  $H^+$ /ha and 6.6 kg S/ha. At Hubbard Brook, the deposition of these species averaged 970  $\mu$ eq  $H^+$ /ha (Likens, 1976) and 12.7 kg S/ha (Likens et al. 1977) in the 10-year period 1964-65 to 1973-74. Thus northern Florida receives about one-third to one-half of the hydrogen ion deposition and 50 to 90% of the sulfate deposition as that in the most impacted region of the United States.

## Chapter 6. Effects of Acidification on Softwater Lakes in Florida.

A total of 20 lakes in two geographical regions were selected for sampling during 1978-79, for a variety of physical, chemical and biological parameters. The sampling was designed to evaluate chemical and ecological impacts of acidic precipitation on sensitive aquatic systems. The lakes were selected on the basis of two main criteria: 1) softwater, making the lakes susceptible to acidification, and 2) availability of historical data to determine whether there have been any measurable changes (i.e. decreases in lakewater pH and alkalinity) over the last decade or so.

This chapter describes the sampling program we conducted on these lakes, temporal trends in chemical composition of the lakes over the past 20 years, and the variations in composition of the major trophic groups in the lakes as a function of pH.

### Previous Studies on Effects of Acid Precipitation on Aquatic Ecosystems

Acid rain in North America and Europe has contributed to the acidification of many aquatic habitats, with subsequent effects on the biota (Gorham 1976; Hornbeck et al. 1976; Oden 1976; Overrein 1976; Schofield 1976; and Likens et al. 1979). With increased acidity, effects have been documented for all trophic levels and include reduced species richness, deformities, reproductive failures, retarded growth rates and deteriorated health. In

some severe cases the complete loss of an entire class of organisms can be traced to increases in acidity (Beamish 1976; Stokes and Hutchinson 1976 and Andersson et al. 1978).

Much valuable information on the effects of increased acidity on aquatic systems has been obtained from studies of acid mine drainage (Harp and Campbell 1967 and Parsons 1968, 1976). Although the rate of acidification by mine drainage is often more rapid than by acid rain, the general responses by the biota are often similar.

The impact of acidification on lakes in Norway has led to the development of a comprehensive project by the Norwegian Research Council (Braekke 1976) designed to investigate the effects of air pollutants on soil, vegetation, water, and freshwater fish (Overreim 1976). Literature reviews on the responses of aquatic organisms to increased acidity are presented in EIFAC (1969), Giddings and Galloway (1976), and Wright (1976).

#### Phytoplankton

Effects of increased acidity on phytoplankton communities include reductions in species richness and alterations in the proportions of the species present (Leivestad et al. 1976). As species richness decreases, species normally found in low abundance often disappear, while acid tolerant species such as Euglena sp. increase in dominance. In a study of growth rates of 34 species of freshwater algae, Moss (1973) found Euglena gracilis and Eunotia sp. to be very acid tolerant and to survive at pH 3.65 and 3.9 respectively. Leivestad et al. (1976) reported that periphytic algae become dominant in acidic streams. In their study, the periphytic diatom Tabellaria flocculosa and the green alga Mougeotia sp. accounted for 70% or more of the total number of algae cells in a stream acidified to pH 4.0 - 4.3. Very few periphytic algae were found in streams at pH 6.0. The high abundance

of periphytic algae in the acidic stream, resulted in a higher algal biomass at pH 4 than pH 6.

The effects of increased acidity on phytoplankton communities can be caused by direct physiological damage or synergistic interactions between acid and toxic substances such as heavy metals (Stokes and Hutchinson 1976). Giddings and Galloway (1976) have suggested that increased free CO<sub>2</sub> concentrations in acidic lakes could favor some species while inhibiting others.

Changes in pH have been shown to affect interspecific competition in phytoplankton. In a study by Kroes (1971), the inhibitory effect of Chlorococcum ellipsoidum on Chlamydomonas globosa was found to be the result of a change in pH brought about by C. ellipsoidum.

#### Macrophytes

Macrophyte communities in temperate lakes have been shown to be greatly reduced in species richness by acid precipitation (Hultberg 1976). In a study by Grahn (1976), the natural vegetation of an oligotrophic lake in Sweden was reduced from Lobelia dortmanna, Littorella uniflora and Isoetes lacustris to a monoculture of Sphagnum spp.

#### Lake Productivity

Acid precipitation has the overall effect of decreasing the productivity of a body of water (Grahn 1976). This process is known as oligotrophication and involves a decrease in available plant nutrients caused by chemical and biological changes in acidified systems (Overrein 1976). Planktonic productivity is reduced by large mats of Sphagnum because of their ability to concentrate cations and their formation of a physical barrier between the sediment and the water column (Grahn 1976). Another aspect of oligotrophication involves a reduction in the rate of biological decomposition of organic matter. Andersson et al. (1978) have shown a replacement of bacteria

by fungi as the major agents of biologic decomposition in acid waters. This replacement has the overall effect of decreasing nutrient recycling and thus lowering productivity.

### Zooplankton

Zooplankton communities have been shown to be adversely affected by acid precipitation, with decreases in species diversity and abundance of individuals occurring in acidified lakes (Hagen and Langeland 1973; Hendrey et al. 1976). Sprules (1975) reported that pH was the factor having the major effect on the structure of zooplankton communities. The greatest effect was noted in lakes of pH 5.0 or less, where many species were completely eliminated. Some acid-tolerant species were found by Sprules to occur throughout the pH range (3.8 - 7.0) observed in his group of lakes, including Mesocyclops edax, Cyclops bicuspidatus, Diaptomus minutus, Holopedium gibberum and Bosmina sp. Species absent from lakes of pH 5 or less were Tropocyclops prasinus, Diaptomus oregonensis, Leptodora kindtii and several species of Daphnia.

When determining the acid tolerance for a particular species, both the pH level for survival of adults and the pH at which reproduction stops must be considered. Davis and Osburn (1969) conducted tolerance studies on Daphnia pulex and found a survival time of at least 32 hours over a wide range of pH (4.3 - 10.4). However, the organisms reproduced successfully only within the pH range 7.0 - 8.7. Consequently, Daphnia is not commonly found in acid waters. On the other hand, Yan (1979) found the small cladoceran Bosmina longirostris comprised 89% of all adult crustacea in a group of acidified Canadian lakes. Because of the reduced biomass (resulting in part from the small size of dominant species), Yan proposed that zooplankton exert less control over phytoplankton communities in acid-stressed lakes than in neutral lakes.

The ability of some zooplankton species to adapt to acidic conditions was demonstrated by Parsons (1968). In this study, acid and non-acid waters were found to contain some of the same species. When individuals from a species common to both types of water were removed from the monacidic water and subjected to acidic conditions, a high rate of mortality was observed.

#### Benthic Invertebrates

Benthic invertebrate populations have lower species richness and reduced numbers of individuals in acidic waters (Tomkiewicz and Dunson 1976). Harp and Campbell (1967) found that Chironomus plumosus was the only chironomid established in water of pH 6.0 or below. The presence of C. plumosus was also highly correlated with the presence of leaf litter and sediment type.

Gastropods are sensitive to low pH, as demonstrated in a study by Økland (1969) in which snails were absent from Norwegian lakes with a pH below 5.2. Benthic crustaceans such as amphipods are an important food source for many fish, and they are adversely affected by high acidity (Hutchinson and Havas 1979). Avoidance of acidic conditions by Gammarus pulex was shown by Costa (1967). G. pulex showed negative responses to pH levels of 5.4 or less, with graded avoidance between 5.6 and 6.4. Bell (1971) found caddis flies to be most acid tolerant with mean 30-day survival limits of pH 2.45 to 3.38 and a 50% failure of emergence at pH 5.9.

#### Fish

Losses of commercial and sport fishing from many lakes in Scandinavia have been reported (Wright and Snekvik 1978). Similar losses in the northeastern United States and Canada have been reported (Parsons 1968; Beamish and Harvey 1972; Schoefield 1976.) The loss of fish populations from acidic waters can be traced to a number of factors, such as increased toxicity of heavy metals, ionic imbalances, and especially increased concentrations of aluminum



in acidic waters (Schofield 1979; Packer and Dunson 1970).

In studies by Leivestad et al. (1976) and Wright and Snekvik (1978), reproductive failures were noted prior to the loss of fish populations from acidic lakes. Beamish (1974,1976) found abnormally low levels of serum calcium in the ovaries of female trout exposed to low pH levels. Females with low calcium levels failed to release their ova for fertilization and reabsorbed much of the ovarian tissue back into their bodies (Beamish 1974).

Acid precipitation can contain high concentrations of heavy metals and increase leaching of cations from soils (Beamish and Harvey 1972; Schofield 1976; Cronan and Schofield 1979; Malmer 1976). Among the metals associated with acid precipitation, aluminum has been shown to exert detrimental effects on organisms at high concentrations (Dickson 1978). Dickson (1978) suggested that unsuccessful attempts to restock some Swedish lakes with rainbow trout after the pH had been increased by liming may be due to aluminum toxicity. However, aluminum is highly insoluble at neutral pH, and it should precipitate rapidly in limed lakes.

Parsons (1976) proposed that three major parameters be investigated in assessing the impact of increased acidity on an ecosystem: 1) quantitative analysis of populations, 2) community structure and 3) the ability of the various species to establish a complete life cycle.

## DESCRIPTION OF THE STUDY REGIONS AND LAKES

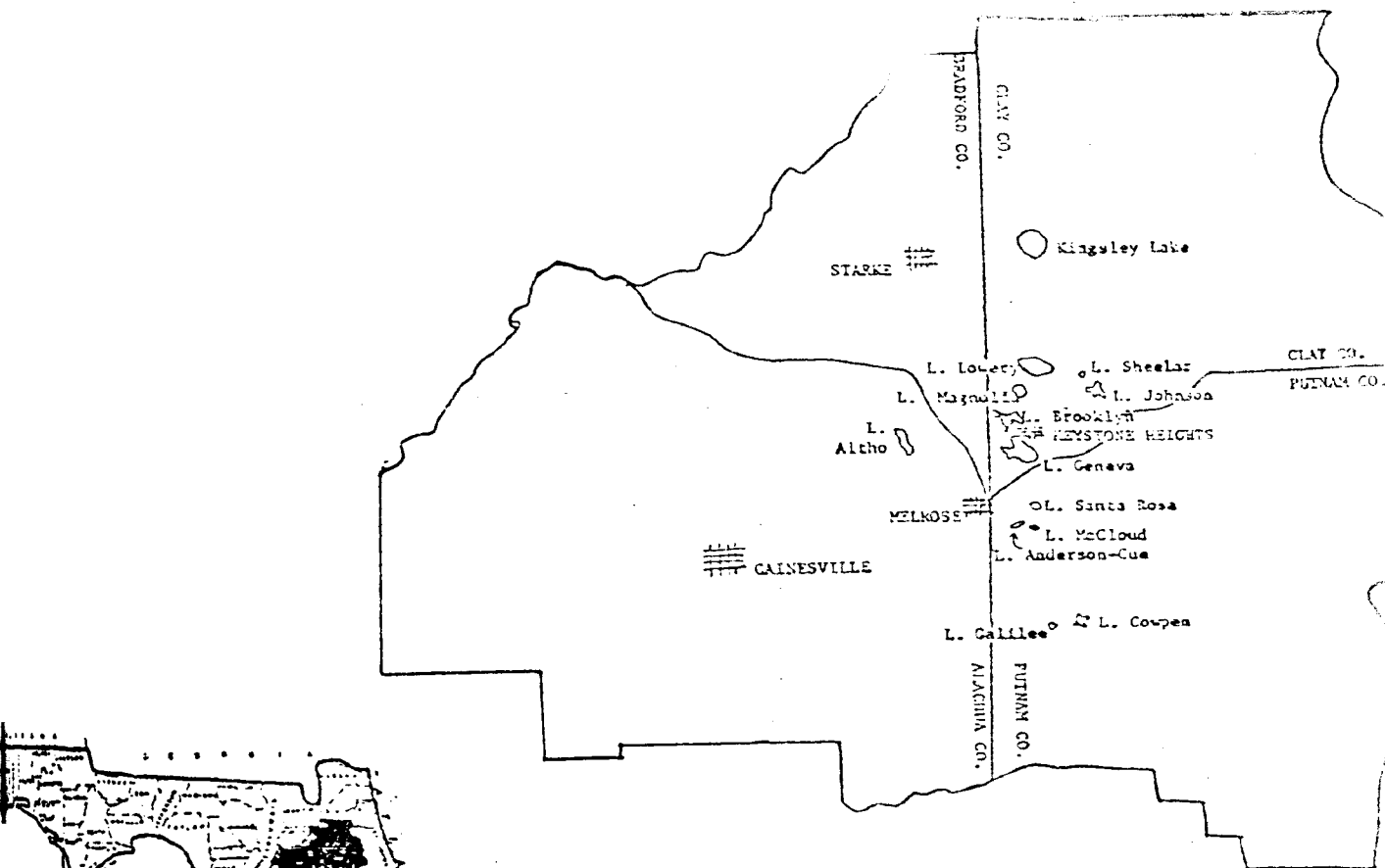
Two groups of soft-water lakes were chosen for study of the effects of precipitation on lake water chemistry and biology: a northern group (Trail Ridge Group) of 13 lakes in the Alachua, Clay, and Putnam Counties and a group of 7 lakes (Highlands Ridge Group) in Highlands County in south-central Florida. Figure 6-1 shows the location of the two lake groups, and Table 6-1 lists each lake, its surface area, elevation, and county location.

### Topography

The two lake districts are topographically similar. Each group is located along a ridge (the Trail Ridge (north) and Highlands Ridge (south) ) within the topographic division of the state known as the Central Highlands (Clark et al. 1962). The Trail Ridge extends southward along the Bradford-Clay County line as a series of hills, with the highest elevation being 75 m (250 ft) above MSL just south of Kingsley Lake. From this point, the land slopes in a southerly direction and fans out into a wider area of sand-hills dotted with lakes. The Highland Ridge is a narrow, elongated area of rolling uplands containing numerous hills and lakes, extending from north-western Highland County, southwestward almost to the Glades-Highlands County line, and ranges in elevation from about 60 m (200 ft) to 12 m (40 ft) above MSL.

### Geology

The two regions are also geologically similar (Figure 6-2), underlain by several hundred feet of unconsolidated to semiconsolidated marine and non-marine deposits of sand, clay, marl, gravel, limestone, dolomite, and dolomitic limestone. The oldest formation penetrated by water wells in both areas is the Lake City limestone of Eocene Age (Clark et al. 1964; Bishop 1956). The Eocene series is comprised, in addition to the Lake City limestone,



TRAIL RIDGE LAKE DISTRICT

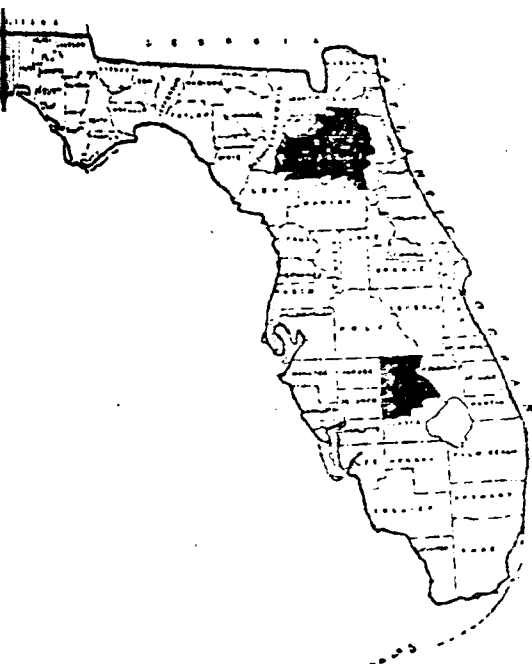
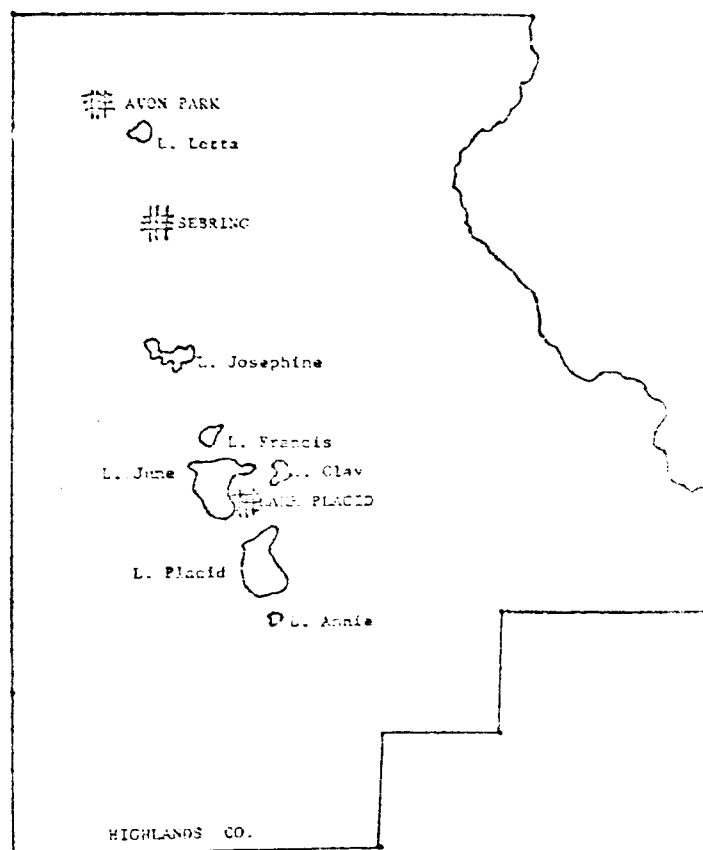


FIGURE 6-1. Location of the lakes in the survey.



HIGHLANDS RIDGE LAKE DISTRICT

Table 6-1. Locations and Physical Data on Lakes in Survey.

Lake	Surface Area (ha)	Mean Depth (m)	Maximum Depth (m)	Elevation (m above MSL)	Location (County)	Previous Studies (Ref.)
<u>Trail Ridge Group</u>						
Altho	216	3.6	5.8	45	Alachua	2,6
Anderson-Cue	8	2.0	4.6	38	Putnam	5,6
Brooklyn	256	5.7	10.4	35	Clay	1,3
Cowpen	223	3.7	8.8	21	Putnam	6
Galilee	34	3.5	5.8	27	Putnam	6
Geneva	650	4.1	8.8	32	Clay	1,3
Johnson	140		4.0	27	Clay	1
Kingsley	652	7.3	26.0	54	Clay	1,3
Lowery (Sand Hill)	500	4.8	12.0	40	Clay	1,4
Magnolia	83	8.0	15.0	38	Clay	1,6
McCloud	10	2.0	5.0	27	Putnam	5,6
Santa Rosa	42	8.1	13.4	30	Putnam	6
Sheeler	7		17.0	49	Clay	
<u>Highlands Ridge Group</u>						
Annie	35	8.3	20.0	34	Highlands	
Clay	147	4.0	8.0	24	Highlands	7
Francis	216	2.9	8.0	21	Highlands	2
June (Stearns)	1403	6.0	12.0	22	Highlands	3,7
Josephine	494	2.0	3.0	22	Highlands	7
Letta	191		3.0	30	Highlands	3
Placid (Childs)	1329	8.0	17.0	28	Highlands	7

) Clark et al. (1964). Semi-annual sampling 1957-60.

) Hennessey and Holcomb (1967); Holcomb (1968), (1969); Duchrow (1970,71,72); Holcomb and Starling (1973). Annual sampling 1966-73.

) Holcomb (1968,69); Duchrow (1970,71,72); Holcomb and Starling (1973). Annual Sampling 1967-72.

) Duchrow (1970,71,72); Holcomb and Starling (1973). Annual sampling 1969-72.

) Brezonik et al. (1969). Biweekly and monthly sampling 1967-68.

) Shannon (1970). Quarterly sampling 1969.

) Milleson (1978). Quarterly sampling 1974-76.

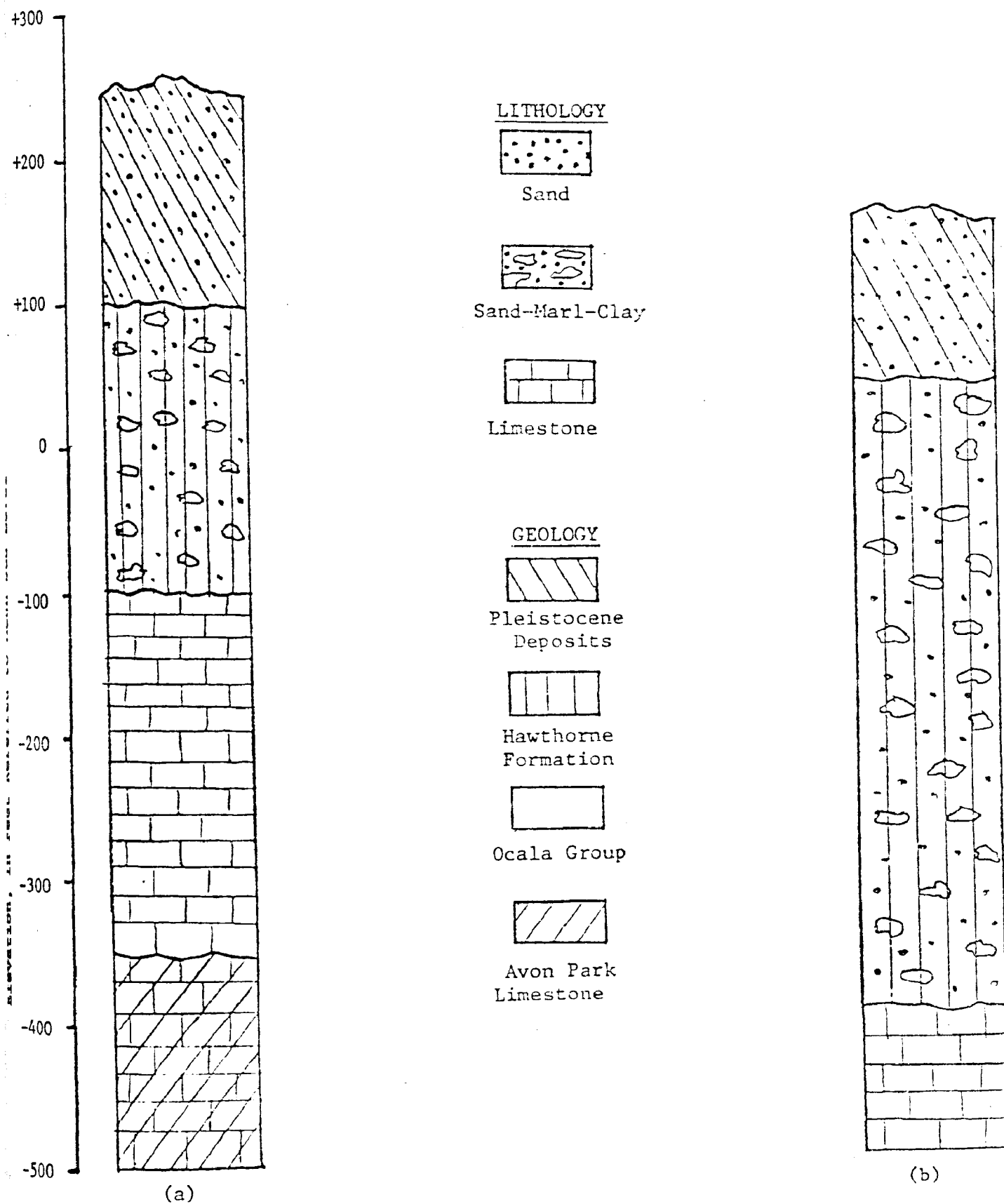


Figure 6-2. Geologic cross-sections of the (a) Trail Ridge Lake District (Clark et al. 1962) and (b) Highlands Ridge Lake District (Bishop 1956).

of the Avon Park and Ocala Group limestones, which collectively are referred to as the Florida Aquifer, and are the major source of fresh water supplies in the state. The top of the uppermost limestone layer, is approximately 30 m (100 ft) below mean sea level in the Trail Ridge area and 120 - 150 m (400 - 500 ft) below MSL in the Highlands Ridge.

The relatively thick and impermeable Hawthorne formation (Miocene Series), which consists chiefly of thick clays and clayey sands overlying the Ocala Group, is a confining bed that holds water under artesian pressure in the Florida Aquifer. The high terraces that form both the Trail Ridge and Highlands Ridge consist of loose sands deposited on the Hawthorne Formation during the interglacial stages of the Pleistocene. The sand deposits forming the surface of the ridges have been reworked by wind and wave action, but ancient sand dunes and sand bars are well preserved.

The lake regions exemplify typical karst topography, with many circular to elliptical basins among the sand hills. Lake basin formation along the ridges resulted from the dissolution of the underlying limestone beds and the collapse of the impervious Hawthorne layer and overlying veneer of Pleistocene sands. The basins subsequently filled with water from precipitation, resulting in perched, soft-water lakes in the sand deposits above the confining Hawthorne formation.

#### Soil Characterization

The sand deposit of the Central Highlands region is classified as an entisol (Asatatula fine sand-quartzipsamment), an excessively drained soil with very highly permeability. Native vegetation, reflecting the nutrient-poor status of the sands, primarily consists of mixed turkey and scrub oak and sand pine. A typical soil profile for this region from the surface (A horizon) to 300 cm depth (C6 horizon) generally consists of grey to light

brown fine to coarse sands, strongly acidic, with a cation-exchange capacity (CEC) of 1 meq/100 g or less and zero percent base saturation (Carlisle et al. 1978). The soil thus has very little neutralization capacity toward acidic precipitation.

#### Description of individual study lakes

The surface areas and elevations presented in Table 6-1 are from data published by the U.S. and Florida Geological Surveys, Water Resources Division, or from interpretation of topographic maps when no other information was available. Some of the lakes undergo severe fluctuations in lake stage during times of excess and below normal rainfall. The severe drought of 1955-57, for example, caused Lake Brooklyn at Keystone Heights to be lowered 7 m (20 ft) and reduced to one-half its normal size (Clark et al. 1964). The areas and elevations given in Table 6-1 are for normal lake stage levels. The lakes are described below in order they appear in that table:

1. Lake Altho, located near Waldo in Alachua County, is in the Santa Fe River drainage basin. It has a surface area of 216 ha at an elevation of 45 m MSL. Lake depth at the mid-lake sampling station was 5 m. The lake drains through the Santa Fe Canal into Little Santa Fe Lake. There is some residential development along the shoreline, but most of the shoreline is lined with cypress that grades rapidly into pine forest in the uplands. The lake is moderately colored because of runoff of humic material from the surrounding forest.

2. Anderson-Cue lake, in Putnam County, has an area of 8 ha at a surface elevation of 37 m. The lake level was low during this study and its area was reduced by almost 50% compared to normal conditions. Depth at the mid-lake station during this study was 3.8 m. The lake has no influent or effluent streams and obtains its water from direct precipitation and

subsurface seepage. Its small drainage basin is delineated by the surrounding high sand hills with elevations of 55 m. There is no human habitation in the drainage basin.

3. Lake Brooklyn in Clay County near the town of Keystone Heights, is the fourth lake in a chain forming the upper Etonia Creek Drainage Basin (Clark et al. 1963). It has a surface area of 256 ha at its normal stage. It is underlain by extremely permeable soils, and its level recedes as much as 7 m during years of below average rainfall. During this study the lake was at a very low stage, having received below normal rainfall for several consecutive years. The depth at the sampling station was 5 m. There is residential development along the south and southwest shore of the lake while the north shore is relatively free of development.

4. Lake Cowpen, located in Putnam County, has an area of 223 ha at 20 m elevation and was 4 m deep at the sampling station. The lake was extremely low during the study and primarily consisted of several circular pools. Sampling was done at the center of the largest of these pools where there was a public boat ramp. There is some residential development along the portions of the shoreline.

5. Lake Galilee is also located in Putnam County approximately 4 km east of Lake Cowpen. It has an area of 34 ha at an elevation of 27 m. Lake Galilee was also low during the sampling period, but its level was less affected by the drought than the level in Lake Cowpen was. The depth was 3 m at the mid-lake sampling station. There are a few residents along the south shore of the lake.

6. Lake Geneva is located in Clay County just south of the town of Keystone Heights. The depth at the sampling site was 5.5 m. It is the largest lake (650 ha) in the Etonia Creek Drainage Basin (Clark et al. 1964).



It receives drainage from a chain of 5 upstream lakes, during years of average or above average rainfall. Lake Geneva is almost completely surrounded by residential development.

7. Lake Johnson (140 ha) is located in Gold Head Branch State Park in Clay County. It receives influent flow from Gold Head Branch Creek which arises from rainfall percolating through sandhills having elevations of 65 m in the immediate area. The lake depth at the sampling station was 3.3 m. The only development along the shoreline is a swimming and picnic area and several rental cottages.

8. Kingsley Lake (Clay County) is 26 m deep at its deepest point and is thought to be the deepest lake in north Florida (Clark et al. 1964). The lake is nearly a perfect circle with an area of 652 ha. Water level fluctuation is small (only ~ 1 m during the period 1945 to 1963) compared to nearby Lake Brooklyn. There is moderate residential development along the north side of the lake.

9. Lake Lowery (Sand Hill Lake) located in Clay County is the second of a chain of lakes in the Etonia Creek basin. It receives flow from Blue Pond, and its surface outflow goes into Magnolia Lake. Lake Lowery has a surface area of 500 ha and a maximum depth of 12 m. The depth at the sampling station was 7 m. The shoreline is completely natural (forest) with the exception of a boat ramp.

10. Lake Magnolia, located near Lake Lowery, is the third lake in the Etonia Creek Basin Chain. During years of average or above average rainfall the lake supplies water to Lake Brooklyn through Alligator Creek. It has an area of 83 ha and a maximum depth of 15 m. The depth at the sampling station was 15 m. The shoreline also is in a natural state, with no development other than a boat ramp.

11. Lake McCloud (Putnam County) is approximately 750 ha north-east of Lake Anderson-Cue. It is totally enclosed, with surrounding sand hills rising to elevations of 45 m. There are no influent or effluent streams. The lake was low during this study, and the depth at the mid-lake station was 5 m. Normally, it has a surface area of 10 ha at an elevation of 90 ft. There is no human habitation in the drainage basin.

12. Lake Santa Rosa (Putnam County) is a seepage lake with an area of 42 ha at an elevation of 30 m. It was also low during this study, and the ends of docks and piers were 10 - 20 m from the edge of the water. The depth at the mid-lake station was 10 m. There are numerous permanent and seasonal cottages in the drainage basin.

13. Lake Sheeler is a small (7 ha) seepage lake near Lake Johnson in Gold Head Branch State Park (Clay County). It is nearly circular with a deep (17 m) conical-shaped basin. The extreme clarity and depth of the lake make it attractive for SCUBA diving and the park reserves it for this sport. The watershed and shoreline is completely undeveloped except for a trail to the water's edge.

14. Lake Annie (Highlands County) has a surface area of 35 ha at an elevation of 34 m. The lake is part of the Archbold Biological Station preserve; its drainage basin is uninhabited and consists totally of native vegetation. The basin is of typical sinkhole formation, being nearly circular and quite deep (20 m). A small stream flows from the north side of Lake Annie into Lake Placid.

15. Lake Clay is situated approximately 1 km east of Lake June in Highlands County and has a surface area of 148 ha. Sampling was performed at the mid-point of the deepest pool of the lake, where the depth was 7.5 m. Lake Clay drains northward into Josephine Creek which flows to Lake

Istokpoga. Lake Clay is completely surrounded by residential development.

16. Lake Francis, located 5 km northwest of the town of Lake Placid (Highlands County), is in a chain of lakes. It receives surface flow from Lake Placid and June to the south, and drains north through Josephine Creek to Lake Istokpoga. Lake Francis has a surface area of 216 ha at surface elevation of 21 m. The depth at the mid-lake station was 8 m. The shoreline consists of approximately equal residential development and native vegetation.

17. Lake June or June-in-Winter (formerly Lake Stearns), located in Highlands County, receives water from Lake Placid via Catfish Creek to the south, and its water drains northward through Stearns Creek. The lake is the largest in this study, with an area of 1403 ha. The depth at the mid-lake station was 7 m. Land use along the north and south shorelines is predominantly residential, while citrus groves occupy the eastern shoreline. The west shore is primarily native vegetation.

18. Lake Josephine (Highlands County) is relatively shallow, with the depth at the mid-lake station being 3.5 m. At an elevation of 21.5 m it has a surface area of 494 ha. It receives water from Wolf and Jackson Creeks and overflows through Josephine Creek into Lake Istokpoga. Residential development occupies the south side of the lake, and trailer camps occur along the east side. Native vegetation and improved pasture are found to the north.

19. Lake Letta, the northern-most of the Highlands Ridge Group, is located near the town of Avon Park. At an average lake stage of 30 m it has a surface area of 191 ha. Lake Letta was low during this study, and the depth at the mid-lake station was 2.5 m. The lake has two inlet streams and drains into Bonnet Lake. The east and north shore of the lake is resi-

dential and the southern and eastern shore is dominated by native vegetation.

20. Lake Placid (formerly Lake Childs) is south-southwest of the town of Lake Placid in Highlands County. It is the second largest lake in this survey, with a surface area of 1329 ha. It receives water from Lake Annie and drains northward through Catfish Creek to Lake June. The depth at the mid-lake station was 7.5 m. The shoreline along the western and northern edge is primarily residential, and citrus groves and native vegetation predominate along the eastern and southern shores, respectively.

#### Previous Lake Studies

Historical data exist for all the study lakes, except Lakes Sheeler and Annie (Table 6-2). Data for some of the Trail Ridge lakes date back over two decades.

Clark et al. (1964) reported lake water chemistry data for semi-annual sampling of lakes Brooklyn, Geneva, Magnolia, Lowery (Sand Hill), Johnson, and Kingsley in the Trail Ridge Lake District. The sampling survey was initiated in July, 1957, and ended in September, 1960. Included in the analyses were pH, major ions, and nutrient forms.

Ten years later, the Florida Game and Fresh Water Fish Commission as part of a state-wide survey of Florida lakes reported data on pH, major ions, and nutrient forms for five of the Trail Ridge lakes (Brooklyn, Geneva, Lowery, Kingsley, and Altho) and three lakes (Francis, June, and Letta) in the Highlands Ridge Group. Sampling was performed on an annual basis from 1966 to 1973 (Hennessey and Holcomb 1967; Holcomb 1968, 1969; Duchrow 1970, 1971, 1972; Holcomb and Starling 1973).

Brezonik et al. (1969) conducted intensive sampling of Lakes Anderson-Cue and McCloud located in the Trail Ridge District during 1967-68 and reported data for pH, major ions, and nutrient forms. Sampling was biweekly

Table 6-2. Historical pH, alkalinity and sulfate data for the Trail Ridge Lake Group.

Lake	1957-60 <sup>*</sup>			1968-69 <sup>**</sup>			1967-72 <sup>+</sup>			1978-79 <sup>++</sup>		
	pH	Alk. mg/L as CaCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> mg/L	pH	Alk. mg/L as CaCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> mg/L	pH	Alk. mg/L as CaCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> mg/L	pH	Alk. mg/L as CaCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup> mg/L
Brooklyn	5.5	2.5	4.1	5.5	0.5	4.0	5.1	0.9	3.2	5.0	0	4.6
Lowery	5.4	2.5	2.0	5.3	0.3	3.8	5.1	0	2.5	5.2	0	3.4
Magnolia	5.6	2.5	2.4	5.5	0.4	3.3				5.1	0	3.0
Geneva	5.4	1.6	5.8	6.3	1.2	5.4	6.1	4.3	6.0	6.1	6.5	9.0
Kingsley	6.3	5.7	4.9	6.9	5.7	5.2	6.6	7.0	5.1	6.7	10.8	7.3
Johnson	5.5	2.5	2.5							5.2	0	2.1
Anderson-Cue				4.8	0	4.4				4.9	0	5.2
Cowpen				5.4	0.4	5.8				4.9	0	13.9
Galilee				5.6	0.6	6.1				5.0	0	11.8
McCloud				4.9	0	4.5				4.7	0	6.8
Santa Rosa				5.2	0.3	4.7				5.1	0	5.3

\* Semi-annual sampling during 1957-60 (N=6); Clark et al. (1964).

\*\* Sampling every four months during 1968-69 [N=3; except Anderson-Cue, McCloud (N=6); Geneva, Kingsley (N=5)]; Shannon (1970).

+ Annual sampling 1967-72 (N=6); Holcomb (1968, 1969); Duchrow (1970, 1971, 1972).

++ This study. Sampling during 1978 (N=4).

during 1967 and on a monthly basis during 1968.

Shannon (1970) and Shannon and Brezonik (1972) conducted quarterly sampling of 55 north-central Florida lakes during 1969, including all the Trail Ridge Group of lakes in this study, except lakes Johnson and Sheeler.

Milleson (1978) recently conducted a survey of seven lakes in Highlands County, including four lakes studied in this project (Placid, June, Clay, and Josephine). Sampling was on a quarterly basis during the period 1974-76, and included major ions, pH, and nutrient forms.

#### SAMPLING AND ANALYTICAL METHODS

The 20 lakes were sampled on a seasonal (quarterly) basis beginning in spring (April - May) 1978 and ending in winter (January - February) 1979. A mid-lake sampling station was selected in each lake at either the deepest part of the lake or the center of the largest pool, if the lake consisted of several pools. The same station was used on all four sampling dates. Temperature and dissolved oxygen were measured with a YSI Model 51A oxygen meter at three depths in the water column, surface (0.5 m), midway between the surface and bottom, and 1 m from the bottom. Secchi Disk transparency was also measured at each sampling station.

Water samples for chemical analyses were collected with an acrylic Kemmerer sampler at the three depths described above, and a composite sample was taken by mixing equal volumes of water in a plastic bucket. Samples for nutrient analyses were preserved with 1 mL saturated  $\text{HgCl}_2/\text{L}$ , placed on ice in the field, and stored at 4°C in the laboratory. An aliquot of the preserved sample was filtered in the laboratory for analysis of inorganic nutrients.

Field pH measurements were made using Model 401 Ionalyzer field pH meter on the composite sample following standardization with two (pH 4.0 and 7.0) buffers at ambient water temperature.

*alkalinity. This is not a good method for very low alkal values.*

Analytical methods for chemical determinations on lake water samples are summarized in Appendix <sup>I</sup> A. Analyses were performed according to standard methods (APHA 1976) and/or the EPA water analysis manual (EPA 1976). Analyses for inorganic nutrient forms, chloride, and sulfate were run by automated methods on an AutoAnalyzer, except for orthophosphate (i.e. "soluble reactive phosphate"), which was done manually using the single reagent method. Total Kjeldahl nitrogen and total phosphate were determined by manual semi-micro digestion of unfiltered samples followed by colorimetric analysis for ammonium (indophenol method on AutoAnalyzer) and orthophosphate (manual single reagent method) on the neutralized digestate.

Samples for chlorophyll analysis were collected at 0.5 m for lakes <5 m and at the top, middle, and bottom of the water column for lakes >5 m by a 2.2 L Kemmerer sampler. Samples for lakes >5 m were composited with depth, and a single chlorophyll sample was taken. All samples were placed in opaque plastic bottles and stored in ice. In the laboratory, a minimum of 100 mL of sample was filtered through Whatman 4.25 GF/A glass fiber filters. To the final mL of sample, 5 drops of aqueous saturated magnesium carbonate were added. The filters were placed in glass test tubes containing 5 mL of acetone and ground with a Wheaton tissue grinder. The ground samples were stoppered, and extracted in the dark at -14°C for 24 h. The extracts were filtered through glass fiber filters using a Millipore Swinnex filter attachment and disposable syringes, and the filtrates were brought to final volume of 10 mL with acetone. Absorbance was read on Beckman DBG spectrophotometer according to Standard methods (APHA 1976). Chlorophyll a is the active form of the pigment (i.e. total chlorophyll corrected for phaeophytin [APHA 1976]).

Phytoplankton samples (80 mL) were collected by a 2.2 L. Kammerer sampler at 0.5 m for lakes < 5 m and at the top, middle and bottom of the water column of lakes > 5 m. Samples were taken in the center of each lake, placed in screw-cap glass bottles, and preserved with 2 mL of acidified Lugol's solution. In the laboratory, sample aliquots were allowed to settle in an Utermohl chamber and identified using a Unitron inverted microscope using taxonomic keys in Whitford and Schumacher (1973), Cocke (1967), Weber (1971), Prescott (1954), and Smith (1950).

Zooplankton samples were obtained by a vertical tow through the entire water column near the center of each lake with a number 20 (mesh 80  $\mu$ m) preserved 10% buffered formalin and identified using taxonomic keys in Edmondson (1959) and Pennak (1953). At least 100 individuals were counted in each sample under a dissecting microscope at 250x. Zooplankton biomass was obtained by multiplying the number of individuals for each species by an appropriate biomass conversion factor (Dumont et al. 1975).

Two habitats of benthic invertebrate communities were sampled in each lake. Duplicate grabs were taken at both a shallow-sand station and a deep-mud station. The importance of substrate characteristics in the distribution of benthic communities has been pointed out by Bloom et al. (1972), Parsons (1968), and Mahadevan et al. (1977). Samples were taken with a Ponar grab (Powers and Robertson 1967) with a sampling area of 0.02 m<sup>2</sup> and a penetration of about 10 cm in mud (slightly less in harder substances such as sand). Samples were washed in the field through a 0.66 mm mesh sieve to remove excess sediment. Remaining organisms were preserved in 10% formalin and stained with rose bengal. Samples were sorted in a white pan in the laboratory and identified using both a dissecting and a compound microscope. Biomass measurements were determined for each lake station. All individuals from a single Ponar sample were placed in a tared crucible and dried at 150°C for 24 h to determine dry weights. Ash-free dry weights were determined by combusting samples in a muffle furnace at 550°C for one hour. Statistical analysis was conducted



using a package of computer programs developed by Bloom et al. (1977) on an Amdahl 470 at the University of Florida.

## RESULTS OF LAKE STUDY: WATER CHEMISTRY

Discussion of the water chemistry of the 20 survey lakes is best accomplished by segregating the lakes into groups according to pH. In the original selection of lakes for study, a geographic grouping (Trail Ridge vs. Highlands Ridge) was used, reflecting the difference in precipitation acidity (Figure 5-1) at the northern (Trail Ridge) site compared to the southern site (Highlands Ridge). However, a one-way ANOVA and Duncan's multiple range test (SAS; Barr et al. 1976) indicate that the lakes (Figure 6-3) also can be divided into two groups based on pH (i.e. acidic and non-acidic). The boundary pH between the two groups is 5.6, which coincidentally is the geochemical equilibrium pH of pure water in contact with atmospheric  $\text{CO}_2$ . The grouping based on pH compares closely with the geographical grouping (Table 6-1), except that the three largest lakes of the Trail Ridge group, Kingsley, Geneva, and Altho, were grouped with the Highlands Ridge lakes. These three Trail Ridge lakes have higher pH levels than the other Trail Ridge lakes, possibly because of their size, depth, and extent of shoreline development. The following discussion thus divides the 20 lakes into two groups: an acidic lake group (pH < 5.6) and an non-acidic group (pH > 5.6).

### Lake Transparency

As discussed earlier, the lakes located along the Trail and Highlands Ridges were formed in basins consisting of sandy deposits, and they have little or no input of surface runoff. Thus these lakes have the most transparent waters of any lakes in the state. Except for two highly colored lakes, Altho and Josephine, which had mean annual color levels of 194 and 154 CU, most of the lakes had color values of 20 CU or less. Both Altho and Josephine are a typical of the other Ridge lakes in that cypress wetlands are located within

<u>GROUPING</u>		<u>MEAN pH</u>	<u>N</u>	<u>LAKE</u>	
	A	6.795	4	Francis	NONACID LAKE GROUP
	A				
	A	6.742	4	Kingsley	
	A				
	A	6.710	4	Clay	
	A				
	A	6.670	4	June	
	A				
	A	6.535	4	Placid	
	A				
	A	6.497	4	Letta	
	B	6.145	4	Geneva	ACID LAKE GROUP
	B				
	B	6.142	4	Josephine	
	B				
C	B	6.025	4	Altho	
C					
C		5.752	4	Annie	
	D	5.245	4	Johnson	
	D				
E	D	5.195	4	Lowery	ACID LAKE GROUP
E	D				
E	D	5.140	4	Sheeler	
E	D				
E	D	5.097	4	Magnolia	
E	D				
E	D	5.057	4	Rosa	
E	D				
E	D	F 5.025	4	Brooklyn	
E	D	F			
E	D	F 4.980	4	Galilee	ACID LAKE GROUP
E	D	F			
E	D	F 4.940	4	Anderson Cue	
E		F			
E		F 4.857	4	Cowpen	
E		F			
		F 4.715	4	McCloud	

Figure 6-3. Duncan's multiple range test for the annual mean pH of the surveyed lakes. Mean lake pH values with the same letter are not significantly different at the .05 level.

their watersheds, and colored water containing humic material flows from these swampy areas into the lakes. Lowest color concentrations were recorded for two pristine, extremely clear lakes, Sheeler (5CU) and Annie (7CU). Average turbidity levels also were very low in the lakes, ranging from 0.6 NTU (Sheeler and Cowpen) to 4.9 NTU (Josephine). Values for most of the lakes were less than 2 NTU.

As expected for lakes having low color and turbidity levels, transparency (Secchi disk) values were high. For example, Lakes Sheeler, Santa Rosa, and Magnolia (in the Trail Ridge group) had average Secchi transparency depths of 7.9, 5.9, and 5.3 m, respectively. Lake Annie (in the Highlands Ridge) had an average Secchi depth of 5.5 m. The two colored lakes, Altho and Josephine, had the lowest mean Secchi values of all the lakes, 104 and 67 cm, respectively. Greatest Secchi depth values generally were recorded in the winter and spring months. Water levels for several of the Trail Ridge lakes were at a 20 year low as a result of several years of below normal rainfall. Consequently, the Secchi disk sometimes was visible resting on the bottom of some of the lakes. This was particularly true for lakes Cowpen and McCloud.

#### Major Ion Composition

The ionic composition of surface waters is a function of contributions from surface and subsurface runoff within the drainage basin, atmospheric precipitation, and the balance between evaporation and precipitation. In soft-water lakes such as those of the Trail and Highlands ridge districts, the relative abundance of cations and anions is often given as (Wetzel 1975):

Cations:  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ ;

Anions:  $\text{Cl} > \text{SO}_4 > \text{HCO}_3$ .

Table 6-3 lists the mean concentrations and standard deviations of major ions in the two lake groups, and Figure 6-4 presents the average contributions (equiva-

Table 6-3. Means and standard deviations of major ions and specific conductance in the two lake groups.

Parameter	Acidic Group* 10 Lakes (N=40)	Non-acidic Group* 10 Lakes (N=40)
H <sup>+</sup> µg/L	10.5 ± 5.0 (pH 4.98)	0.62 ± 0.62 (pH 6.21)
Specific µS/cm Conductance @ 25°C	41.5 ± 18.2	92.9 ± 39.8
Na <sup>+</sup> mg/L	2.88 ± 1.27	5.92 ± 2.13
Ca <sup>+2</sup> mg/L	0.99 ± 0.75	3.67 ± 1.52
Mg <sup>+2</sup> mg/L	0.54 ± 0.27	2.15 ± 1.36
K <sup>+</sup> mg/L	0.57 ± 0.35	2.03 ± 1.67
Al <sup>+3</sup> µg/L	58 ± 29	23 ± 15
Cl <sup>-</sup> mg/L	5.51 ± 1.94	11.10 ± 3.55
SO <sub>4</sub> <sup>-2</sup> mg/L	5.51 ± 1.94	13.01 ± 6.51
HCO <sub>3</sub> <sup>-</sup> mg/L	0	8.66 ± 5.28

\* Means for the two groups are significantly different (P < 0.0001 in each case) for each parameter, based on one-way ANOVA (Barr et al. 1976).

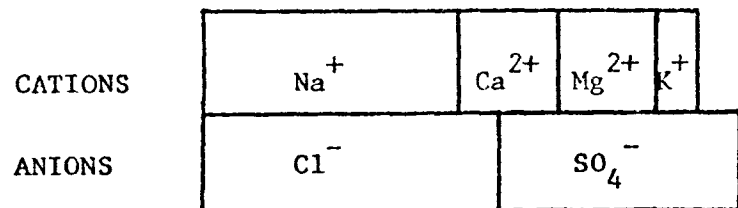
lent basis) of the major ions to the total cation and anion equivalents. For each parameter listed in Table 6-3 there is a statistically significant difference between the mean values in each lake group. The ionic bar graphs show good agreement between the sums of the major cation and anion equivalents. Additionally, theoretical conductivities were calculated from the mean ionic composition of each lake group. These values compare closely to the mean measured conductivities for the two groups:

	Specific Conductance <u><math>\mu\text{S/cm}</math> (at <math>25^{\circ}\text{C}</math>)</u>		
	<u>Actual</u>	<u>Calculated</u>	<u>% Error</u>
Acidic Group	41.5	38.2	8%
Non-acidic Group	92.9	89.3	4%

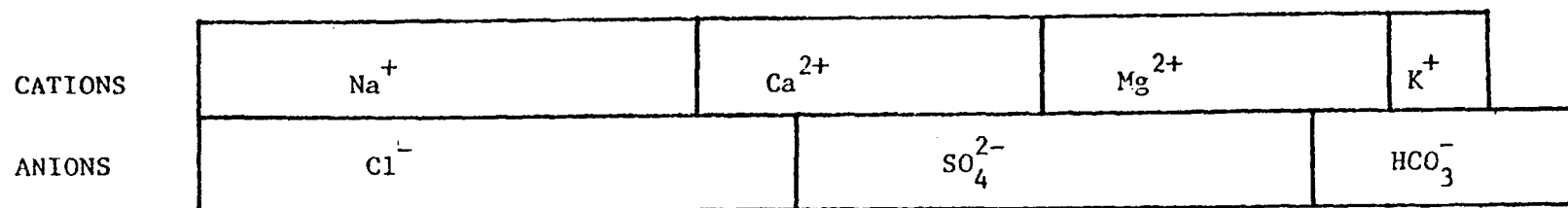
The bar graphs in Figure 6-4 illustrate that on an  $\mu\text{eq/L}$  basis, the order of dominance of cations in both groups of lakes is the same as that given above for typical softwater lakes. The cations in both lake groups are dominated by sodium on both a  $\text{mg/L}$  and a  $\mu\text{eq/L}$  basis. Sodium comprises 50 and 39% of the cationic equivalents in the acidic and non-acidic groups, respectively. The contributions of calcium (20%) and magnesium (18%) are approximately equal in the acidic group as well as in the non-acidic group; Ca (27%) and Mg (26%). Potassium is the least important of the major cations and contributes 6-8% of the cationic equivalents in the two groups. Hydrogen ( $\text{H}^+$ ) and aluminum ion provide small contributions ( $< 5\%$  each) to the cation equivalents of the acidic lake group.

The major anions in the acidic lake group are chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ), which comprise 57 and 43% of the total anion equivalents,

100  
μEQ/L  
SCALE



ACIDIC LAKE GROUP



NON-ACIDIC LAKE GROUP

Figure 6-4. Distribution of major cations and anions in the two study lake groups.

respectively. In the non-acidic group the major anion species are  $\text{Cl}^-$  (43%),  $\text{SO}_4^{2-}$  (37%) and bicarbonate,  $\text{HCO}_3^-$  (20%), but there is no contribution by  $\text{HCO}_3^-$  to the anion component for the acidic group. The low bicarbonate levels that existed in these lakes in the 1950s and 1960s have been titrated by inputs of acidic precipitation over the last decade. This matter is discussed in greater detail in the section dealing with historical lakewater chemistry trends.

Specific conductance values from the survey lakes were low, as expected for soft-water lakes. All the lakes had annual mean values less than 150  $\mu\text{S}/\text{cm}$ , and 9 of the 20 lakes had mean values less than 50  $\mu\text{S}/\text{cm}$  (Figure 6-5). The mean conductivity for the acidic group was 41.5  $\mu\text{S}/\text{cm}$  (range of 19 to 78  $\mu\text{S}/\text{cm}$ ). For the non-acidic group the mean was 92.9  $\mu\text{S}/\text{cm}$  (range of 35 to 147  $\mu\text{S}/\text{cm}$ ). As shown in Figure 6-5 the lakes with the higher pH values also tended to have higher conductivity values indicating somewhat harder, more buffered waters.

The mean pH of the acidic lake group was 4.98, and annual means ranged from 4.71 (McCloud) to 5.21 (Johnson). The mean for the non-acidic group was 6.21, and annual means ranged from 5.73 (Annie) to 6.70 (Clay). The lowest measured pH during the study was 4.60 for McCloud (winter), while the highest value was 7.02 for Francis (fall). Seasonal variations generally were less pronounced for the acidic lake group than the non-acid group. The very acidic Lake McCloud, for example, had pH values that ranged from 4.60 (winter) to 4.82 (spring), while Lake Francis, a non-acid lake, had pH values ranging from 6.35 to 7.02 (spring and fall, respectively). The larger seasonal fluctuations of pH in the non-acidic lakes likely reflect higher productivities in these lakes than the acidic lakes. As shown in Table 6-3 there is a statistically significant difference between the mean pH values of each group.

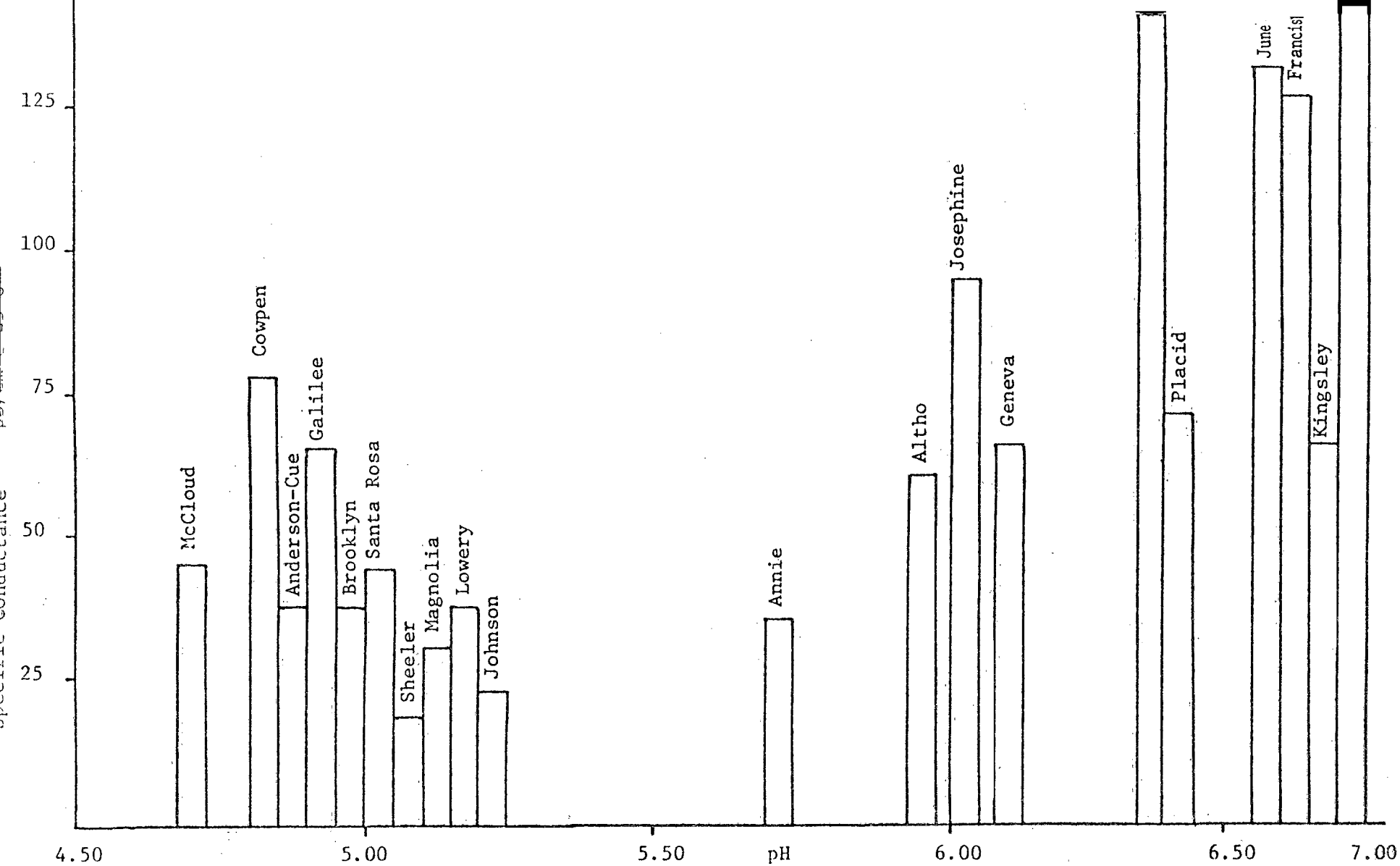


Figure 6-5. Annual mean specific conductance as a function of pH for the 20 survey lakes.



## Nutrient Forms

To properly assess the effect of acidification on the biota and productivity of the survey lakes it is necessary to also consider nutrient levels in the lakes. The most important nutrients controlling the productivity of lakes are phosphorus and nitrogen. Silica concentrations can be important in controlling algal species composition, i.e. in limiting the growth of diatoms.

Table 6-4 presents the means and standard deviations of major phosphorus forms in each lake group. In the acidic lake group, annual average soluble reactive phosphate (SRP) levels ranged from 4 (Sheeler) to 18  $\mu\text{g/L}$  (Anderson-Cue) and total phosphate (TP) concentrations ranged from 7 (Sheeler) to 40  $\mu\text{g/L}$  (Anderson-Cue). In the non-acidic group, SRP ranged from 4  $\mu\text{g/L}$  (Annie) to a high of 27  $\mu\text{g/L}$  (Josephine). The annual average TP concentration also was lowest in Annie (8  $\mu\text{g/L}$ ) and highest in Josephine (68  $\mu\text{g/L}$ ). Statistical analysis (ANOVA) showed no significant difference (0.05 level) between the mean SRP concentrations in the two lake groups, but a significant difference was found for the TP and ORG/P levels (Table 6-4).

Mean and standard deviations for the major forms of nitrogen in the two lake groups are listed in Table 6-4. Average inorganic nitrogen concentrations (in mg N/L) in the acid lake group ranged from 0.037 (Cowpen) to 0.37 (Anderson-Cue), while the range in the non-acid group was 0.026 (Annie) to 0.106 (Placid). Organic nitrogen levels (in mg N/L) ranged from 0.10 (Cowpen) to 0.46 (Anderson-Cue) in the acid lake group and from 0.23 (Annie) to 0.68 (Josephine) for the non-acid lakes. Statistically significant differences between the means of each group were not found (Table 6-4) for the inorganic species ( $\text{NH}_4^+$ , and  $\text{NO}_3^-$ ), but TON and TN levels were different (at the 0.0001 and 0.005 levels, respectively).

Table 6-4. Means and standard deviations of nutrients in the two lake groups.

Parameter	Acidic Group 10 lakes (N=40)	Non-acidic Group 10 lakes (N=40)	Probability* means are not different
$\text{NH}_4^+\text{-N}$ $\mu\text{g/L}$	72 $\pm$ 99	41 $\pm$ 48	.0812
$\text{NO}_3^-\text{-N}$ $\mu\text{g/L}$	21 $\pm$ 41	16 $\pm$ 17	.4158
TON $\mu\text{g/L}$	199 $\pm$ 131	405 $\pm$ 193	.0001
TN $\mu\text{g/L}$	292 $\pm$ 219	462 $\pm$ 196	.0005
SRP $\mu\text{g/L}$	7 $\pm$ 6	10 $\pm$ 11	.0940
TP $\mu\text{g/L}$	16 $\pm$ 12	26 $\pm$ 22	.0109
ORG P $\mu\text{g/L}$	9 $\pm$ 9	16 $\pm$ 19	.0353
TOC $\text{mg/L}$	4.6 $\pm$ 3.4	7.0 $\pm$ 3.9	.0039
$\text{SiO}_2$ $\mu\text{g/L}$	459 $\pm$ 341	420 $\pm$ 416	.65481

\*Probabilities listed are from ANOVA (Barr et al. 1976) on the annual means for each parameter in each group. If  $P < .05$ , means are accepted as statistically different.

Silica concentrations can be important in controlling productivity in fresh waters especially if the phytoplankton population is composed largely of diatoms. As shown in Table 6-4, the mean values of  $\text{SiO}_2$  in the two lake groups are similar, and the large standard deviations for each mean indicate considerable scatter in  $\text{SiO}_2$  concentrations within the groups. For example,  $\text{SiO}_2$  mean concentrations ranged from 51 (Cowpen) to 950  $\mu\text{g/L}$  (Lowery) in the acid lake group, and in the non-acid group silica ranged from 115 (Geneva) to 1180  $\mu\text{g/L}$  (Josephine). Consequently, statistical analysis indicated no significant difference in mean  $\text{SiO}_2$  between the two groups of lakes.

Since significant differences were found in the mean levels of organic constituents (TON, ORGP, TOC) and total nutrients (TN, TP) between the two lake groups (Table 6-4), the non-acidic lakes (with higher values for these parameters) would appear to be more productive than the acidic lakes. As discussed in a later section, the difference in chlorophyll a levels between the two lake groups support this conclusion. Reasons for the increased levels of total and organic nutrients in the non-acidic lakes are not certain, but it may reflect lower rates of mineralization in acidic waters. On the other hand, the lower nutrient concentrations may simply reflect lower nutrient loading rates to the acidic lakes, many of which are in small pristine watersheds. Further studies are necessary to evaluate these alternate explanations.

#### Aluminum

Atmospheric inputs of acidity ( $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) to the drainage basins of lakes results in increased weathering and mobilization of metals within the watersheds of the lakes. In noncalcareous soils, increased deposition of acidity leads to increased concentrations of dissolved aluminum in surface and ground waters (Cronan and Schofield 1979; Gjessing et al. 1976). An important ecological consequence of increased aluminum levels in lake waters

is the loss or diminution of game fish populations because of the toxic effect of free aluminum ion ( $\text{Al}^{3+}$ ) and its hydroxo-complexes ( $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ). Laboratory studies have shown that brook trout exhibit a toxic response when aluminum levels are above 200  $\mu\text{g/L}$  in the pH range 4.4 to 5.9.

Since the watersheds of the Trail and Highlands Ridge lakes are typically noncalcareous, aluminum analyses were included in the chemical determinations of the lakes. The mean aluminum concentrations and within-year ranges for each lake are presented as a function of the mean lakewater pH in Figure 6-6. Highest aluminum levels were found in the lakes with the lowest mean pH values. The average aluminum concentration for the acidic lake group was 58  $\mu\text{g/L}$ , while the mean for the non-acidic group was 23  $\mu\text{g/L}$ . These mean values are statistically different at the 0.0001 level (Table 6-3). The mean aluminum concentrations ranged from 116 (Cowpen) to 33  $\mu\text{g/L}$  (Sheeler) in the acidic lake group and 43 (Annie) to 24  $\mu\text{g/L}$  (Geneva) in the non-acidic group. The highest Al concentration found during the survey was 150  $\mu\text{g/L}$  in Lake Cowpen in winter of 1978. Since precipitation contains very little aluminum ( $< 10 \mu\text{g/L}$ ), the aluminum levels in the lakes have resulted from leaching of soils within the watersheds.

#### Analysis of historical trends in chemical composition of the lakes

Water chemistry data on some of the lakes in the Trail Ridge region are available for over a 20 year period, and thus it is possible to examine the results of the present lake survey in a historical context. However, it should be pointed out that in most cases the historical record is rather sparse. No measurements are available for many years, and the number of samples collected in any year was very small (one or two) for most of the historical studies. Table 6-2 lists data on pH, alkalinity ( $\text{mg/L}$  as  $\text{CaCO}_3$ ), and sulfate for eleven of the Trail ridge lakes in a generally chronological

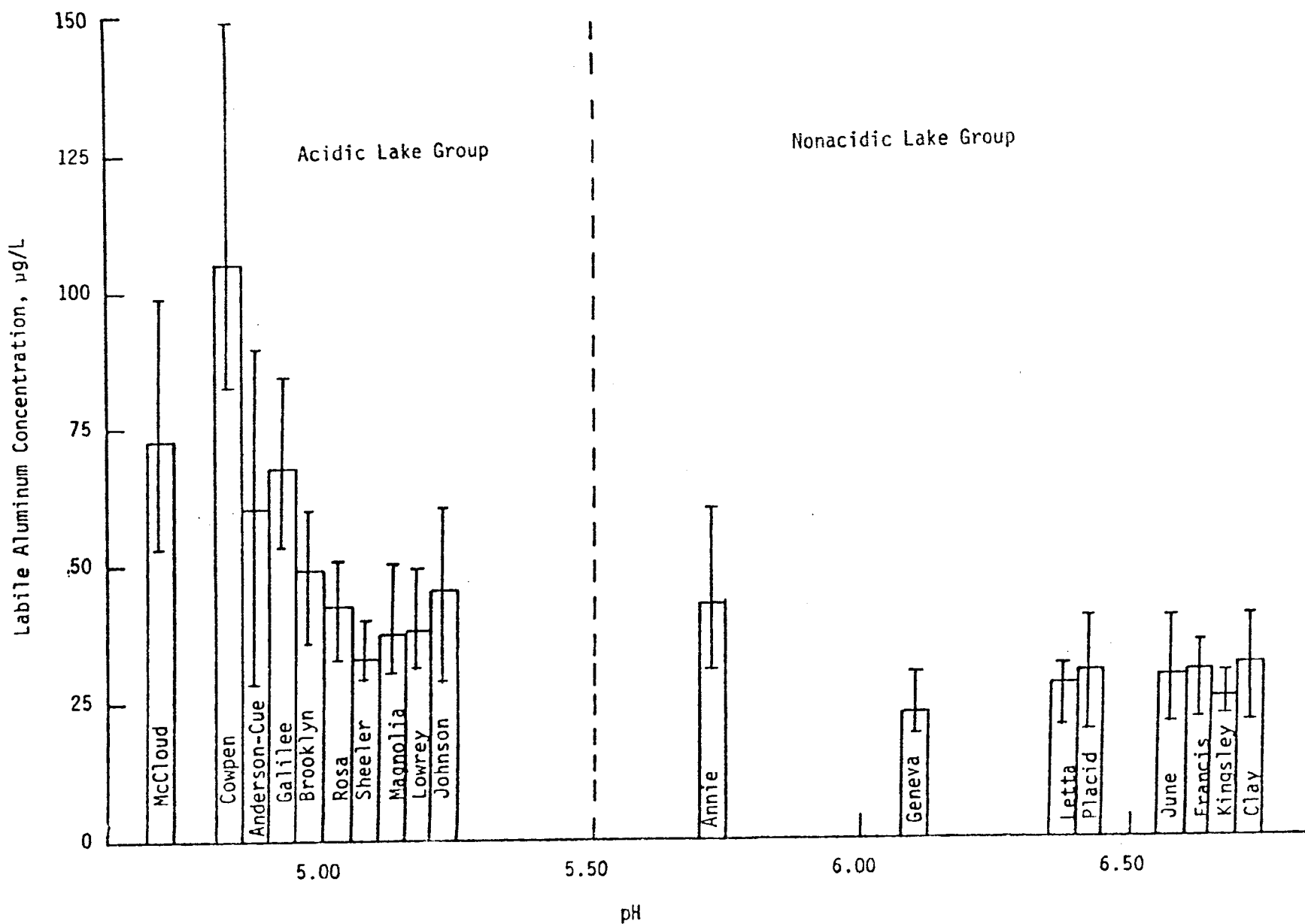


Figure 6-6. Range and mean annual concentration of aluminum as function of pH for the survey lakes.

sequence. These parameters were chosen for historical comparison because they most likely would reflect lakewater chemistry changes brought about by increased deposition of acidic precipitation. Approximately 70% of the free acidity in precipitation in Florida is  $\text{H}_2\text{SO}_4$  (see Chapter 5). The data indicate that changes in water chemistry have occurred for all the lakes within the time period of the data collection. Except for Lakes Geneva and Kingsley, the lakes show a decrease in pH and/or alkalinity, presumably due to atmospheric inputs of sulfuric and nitric acids. Increases in the  $\text{SO}_4^{2-}$  content of the lakes are also evident for most of the lakes. Interestingly, Lakes Geneva and Kingsley show increases in both pH and alkalinity over the past 20 years. These lakes are the largest of the Trail Ridge lakes (Table 6-1), and they have experienced extensive shoreline development during this time period. There apparently are no historical data on Lake Sheeler with which comparisons may be made.

Previous data for Lakes June, Francis, and Letta (Highlands Ridge) collected during 1967-72 (Holcomb 1968,69; Duchrow 1970,71,72) indicate these lakes have shown little change in pH and alkalinity over the last 10 years.

It has been estimated (Likens et al. 1979) that lakes with about 80  $\mu\text{eq/L}$  of  $\text{HCO}_3^-$  (alkalinity equal to 4.0 mg/L as  $\text{CaCO}_3$ ) and a pH of approximately 6.5 will lose their bicarbonate buffer to the point where the lakewater pH drops below 5, if the long-term mean pH of precipitation is about 4.3. Less acidic precipitation could bring about similar changes in lakes with originally lower bicarbonate levels. As shown in Table 6-2, the alkalinity of the soft-water Trail Ridge lakes has essentially been completely titrated by acidic precipitation. Consequently, these lakes are very sensitive to further acidic inputs.

## Results of Lake Survey: Biological Communities

### Phytoplankton and Chlorophyll

As the base of the aquatic food chain, phytoplankton are an essential component of lake ecosystems. Variations in the number of individuals, in species richness, or in productivity may affect all trophic levels. The effects of increased acidity on phytoplankton communities include a decline in species richness, a reduction in algal abundance, decreased algal productivity, and a replacement of blue-green algae by green algae as the dominant phytoplankters (Lackey 1938; Leivestad et al. 1976; Yan and Stokes 1978).

The concentration of total phosphorus (TP) is important to the productivity of phytoplankton communities (Vollenweider, 1968). The mean TP concentration in the 10 acidic lakes was 15  $\mu\text{g/L}$ , whereas the less acidic group had a mean of 26  $\mu\text{g/L}$  (Table 6-4). The concentration of phosphorus in lake water can be decreased by lowering pH in part because rates and efficiencies on nutrient recycling from organic matter are thought to be lower under acidic conditions (Grahn 1976). However, most of the lakes in the nonacid group are in watersheds with moderate cultural development (including some orange groves). Watersheds of lakes in the nonacidic group generally have less cultural development, and the lower concentrations of TP in the acidic lakes thus are likely due to a combination of increased acidity and reduced cultural impact.

### Chlorophyll a

Mean annual chlorophyll a concentrations (corrected for phaeophytin) from the 10 acidic lakes (Table 6-5) was 2.74  $\text{mg/m}^3$ , and the mean for the 10 nonacidic lakes was 10.0  $\text{mg/m}^3$ . Concentrations of chlorophyll a decreased with decreasing pH (Figure 6-7a), although the data exhibit a fair amount of scatter. The mean chlorophyll a concentration in the 5 pH intervals (Figure

Table 6-5. Summary of phytoplankton data for the 20 study lakes.

Lake	pH	Number of Species*	Individuals <sup>2</sup> (#/mL)	Chlorophyll <u>a</u> mg/m <sup>3</sup>
McCloud	4.71	12	7,340	0.9
Cowpen	4.84	9	2,940	1.3
Anderson-Cue	4.89	9	10,870	2.8
Galilee	4.96	12	5,650	2.9
Brooklyn	5.01	8	4,330	3.0
Rosa	5.05	12	3,390	2.2
Sheeler	5.09	11	3,730	1.0
Magnolia	5.10	10	5,460	1.1
Lowery	5.19	12	4,510	1.1
Johnson	5.20	13	8,520	2.5
Annie	5.72	12	8,890	1.5
Altho	6.00	17	8,680	5.5
Josephine	6.07	22	25,580	11.0
Geneva	6.12	11	4,730	3.5
Letta	6.37	19	24,540	10.5
Placid	6.40	17	9,590	7.2
June	6.64	18	9,720	9.7
Francis	6.66	21	24,160	10.9
Kingsley	6.68	12	9,070	2.7
Clay	6.69	16	15,080	12.7

\* Mean values for four sampling periods

1. Mean number of species encountered for four sampling periods.

2. Mean values for four sampling periods



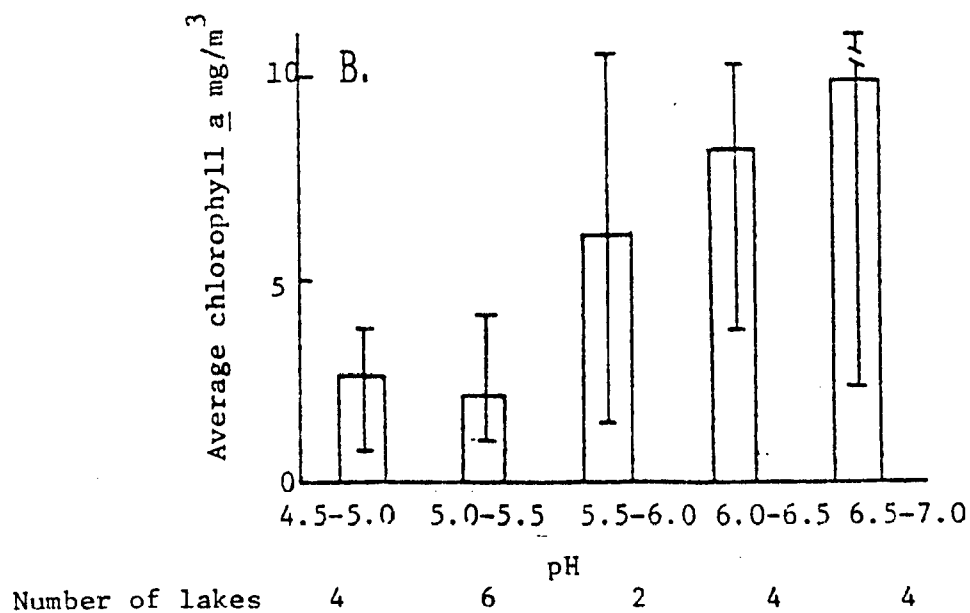
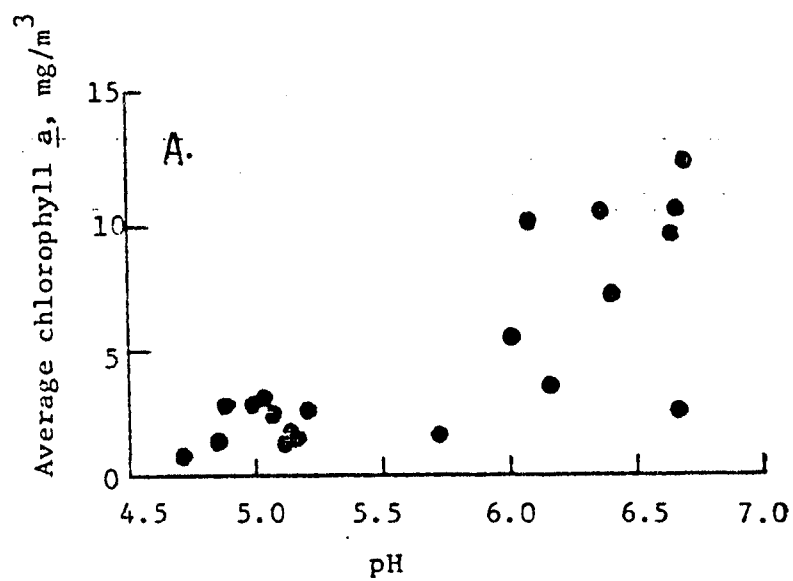


Figure 6-7. Annual average chlorophyll *a* vs. pH (A) and as means of lakes within five pH intervals (B) for the 20 survey lakes.

6-7b) more clearly demonstrates the definite trend of decreasing chlorophyll a with decreasing pH. Using a Kruskal-Wallis rank sum test, the lakes were shown to contain statistically different concentrations of chlorophyll a ( $\alpha = .005$ ).

In addition to a pH-chlorophyll relationship, a phosphorus-chlorophyll relationship also can be discerned in Figure 6-8. However, the absence of lakes with low pH and high total phosphorus concentrations in the sample group precludes the definition of a response surface for pH, total phosphorus, and chlorophyll a over the entire pH range (4.5 - 7.0) in the data base. A sufficient range of TP values exists for lakes with relatively high pH (i.e. values > 6.0) to demonstrate an overall trend of increased chlorophyll a with increased total phosphorus. The limited data for lakes with low pH also suggest a similar trend of increasing chlorophyll with increasing phosphate content.

#### Species Richness and Abundance of Phytoplankton

A reduction in the number of phytoplankton species found in a given sample decreased (Table 6-5), but as shown in Figure 6-9a, a considerable amount of scatter exists in the relationship, especially for lakes with pH > 6.0. In the less acidic lakes, hydrogen ion concentration exerts less control over phytoplankton community than in lakes of lower pH. Using a Kruskal-Wallis rank sum test, the 20 lakes were found to contain statistically different number of phytoplankton species ( $\alpha = .005$ ).

The mean number of species in the 10 acidic lakes ( $\text{pH} \leq 5.2$ ) was 10.8, with a range of 8 to 13, and the mean number of species on the non-acidic lakes ( $\text{pH} \geq 5.7$ ) was 16.5, with a range of 11 to 22. By grouping the 20 lakes into five pH intervals (Figure 6-9b), the decrease in number of species with decreasing pH is depicted more clearly. The mean number of species increased progressively from 10.5 in the most acidic group of lakes to 17.0 in the least acidic group of lakes.

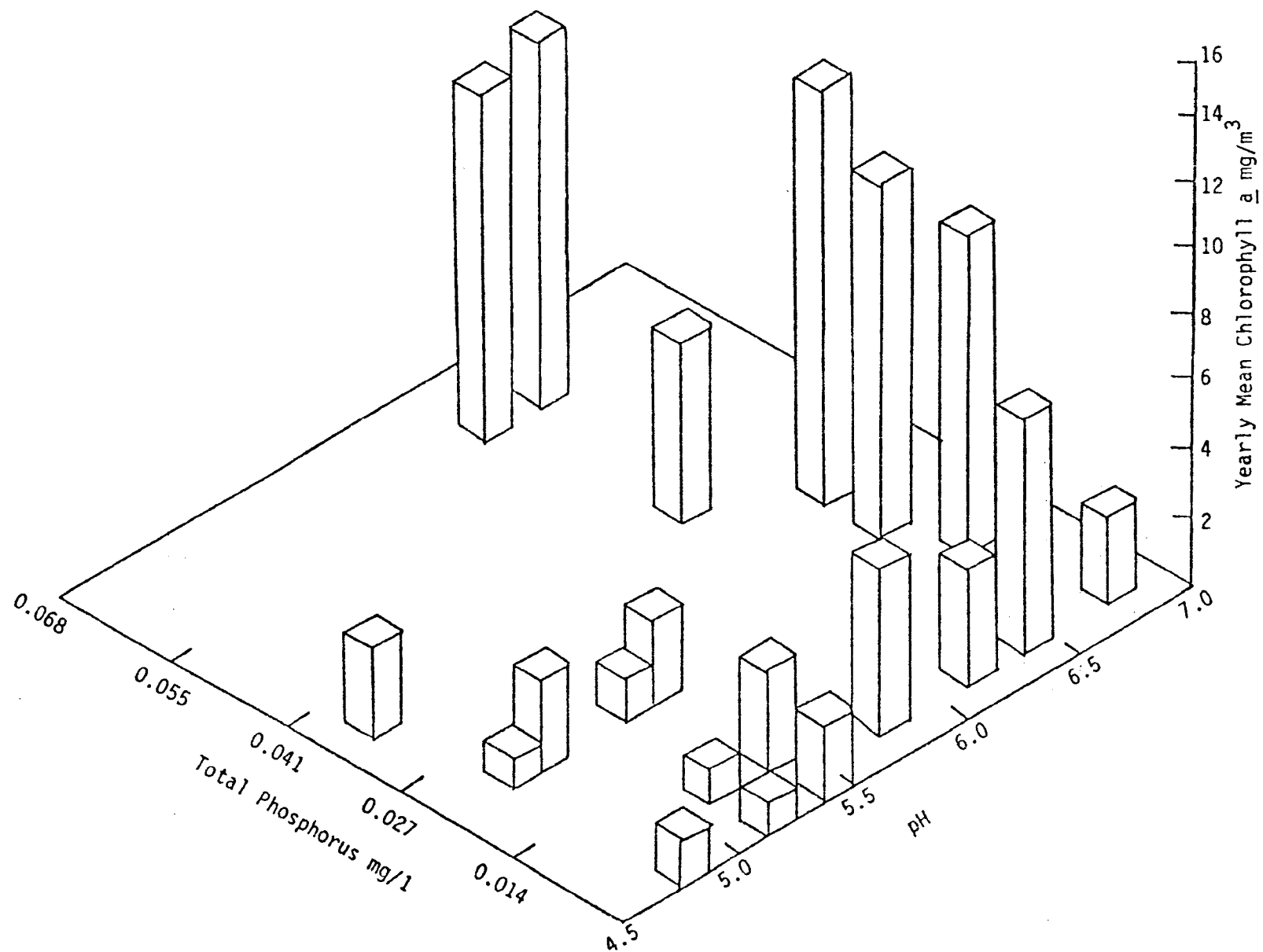


Figure 6-8, Three dimensional plot of chlorophyll  $a$  level as a function of pH and total phosphate levels in the 20 lakes.

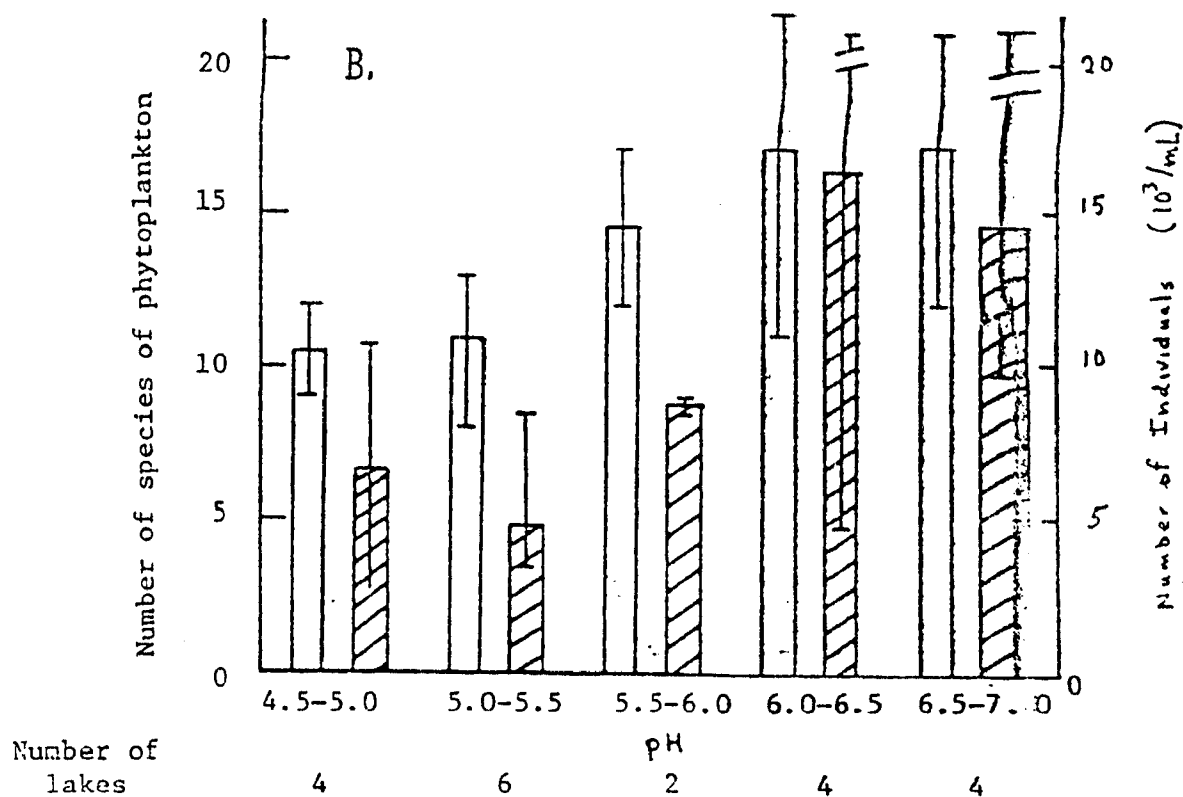
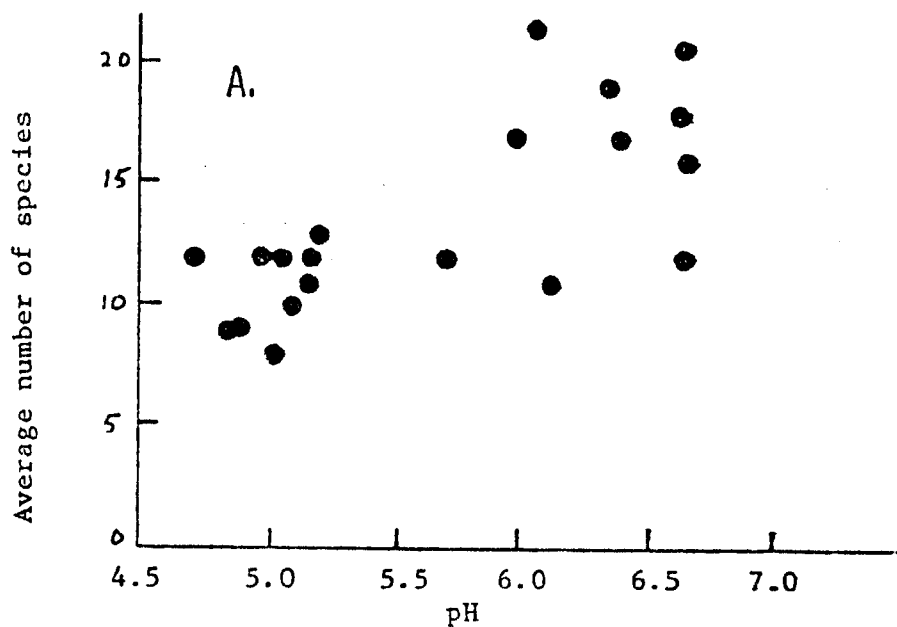


Figure 6-9. Average number of species of phytoplankton vs. pH (A) and bar graphs of average number of species and average number of individuals per lake within five pH intervals (B) for the 20 survey lakes.

Similarly, the number of phytoplankton individuals decreased with decreasing pH (Figure 6-10), but again the data are highly scattered. Using a Kruskal-Wallis rank sum test, the 20 lakes were found to have statistically different phytoplankton abundances ( $\alpha = .0005$ ). The mean number of individuals from the 10 acidic lakes was 5,670/mL, with a range of 2,940 to 10,900/mL. The mean number of individuals from the nonacidic lakes was 14,000/mL, with a range of 4,730 to 25,600/mL. The mean number of phytoplankton individuals in each of the 5 pH intervals (Figure 6-9b) more clearly illustrates the increase in the number of individuals in the pH range of 6.0 - 7.0.

The isometric plot in Figure 6-11 illustrates the dependence of phytoplankton abundance on both pH and total phosphorus concentration. The absence of lakes with low pH and high total-phosphorus in the data base again precludes definition of the complete response surface. Based on available data, phytoplankton abundance increased with increasing pH at all levels of total phosphorus encountered in the 20 study lakes. A similar but less complete trend of increasing phytoplankton abundance with increasing total phosphorus was observed at all pH intervals.

The ability of acidic conditions to decrease the concentration of available plant nutrients (such as phosphorus) has been proposed (Dickson, 1978; Grahn 1976; Anderson et al. 1978). The consistently low total phosphorus levels in all acidic lakes except Anderson-Cue, plus reports in the literature of decreased recycling of nutrients in acidic lakes suggest a causal relationship between the low phosphorus concentration and low pH of the lakes. Anderson-Cue lake was the site of a previous eutrophication experiment (Brezonik et. al. 1969) and received relatively high inputs of phosphorus for several years. Further studies are needed to define the relationship among phosphorus, chlorophyll, and lake acidity.

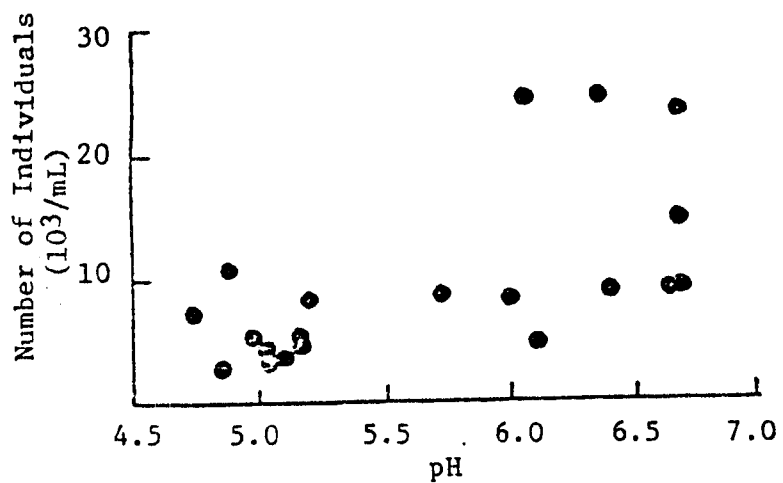


Figure 6-10. Phytoplankton density (number of individuals per mL) vs. pH for the 20 survey lakes.

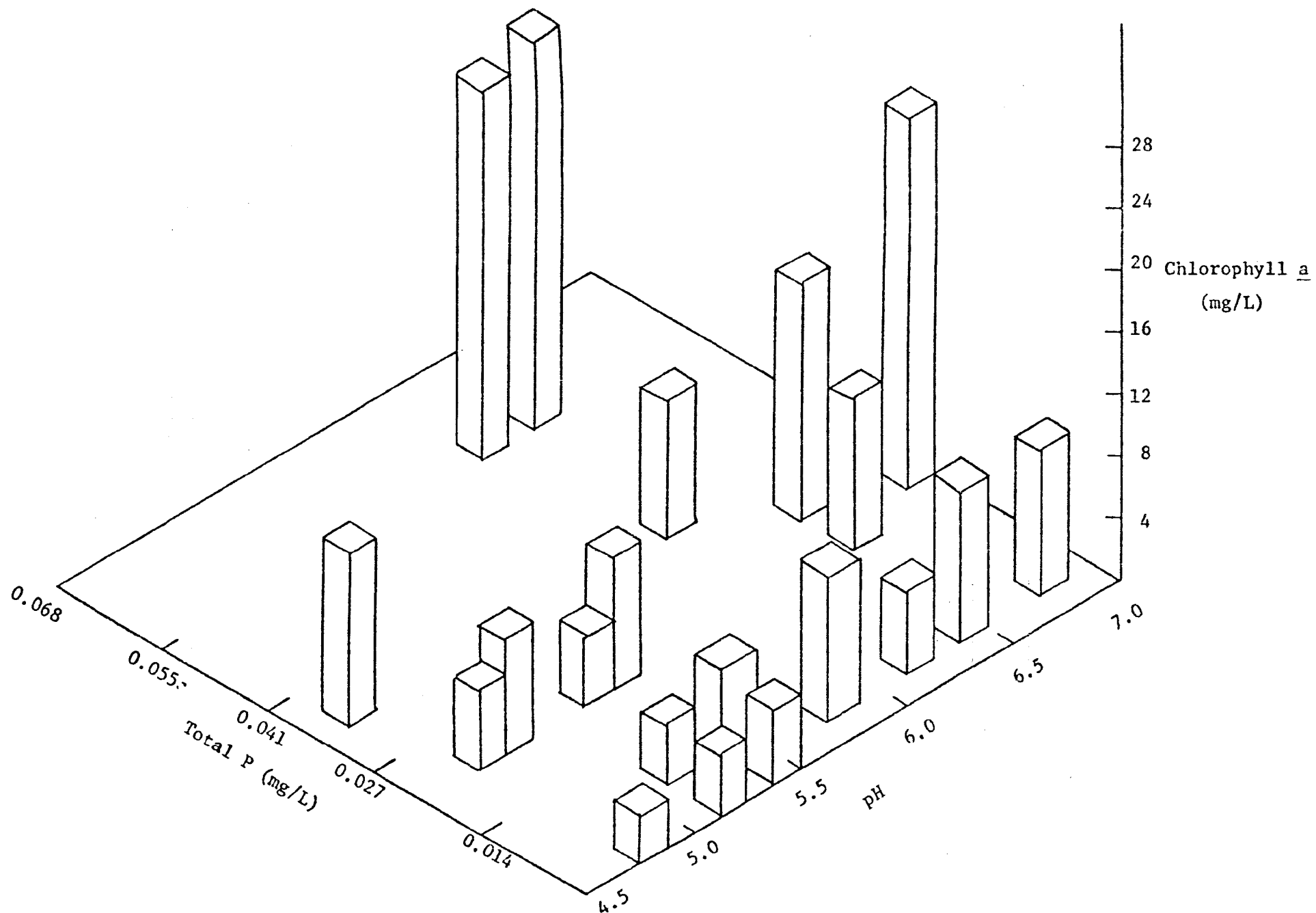


Figure 6-11. Three dimensional plot of phytoplankton density as a function of pH and total phosphate levels in the 20 survey lakes.

### Species Composition

One of the most obvious changes in the composition of phytoplankton communities, both in previous studies (Yan 1975) and in the present investigation, is a replacement of blue-green algae as the dominant group at high pH by green algae as the dominant group at low pH. In lakes of pH 4.5 - 5.0 (Figure 6-12), green algae made up 60% of the total number of phytoplankton individuals, while blue-green algae contributed 25%. In lakes of pH 6.51 - 7.0, green algae were responsible for 31%, while blue-green algae made up 63% of the total number of individuals. Similar results were obtained by Yan and Stokes (1978), who found an increase in the ratio of green algae to blue-green algae with increasing acidity.

A decrease in the number of rare species was strongly associated with decreasing pH, as shown in the species list in Table 6-6. Highly acidic lakes were dominated by Staurastrum spp., Scenedesmus sp., Ankistrodesmus falcatus, Peridinium inconspicuum and several species of small coccoid green algae. Blue-green algae were sparse in the acidic lakes and were represented mainly by Oscillatoria limnetica and Anacystis incerta. Other algae found in the acidic lakes included Euglena sp., Oocystis spp. and Chlamydomonas sp. Diatoms were also rare in the acidic waters, with Tabellaria sp. as the dominant genus and Navicula and Melosira as the principal subdominants. The nonacidic Florida lakes contained more rare species and greater numbers of blue-green species such as Amigdalum quadridentata, Anabaena spp., Spirulina laxissima and Microcystis aeruginosa.

The species composition of the study lakes was similar to that for lakes of comparable pH reported in the literature. Almer et al. (1974) found Chlamydomonas sp., Peridinium inconspicuum, and Oocystis sp. as the dominants in acidified lakes of Scandinavia.



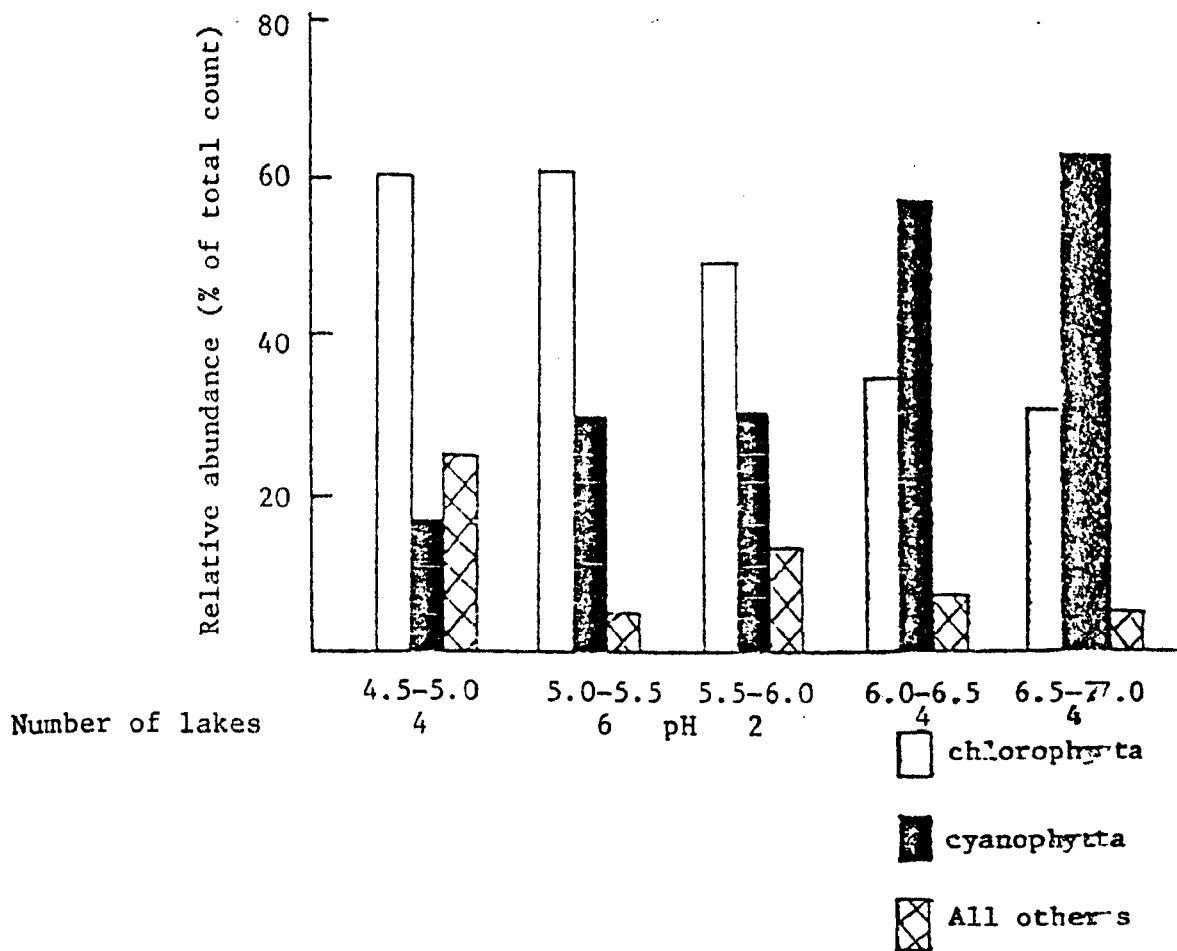


Figure 6-12. Relative abundance of major phytoplankton taxa in the lakes grouped within five pH intervals.

Table 6-6. Phytoplankton distribution with pH from 20 Florida study lakes.

Phytoplankton	4.5-5.0	5.0-5.50	5.51-6.0	6.01-6.5	6.51-6.7
<i>Staurastrum</i> spp.	X		X		X
<i>Synedra</i>	X			X	
<i>Lyngbya</i>	X	X	X	X	X
<i>Oscillatoria limnetica</i>	X	X		X	X
<i>Peridinium inconspicuum</i>	X	X	X	X	X
<i>Chroomonas</i> sp.	X	X	X	X	X
<i>Ankistrodesmus falcatus</i>	X	X	X	X	X
<i>Selenastrum minutum</i>	X	X	X	X	X
<i>Chlamydomonas</i>	X	X	X	X	X
<i>Elakatothrix gelatinosa</i>				X	
<i>Rhabdoderma</i> sp.		X	X	X	X
<i>Anacystis incerta</i>	X	X	X	X	X
<i>Gloetheca linearis</i>	X	X			X
<i>Penate diatom</i> sp.	X	X	X	X	X
<i>Tabellaria</i> sp.	X			X	X
<i>Closterium</i> sp.	X	X		X	X
<i>Euglena</i> sp.	X	X	X	X	X
<i>Small gr. coccoids</i>	X	X	X	X	X
<i>Oocystis pusilla</i>	X	X	X	X	X
<i>Dinobryon</i> sp.	X		X	X	X
<i>Anacystis montana</i>		X	X	X	X
<i>Phacus</i> sp.		X	X	X	
<i>Cosmarium</i> spp.		X	X	X	X
<i>Tetradon minimum</i>		X	X	X	X
<i>Crocococcus limneticus</i>			X	X	X
<i>Synedra</i>		X	X	X	X
<i>Kirchneriella contorta</i>		X	X	X	X
<i>Amigdalum quadridentata</i>		X	X	X	X
<i>Closteriopsis</i>		X	X	X	X
<i>Dactylococopsis raphidioides</i>		X			
<i>Crucigenia tetrapodia</i>		X	X	X	X
<i>Microcystis aeruginosa</i>		X		X	
<i>Chlorella</i> sp.		X	X	X	X
<i>Centric diatom</i> sp.		X	X	X	X
<i>Gomphosphaeria lacustris</i>		X			
<i>Pseudotetraspora</i> sp.		X		X	
<i>Gonyostomum semen</i>			X		
<i>Spirulina laxissima</i>			X	X	X
<i>Aphanothece nidulans</i>			X		X
<i>Asterionella formosa</i>			X	X	X
<i>Anabaena</i> sp.			X	X	X
<i>Melosira herzogii</i>			X	X	X
<i>Rhizosolenia</i> sp.			X	X	X
<i>Chlorogonium elongatum</i>				X	
<i>Oscillatoria angustissima</i>				X	X
<i>Anacystis thermalis</i>				X	X
<i>Echinospaerilla</i> sp.				X	
<i>Gleocapsa rupestris</i>				X	
<i>Staurodesmus dijectus</i>					X
<i>Schizothrix calcicola</i>					X
<i>Mallomonas</i> sp.				X	X

The overall effects of increased acidity on the phytoplankton communities of Florida lakes thus include a reduction in number of species and individuals and lower chlorophyll a. Blue-green algae were found to be dominant in non-acidic lakes, while green algae were the most common group in the acidic lakes. The effects of pH on the phytoplankton community are confounded in part by a trend of lower concentrations of total phosphorus in more acidic lakes.

### Zooplankton

Zooplankton community structure in the 20 study lakes was analyzed based on the number of species, abundance of individuals, and the distribution of individuals among the various species. In addition, two common multivariate statistical techniques were used to reduce the dimensionality of the data and to generate trends from the complicated data base. The first method involved classification of the zooplankton communities in the 20 study lakes based on cluster analysis and a calculated similarity matrix. The second method involved ordination, i.e. extraction of principal coordinates or axes for the 20 lakes from the multidimensional hyperspace based on their zooplankton communities. These statistical methods show correlations between environmental factors and biotic responses but do not imply causation. If similar trends are depicted by each technique, a stronger correlation between pH and zooplankton communities can be deduced.

### Zooplankton Community Structure

Reduced species richness is often associated with acid-stressed environments. As the number of species decreases, the rare species are lost, and species that can tolerate the altered environmental conditions increase in dominance. Increased acidity in freshwater systems has been associated with a general decrease in the number of zooplankton species (Yan 1979; Sprules 1975; Parsons 1968). In the present study, the mean number of zooplankton

species in the nonacidic group was 19, while in the acidic group only 14 species were found (Table 6-7). The Kruskal-Wallis rank-sum test indicated that the number of zooplankton species in the various lakes was statistically different at  $\alpha = 0.005$ . The distribution of species richness across 5 pH intervals (Figure 6-13) showed a monotonic increase in the number of species from the second lowest pH interval (13.5 species at pH 5.0 - 5.5) to the highest interval (19.5 species at pH 6.5 - 7.0). The most acidic group (pH 4.5 - 5.0) had approximately the same number of species (13.7) as the next pH interval. The range of species richness was relatively small over the entire pH spectrum, suggesting that pH does not have an overwhelming effect on zooplankton diversity in Florida lakes.

The number of zooplankton species found in the present study is much higher than the numbers reported in other studies on lakes of comparable pH. In a study of acidic lakes near Sudbury, Ontario, Yan (1979) found about half as many zooplankton species in lakes with pH values comparable to the acidic Florida lakes. Leivestad et al. (1976) found that numbers of zooplankton species in acidic Norweigan lakes were two to three times lower than those observed in the present study. Lower concentrations of toxic heavy metals that are often associated with acid precipitation may be responsible for the higher species diversity found in Florida lakes, but further studies are necessary to evaluate this hypothesis. In addition, subtropical lakes in Florida are not subjected to the harsh seasonal fluctuations that occur in temperate lakes. The range of temperature in the Florida lakes was about 12 to 30°C during the year of sample collection. All 20 lakes are oligotrophic or mesotrophic, and none exhibited anoxic conditions in the water column. With such moderate environmental conditions, the adaptive potential of organisms to an external stress such as increased acidity may be enhanced.

The population density of zooplankton also has been shown to decrease

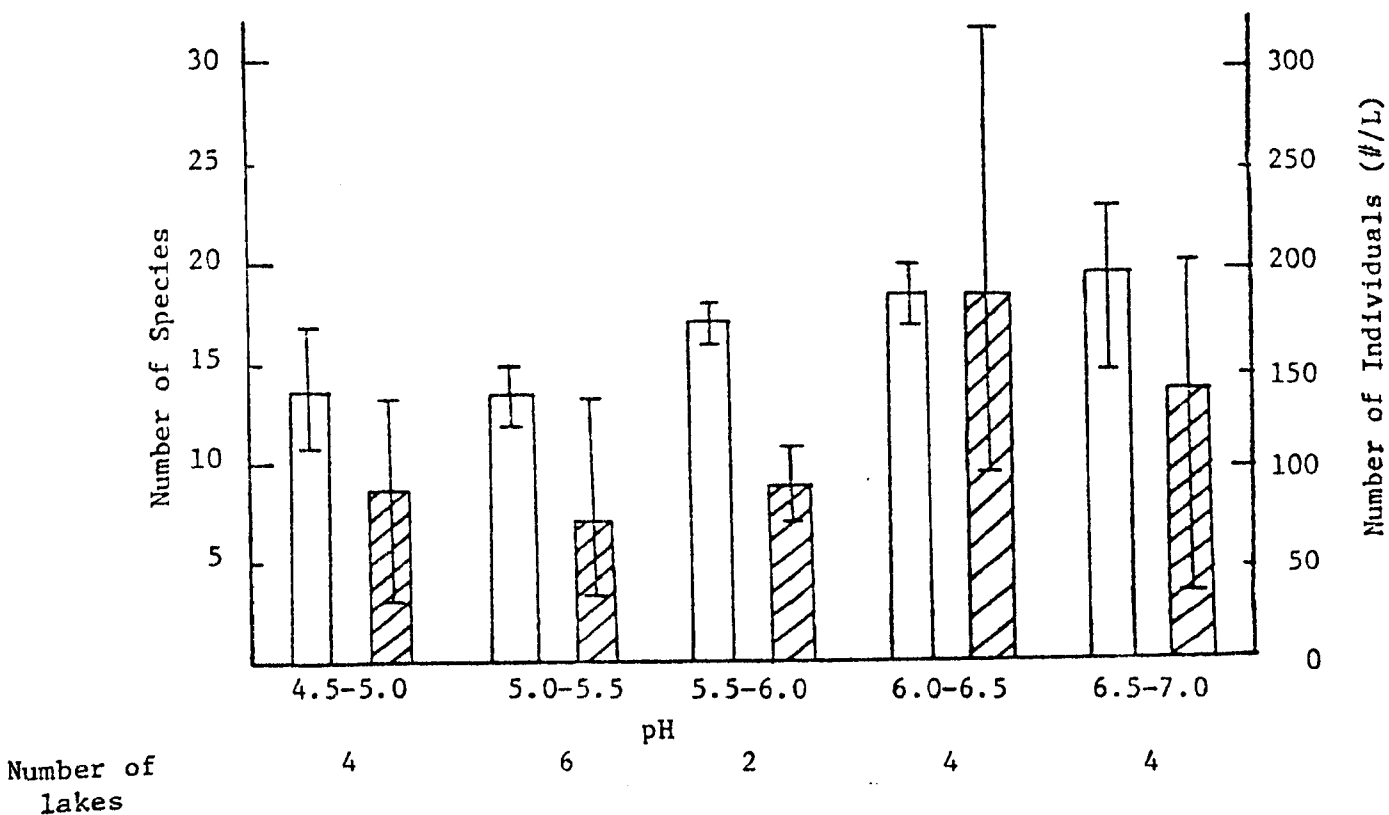


Figure 6-13. Average number of species (per lake) and average number of zooplankton individuals per liter for the 20 lakes grouped into five pH intervals.

with decreasing pH (Yan 1979; Yamamoto 1972; Parsons 1968). The mean abundance of zooplankton in the 10 acidic Florida lakes (Table 6-7) was  $7.5 \times 10^4$  individuals/ $m^3$  (range  $3.0 - 13.8 \times 10^4$ ), while the corresponding values for the 10 nonacidic lakes were  $14.5 \times 10^4$  and  $3.8 - 32.6 \times 10^4$ . The scatter in population values at a given pH precludes delineation of a simple trend between zooplankton population density and pH (Figure 6-14), but the Kruskal-Wallis rank-sum test indicated significant differences ( $\alpha = 0.005$ ) between the mean number of individuals in the lakes. Although a histogram of mean zooplankton numbers for the five pH intervals suggests a trend of increasing numbers with increasing pH, large and overlapping error bars were found for each interval.

The abundance of zooplankton in the lakes was influenced by phytoplankton density, as shown by the correlation between zooplankton numbers and chlorophyll levels in Figure 6-15. Since chlorophyll levels increased with increasing pH, the modest trend noted between zooplankton abundance and pH may reflect changes in overall lake productivity rather than direct effects of pH on zooplankton growth and survival rates.

Mean annual zooplankton biomass (Table 6-7) was calculated from species counts and conversion factors obtained from the literature (Dumont et al. 1975). Mean annual biomass for the 10 acidic lakes was  $93 \text{ mg}/m^3$  (range: 24 to  $175 \text{ mg}/m^3$ ). The mean biomass in the ten nonacidic lakes was  $123 \text{ mg}/m^3$  (range: 49 to  $268 \text{ mg}/m^3$ ). Zooplankton biomass displayed trends similar to those observed for zooplankton abundance. Much of the variation between pH intervals associated with zooplankton biomass, reflects changes in the proportions of species of differing sizes.

Of considerable importance in evaluating the effects of increased acidity on zooplankton communities is the change in species composition with

Table 6-7. Summary data on zooplankton and related diversity indices in the 20 Florida lakes.<sup>1</sup>

Lake	pH	Number of species	Individuals #/m <sup>3</sup>	Biomass mg/m <sup>3</sup>	Shannon- Weaver Index (H')	Evenness (H'/H <sub>max</sub> )	Modified Simpson's Index (SI*)
McCloud	4.71	11	79,400	116	0.86	0.77	0.82
Cowpen	4.84	13	30,500	24	0.86	0.73	0.82
Anderson-Cue	4.89	14	135,500	170	0.87	0.70	0.82
Galilee	4.96	17	86,400	110	0.99	0.76	0.87
Brooklyn	5.01	12	137,800	120	0.85	0.72	0.81
Rosa	5.05	13	77,900	175	0.66	0.55	0.69
Sheeler	5.09	12	33,200	33	0.86	0.75	0.83
Magnolia	5.10	15	47,300	57	0.83	0.66	0.81
Lowery	5.19	15	45,400	60	0.95	0.77	0.86
Johnson	5.20	14	79,000	64	0.89	0.73	0.83
Annie	5.72	16	108,900	72	0.81	0.63	0.79
Altho	6.00	18	70,400	49	0.93	0.71	0.84
Josephine	6.07	20	326,400	268	0.97	0.71	0.85
Geneva	6.12	18	93,500	132	0.89	0.67	0.83
Letta	6.37	18	150,200	92	0.89	0.67	0.80
Placid	6.40	17	154,300	103	0.94	0.74	0.84
June	6.64	21	201,600	137	1.07	0.78	0.88
Francis	6.66	23	194,300	190	1.03	0.74	0.85
Kingsley	6.68	15	109,800	66	0.86	0.68	0.80
Clay	6.69	19	38,400	120	0.95	0.71	0.83

- <sup>1</sup>. Counts and biomass are averages of four (quarterly) samples. Diversity indices are calculated from mean counts of the four sampling dates.

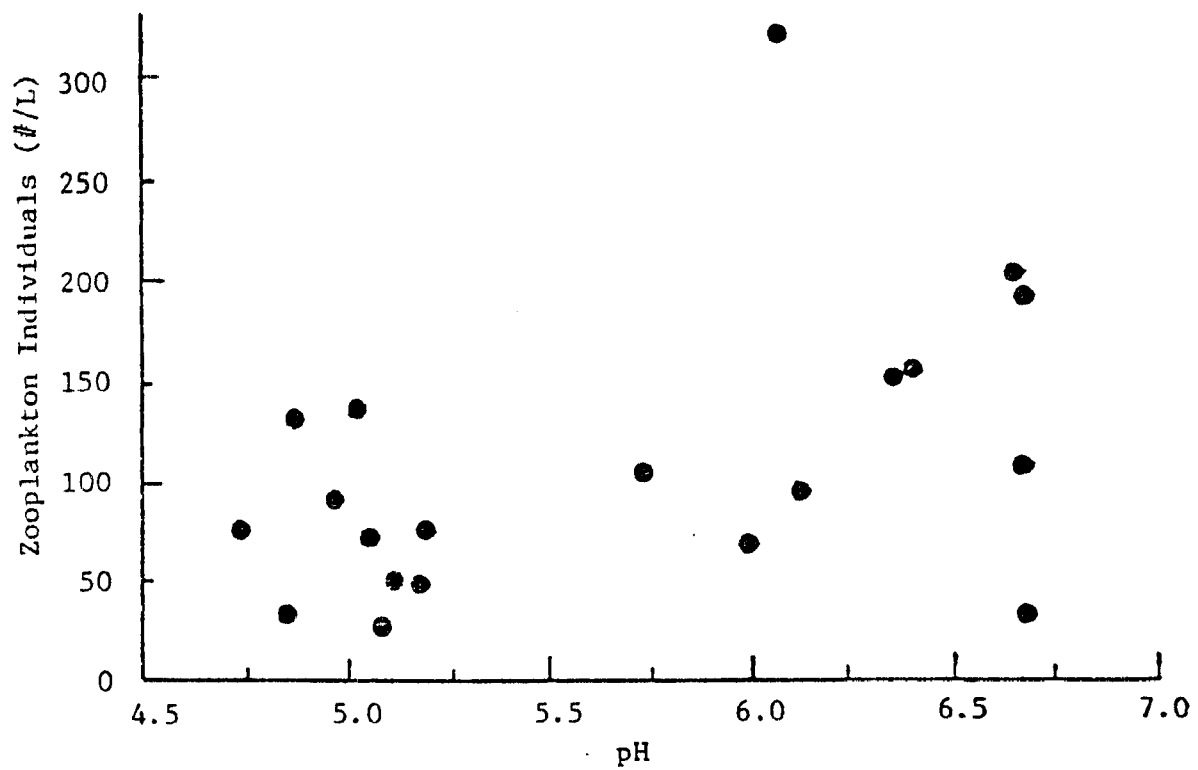


Figure 6-14. Average number of zooplankton individuals vs. pH.



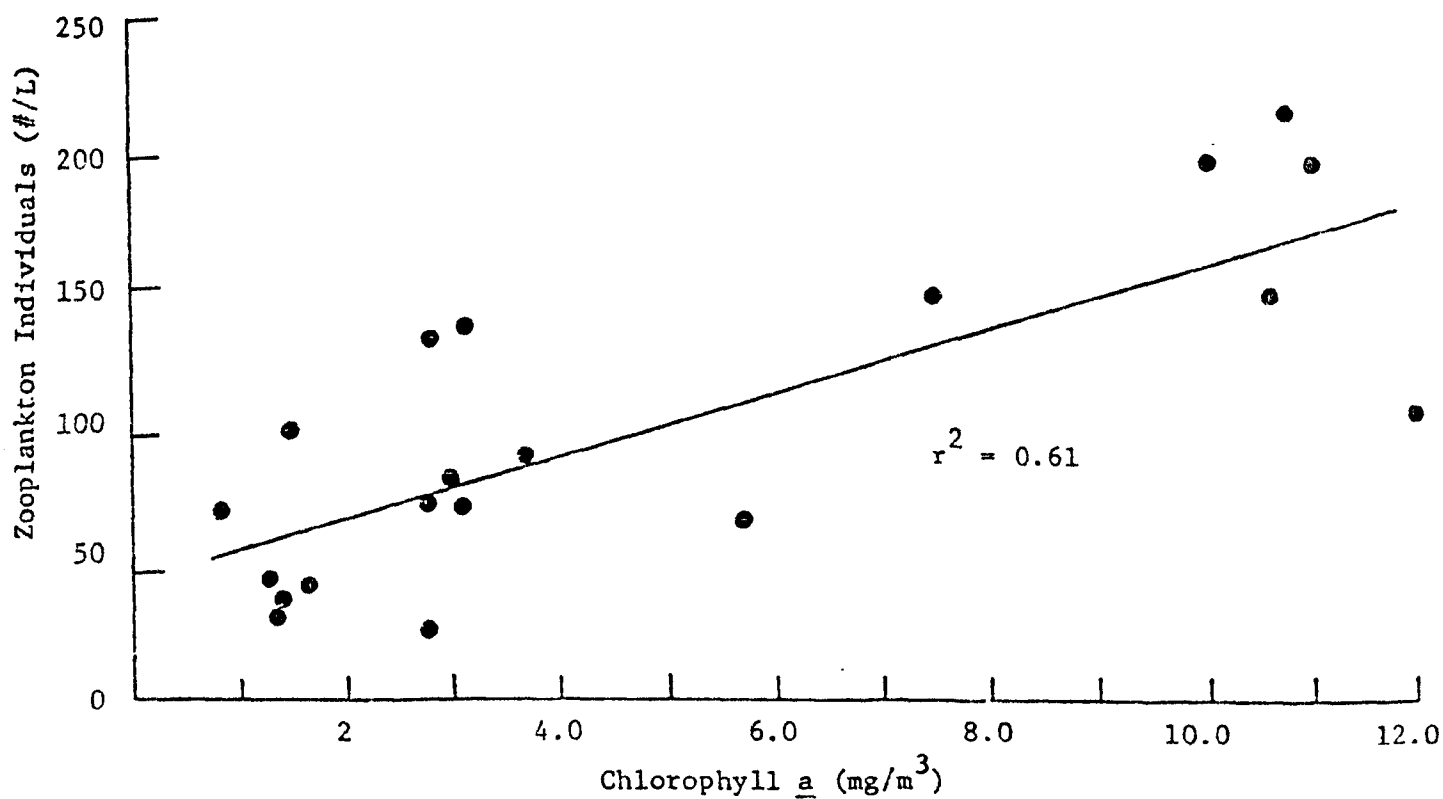


Figure 6-15. Relationship between zooplankton population density and chlorophyll a concentration in the 20 survey lakes. Data are averages for the four sampling dates.

pH. A group of acid-tolerant species was dominant in all lakes (from pH 4.71 to pH 6.69) and consisted of Diaptomus floridanus, Cyclops varicans, Bosmina longirostris, Daphnia ambigua, Keratella cochlearis and Mesocyclops edax (Table 6-8). Other species that were found at all pH levels but were not dominant included Tropocyclops prasinus, Leptodora kindti, Trichocerca multierinus, Conochilus unicornis and Polyarthra vulgaris. The majority of the species restricted to lakes of high pH were rotifers, and these were rare, even in the lakes where they were found. One notable exception is Asplanchna sp., which occurred consistently in lakes with a pH greater than 6.0.

A similar group of zooplankton species dominates both acidic and non-acidic lakes in Canada (Sprules 1975). The dominant acid-tolerant species reported by Sprules include Mesocyclops edax, Cyclops bicuspidatus thomasi, Diaptomus minutus, Holopedium gibberum, Diaphanosoma leuchtenbergianum and Bosmina sp. Five of the dominant genera found by Sprules also were found to be acid-tolerant in Florida. Daphnids have been reported to be absent from acidic lakes in several studies (Yan 1979; Parsons 1968), but Daphnia ambigua was present at all pH levels in the Florida lakes and had a yearly mean abundance of  $6 \times 10^3/\text{m}^3$  in the most acidic lake (pH 4.71).

In order to obtain overall trends of species composition with increasing acidity, the percentage of total number of species contributed by copepods, cladocerans, and rotifers was calculated. Rotifers were the major zooplankters in every pH interval (Figure 6-16a), but their contribution decreased from 58% to 35% of the total number of species from the least acidic to the most acidic group of lakes. Copepods were the principal subdominant group at all pH intervals and displayed an inverse trend to that of the rotifers, i.e. an increase in importance with decreasing pH (21% of the total species at pH 6.5 - 7.0 and 35% of the total species at pH 4.5 - 5.0).

Table 6-8. Composite species list from 20 Florida lakes during four quarters.<sup>1</sup>

	Acid lakes										Non-Acid lakes									
	pH																			
	4.7				to					5.2	5.7				to			6.7		
	McCloud	Coupen	Anderson	Galilee	Brooklyn	Rosa	Sheeler	Magnolia	Lowery	Johnson	Annie	Alto	Josephine	Geneva	Lotta	Placid	June	Francis	Kingsley	Clay
<b>Crustacea</b>																				
<i>Asplanchna floridana</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asplanchna varicans</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asplanchna edax</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asplanchna prasinus</i>	X	X	X	X		X		X	X	X	X		X	X	X	X	X	X	X	X
<i>Asplanchna sp.</i>	X		X	X	X	X			X	X	X		X	X	X			X		
<i>Asplanchna</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asplanchna</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<b>Cladocera</b>																				
<i>Diaphanosoma longirostris</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Diaphanosoma ambigua</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X
<i>Diaphanosoma kindtii</i>	X			X	X	X		X		X	X	X	X	X	X	X	X	X	X	X
<i>Diaphanosoma Cladoceran</i>				X	X	X		X		X	X	X	X	X	X		X	X		X
<i>Diaphanosoma sphaericus</i>				X	X		X					X	X	X			X	X		
<i>Diaphanosoma dietersi</i>											X	X								
<i>Diaphanosoma brachyurum</i>																			X	
<i>Diaphanosoma reticulata</i>																		X		
<i>Diaphanosoma sp.</i>			X																	
<i>Diaphanosoma amazonicum</i>										X										
<b>Gammaridea</b>																				
<i>Asellus cochlearis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asellus multicrinus</i>	X	X		X			X		X	X	X	X	X	X	X	X	X	X	X	X
<i>Asellus vulgaris</i>	X			X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
<i>Asellus longiceta</i>		X	X	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Asellus Unicornis</i>		X	X	X	X		X	X			X	X	X		X	X	X	X		X
<i>Asellus taurocephala</i>		X	X	X	X		X	X	X	X	X			X		X		X		X
<i>Asellus sp.</i>				X		X		X	X	X	X	X	X	X		X	X	X	X	X
<i>Asellus quadridentata</i>			X						X			X					X		X	
<i>Asellus havanaensis</i>							X			X			X	X			X	X		
<i>Asellus sp.</i>					X			X				X	X	X	X	X	X		X	X
<i>Asellus sp.</i>		X				X											X	X		X
<i>Asellus angularis</i>													X		X			X		X
<i>Asellus quadrata</i>				X											X					
<i>Asellus calyciflorus</i>								X					X							
<i>Asellus sp.</i>									X					X						
<i>Asellus sp.</i>												X			X					
<i>Asellus sp.</i>			X																	
<i>Asellus patulus</i>																	X			
<i>Asellus sp.</i>																	X			
<i>Asellus sp.</i>																		X		

Lakes listed in order of increasing pH. X indicates the species was found in the lake at least once during the four quarters.

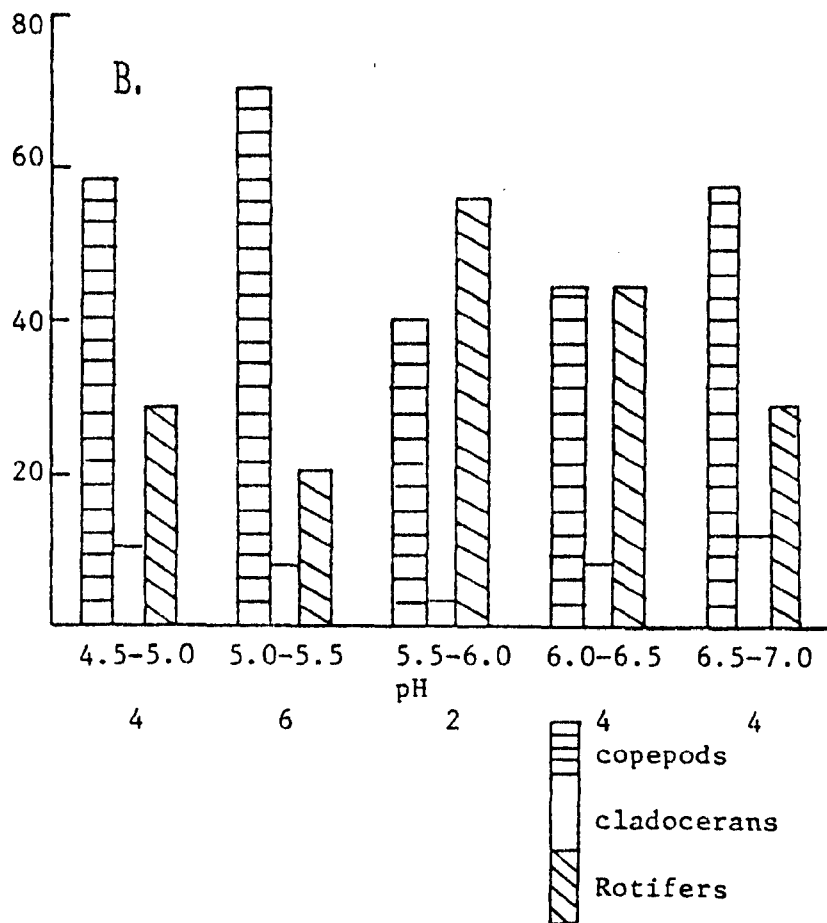
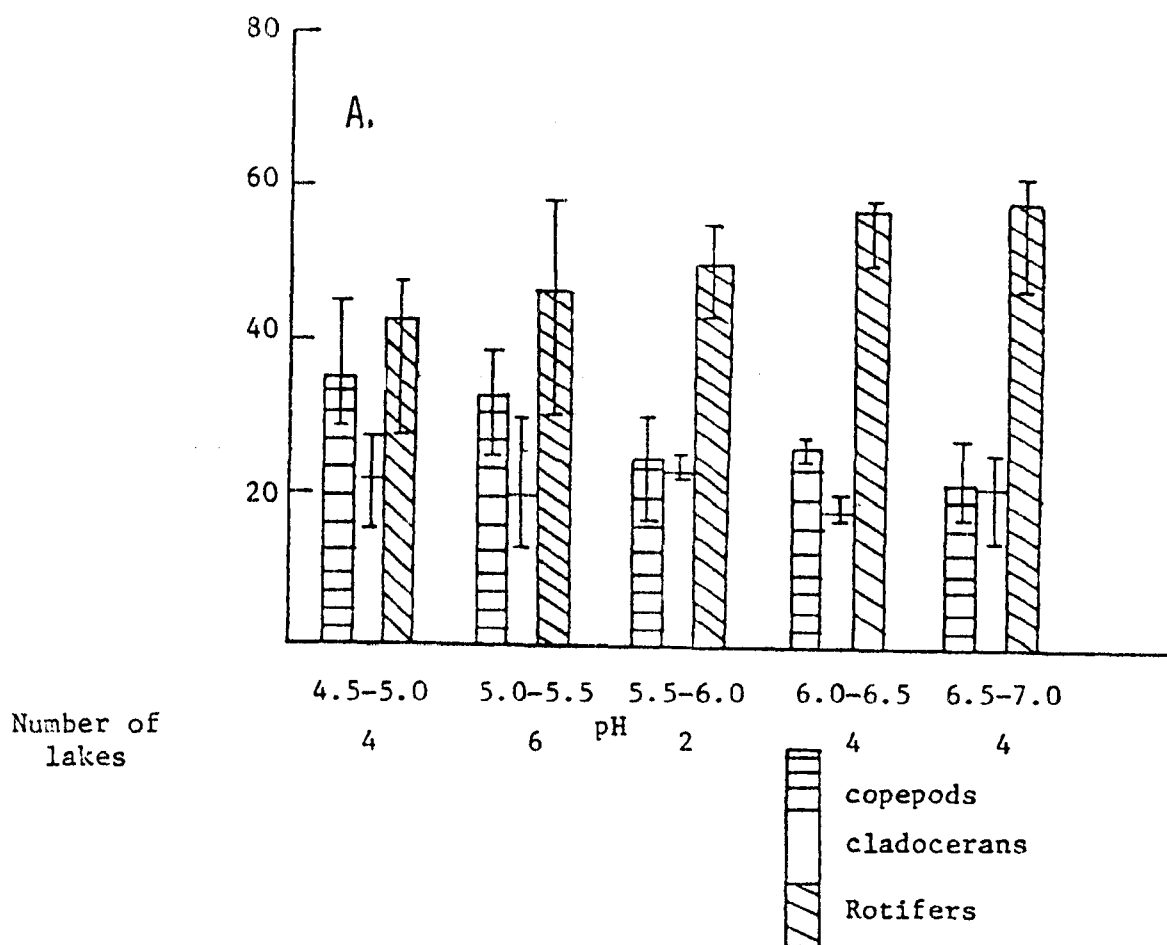


Figure 6-16. Average percent contributions of three major groups of zooplankton to the total number of species (A) and total number of individuals (B) for the 20 survey lakes grouped into five pH intervals.

Cladoceran importance remained fairly constant across all pH intervals and represented between 18 and 22% of the total number of species.

Trends in the percentage of the total number of individuals contributed by the three major groups of zooplankton over the five pH intervals are more complicated (Figure 6-16b). In acidic lakes (4.5 - 5.5), copepods contributed the largest proportion of the total zooplankton abundance (60 to 71%), and rotifers contributed only 21 to 30%. Cladocerans made up only 8 to 11% of the total zooplankton abundance in the acidic lakes. In the pH range 5.51 - 6.5, copepods declined in dominance, while rotifers increased to 46% of the total individuals, but the percentage contribution of each zooplankton component in the pH range 6.5 - 7.0 was nearly identical to that found in the most acidic group of lakes. Based on these results, no clear trends in the percent of total zooplankton abundance can be detected across the pH spectrum.

Species diversity indices have been widely used to describe biotic communities in ecological studies (Sanders 1968; Pielou 1969). In the present study, three diversity measures (Table 6-7) were calculated from the mean annual zooplankton data for the 20 lakes. Simpson's Index [ $SI^* = \sum n_i(N_i - 1) / N(N - 1)$ ] defines the probability that two individuals selected at random will be of the same species (Simpson 1949). In the present study we report  $SI^* = 1.0 - SI$  so that values of 1 and 0 correspond to total evenness and extreme skew, respectively. In addition, both the Shannon-Weiner function [ $H' = \sum p_i \log (1/P_i)$ ] and evenness [ $H'/H'_{max}$ ] were computed.

The mean value of  $SI^*$  from the acidic lakes was 0.82, and the mean value from the nonacidic lakes was 0.83; thus based on this index, no differences in the zooplankton communities can be discerned between the

acidic and nonacidic lakes. The mean value of  $H'$  for the acidic lakes was 0.86, and the mean value for the nonacidic lakes reflects their greater species richness. The two groups of lakes had nearly identical evenness measures ( $E = 0.71$  for the acidic lakes;  $E = 0.70$  for the nonacidic lakes). Since  $H'$  has both an evenness and a species richness component, the higher  $H'$  for the nonacidic lake group thus reflects a higher number of species. Overall, the similar mean values for the three measures of diversity for the two groups of lakes indicates that little difference exists in the species diversity of the zooplankton communities of acidic and nonacidic Florida lakes.

#### Classification of Zooplankton Communities

Cluster analysis was used to identify patterns in the zooplankton communities associated with increased acidity. This method assumes that some general set of controlling factors is acting on the biotic community. Thus, the various species assemblages act as a natural bioassay, permitting the detection of major influences exerted by environmental and biological parameters. Conclusions drawn from this multivariate technique, as well as those from the univariate techniques used earlier in this section, are correlative and do not prove causation. Sneath and Sokal (1973) discussed the principles and techniques of classification in detail, while Poole (1974) has reviewed methods for cluster analysis. Czekanowski's similarity index was used to measure the similarity between the various zooplankton communities (Cormack 1971). Recent studies (Bloom 1979) have demonstrated the superiority of this index over other indices to accurately group assemblages of known similarity. The zooplankton data were log transformed ( $X' = \ln(x + 1)$ ), and no standardization was used. Two types of classifications were generated: standard (Q-mode) analysis, which clusters the lakes according to the similarity of their species composition, and reverse (R-mode) analysis, which clusters the species according to their similarity of occurrence. Both analyses were

performed using quantitative(actual count) data and qualitative (presence-absence) data. The former thus includes information on the relative dominance of species, while the latter disregards abundance.

Results of the cluster analyses are presented as dendrograms, in which groups of similar objects are depicted by the joining of lines into progressively larger groups. The dendrogram generated from Q-mode quantitative classification of quarterly zooplankton data from the 20 lakes (Figure 6-17) shows a strong effect of seasonality on zooplankton communities; clusters of highest similarity generally comprised of various lakes within a single season. At an arbitrarily defined similarity level of 63%, 11 groups of two or more stations were defined, along with a number of solitary stations. Clusters g, h, i, j and k are comprised primarily of acid lakes, and a single season (fall, winter, or spring) dominated each cluster. Two nonacidic lakes (Kingsley and Geneva) also are included in this group. Clusters b and e are mostly from the summer quarter and are made up of both acidic and nonacidic lakes. Clusters c, d and f are dominated by nonacidic lakes from all four quarters. The overall trend suggests that a greater difference in zooplankton communities exists between the acidic and nonacidic groups during the fall, spring and winter quarters and that a higher level of similarity exists during the summer. Results of Q-mode classification based on presence-absence data followed the same patterns described for the quantitative data. The level of similarity of the various groups was higher because the effect of dominance was removed by considering only presence-absence data.

In order to assess the overall yearly trends in zooplankton communities, a classification was conducted on the yearly mean data. A dendrogram obtained from the mean annual quantitative data (Figure 6-18) shows that two major groups are formed at the 68% similarity level. One group is composed of seven lakes with a pH range of 6.00 to 6.69. The second group contains ten acidic

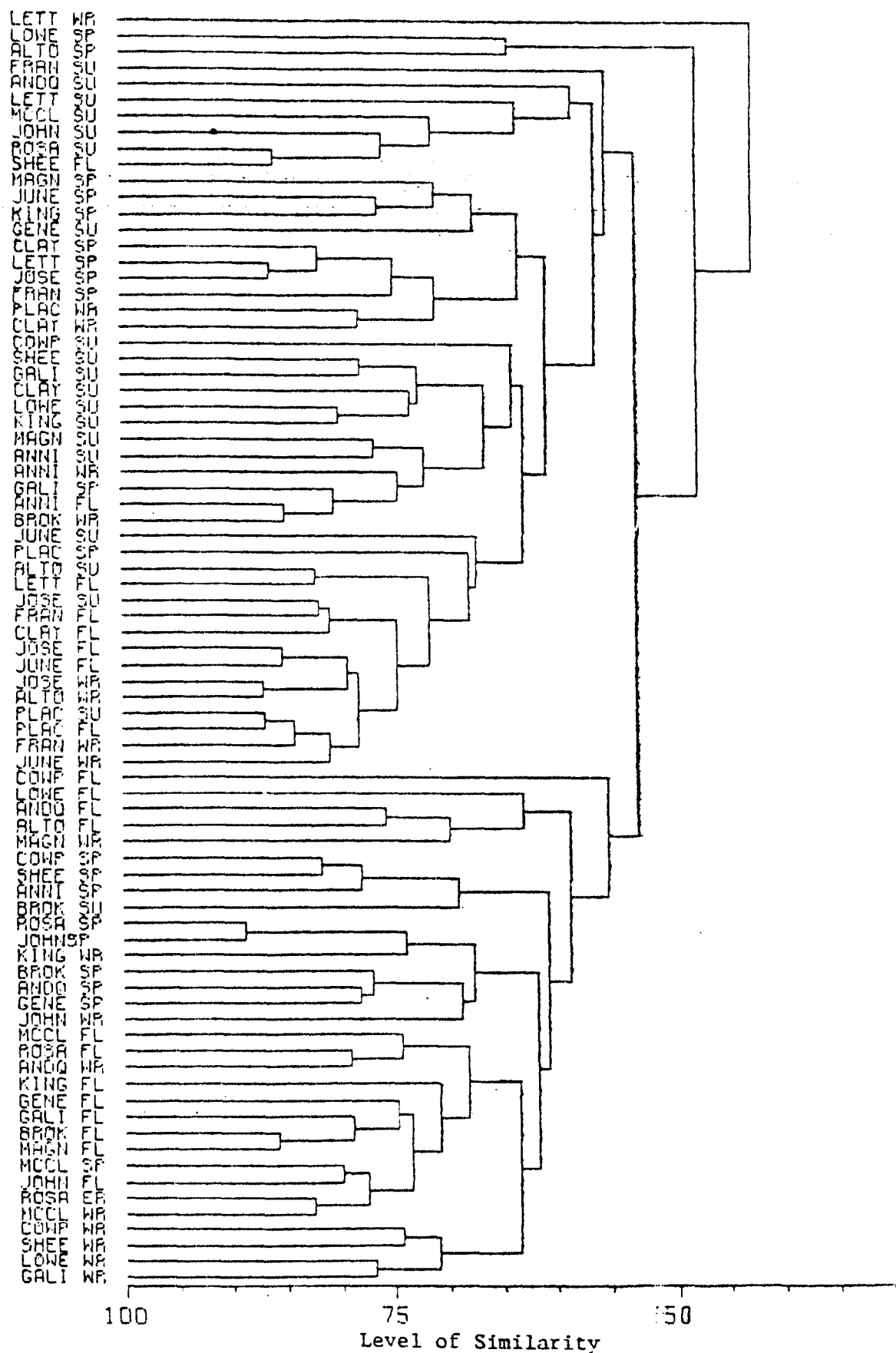


Figure 6-17. Dendrogram of the 20 lakes based on quarterly quantities of zooplankton data. Names on the left represent lakes and seasons sampled.



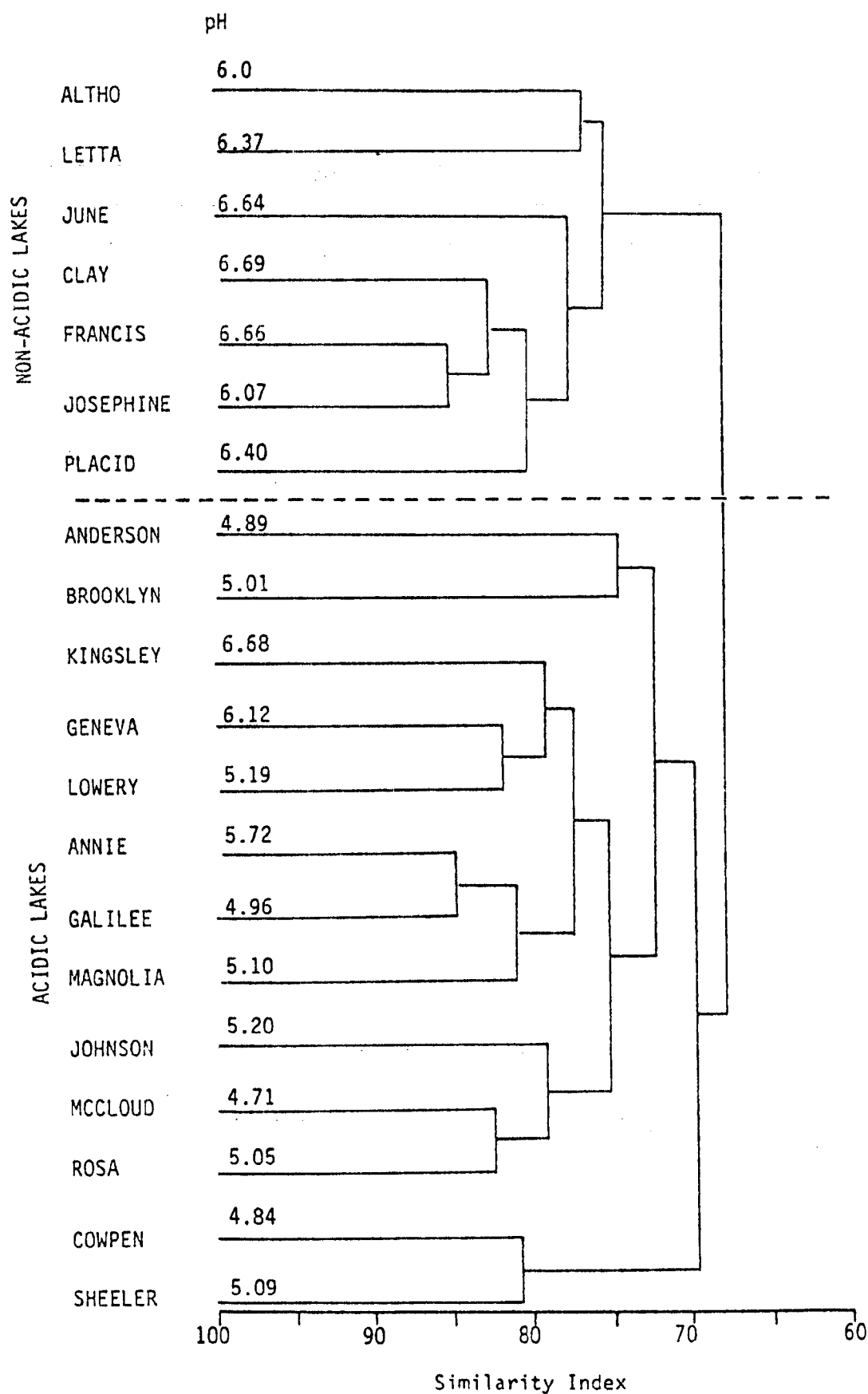


Figure 6-18. Dendrogram of the 20 lakes classified using quantitative zooplankton data (annual average population distributions).

lakes (mean pH 4.71 to 5.2) and three nonacidic lakes. The latter three lakes all are considerably more oligotrophic than the other nonacidic lakes, suggesting that the zooplankton communities are heavily influenced by phytoplankton abundance.

An R-mode cluster analysis using quantitative data on the relationship among the species found in the 20 lakes (Figure 6-19) shows that the group of acid-tolerant species that were dominant at all pH levels grouped together at a high level of similarity. These six species, along with copepodites and nauplii, constitute a group delineated at the 87% similarity level. Species groups were added to this central group of dominant acid-tolerant individuals in order of decreasing occurrence and abundance.

#### Ordination of Zooplankton Communities

Ordination methods are useful in extracting information on underlying factors or trends from a complicated data base. Ordination techniques such as principal component analysis and factor analysis have been used in both terrestrial and aquatic studies (Bray and Curtis 1957; and Shannon and Brezonik 1972). In the present study, principal coordinate analysis (PCOR) was applied to log-transformed data from the 20 study lakes, and a series of principal axes were calculated to account for the variance within the placement of the stations. The principal axes are linear combinations of the variables that explain the maximum possible variance in the original data. In simple terms, the principal axes can be considered as new (derived) variables that reduce the dimensionality of the original data set. The derived variables can be considered as underlying factors explaining the variations in the measured variables. For further explanations of ordination techniques, see Gowers (1966), Sneath and Sokal (1973), and Poole (1974).

Principal coordinate analysis of the zooplankton data was done using the computer program described in Bloom et al. (1977). The zooplankton

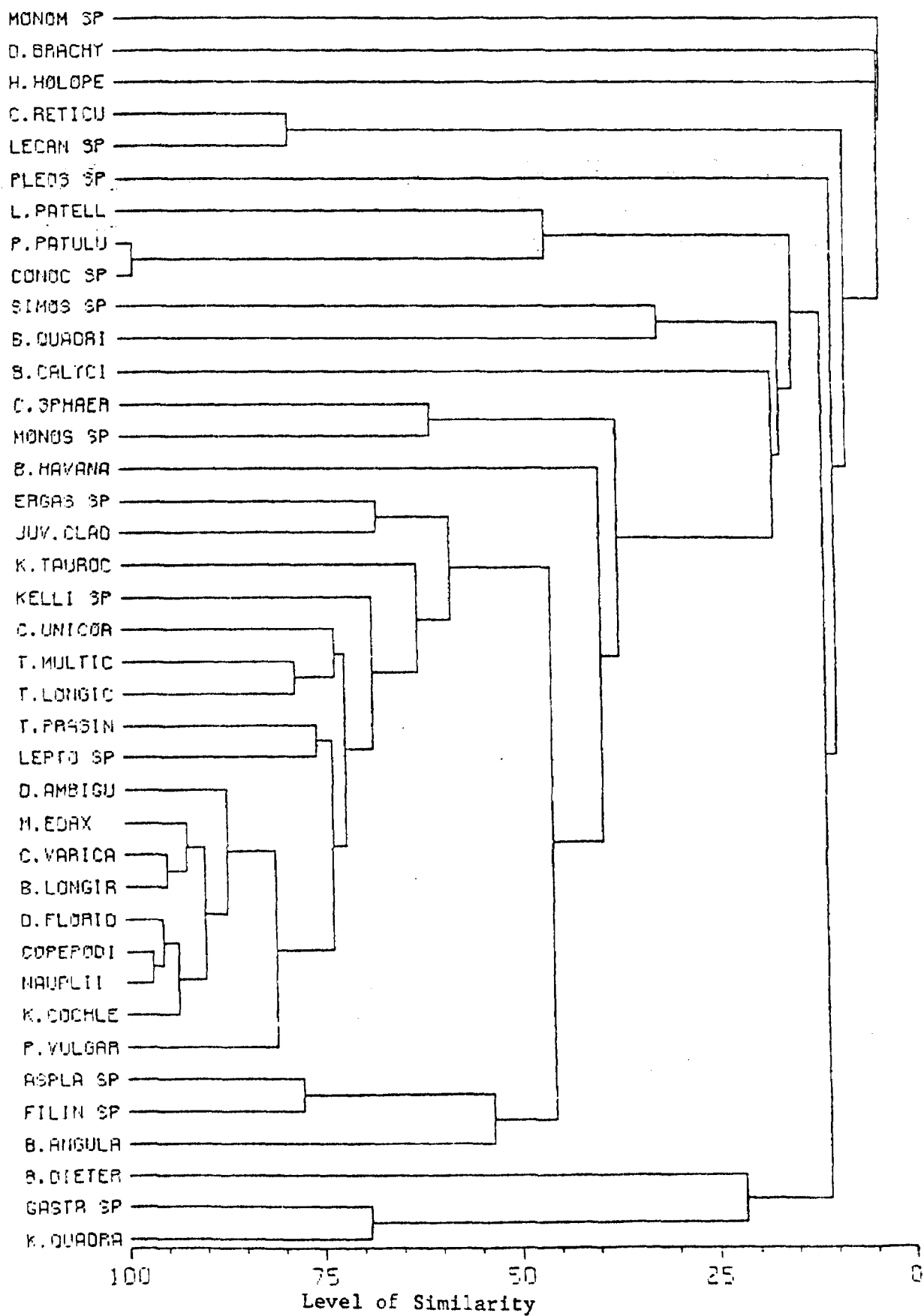


Figure 6-19. Dendrogram from an R-mode classification of zooplankton taxa, based on annual average population densities in the 20 lakes.

counts for each lake were first log-transformed (to obtain normal distributions), and Z-scores for each species were then computed so that all variables had means of zero and unit variance. Figure 6-20a presents a three dimensional view of the 20 lakes plotted on the first three principal axes. These axes account for 54% of the variance in the data, which is rather good for such a complicated data base. The overlap of several of the lakes in Figure 6-20a obscures some of the information, and the exact location of each lake on the three axes can be obtained from Figures 6-20b and c, which show cross-sectional views of the 20 lakes on planes representing axes I and II, and I and III, respectively.

Two main groups of lakes are visible from Figure 6-20b, a dense group of 13 lakes and dispersed group of 7 lakes. The smaller group contains only nonacidic lakes, and the other group consists of ten acidic and three non-acidic lakes. These two groups of lakes agree in composition with the two groups obtained in the cluster dendrogram (Figure 6-18), further indicating a difference in the zooplankton communities of the two groups of lakes. Within the group of seven nonacidic lakes, three lakes (Josephine, Francis and June), are located away from the rest of the group, and they had the highest numbers of individuals and the greatest number of species of all 20 lakes. A further similarity between the clustering and ordination results is the relative positions of Lake Cowpen and Lake Sheeler. Both lakes are highly acidic with low-color content, and both had reduced species richness and low zooplankton abundance. These lakes were the last to be added to the cluster of acid lakes (Figure 6-18), and both are grouped together (and at some distance from the other acidic lakes) in the ordination graphs (Figure 6-20a-c).

The overall pattern depicted by the multivariate analyses suggests that a difference exists between acidic and nonacidic lakes, but low productivity nonacid lakes are grouped with the acid lakes.

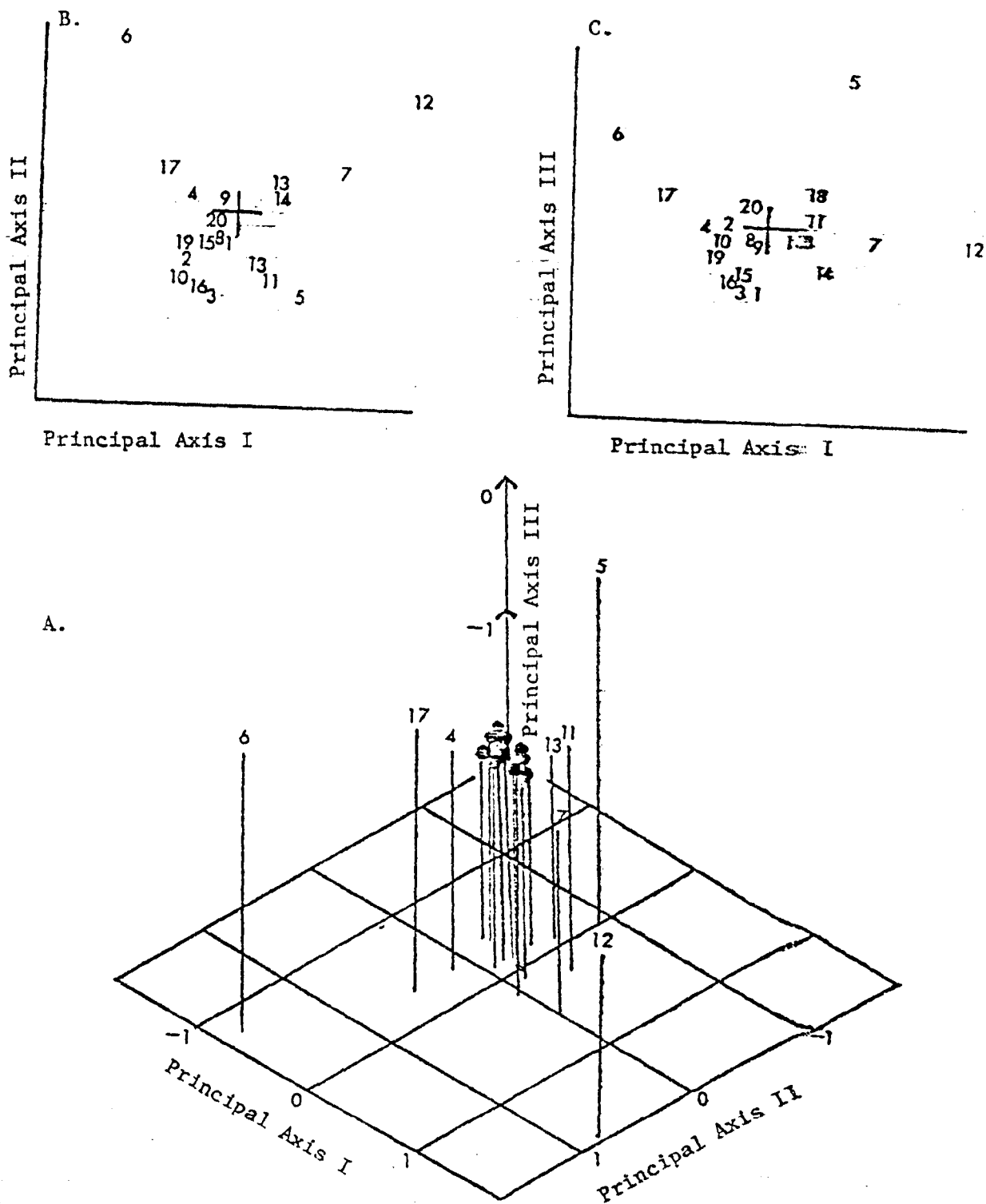


Figure 6-20. Principal coordinate analysis of study lakes based on zooplankton community structure. A. Placement of lakes on first three principal axes. B and C. Placement of lakes on first and second and first and third principal axes, respectively. For lake number code, see Table 6-1. Black circles represent overlapping lakes.

## Benthic Invertebrates

Community structure of the benthic invertebrate assemblages from the 20 study lakes was analyzed based on species richness, abundance of individuals and species diversity. In addition, both cluster analysis and ordination were used to detect differences in the structure of the benthic communities among the 20 study lakes.

### Species Richness

Reductions in the number of benthic species have been related to increases in acidity in lakes (Parsons, 1968; Leivestad et al., 1976). The present data also indicate a slight reduction in the mean number of benthic species with increasing acidity (Table 6-9). The mean number of species in the 10 acidic lakes (pH <5.6) was 24.6 (range of 21 to 30), and the mean in the 10 nonacidic lakes (pH >5.6) was 26.6 (range 17 to 37). The mean number of benthic species within the 20 lakes was found to be statistically different using a Kruskal-Wallis test ( $\alpha = .005$ ). The mean number of species showed considerable variation between lakes in both the acidic and nonacidic groups. The nonacidic group of lakes exhibited the greatest variability, a fact that can be attributed to the greater trophic diversity of this group. Lakes with the highest numbers of species routinely were the most productive. Arranged according to the five previously established pH intervals, a bimodal pattern of species richness emerges with the greatest number of species occurring in lakes of either the highest or lowest pH (Figure 6-21). Such a distribution suggests that species richness in the study lakes is controlled by factors other than pH.

The importance of sediment characteristics as a controlling factor for

Table 6-9. Summary of data on benthic invertebrates and related diversity indices for 20 Florida lakes.<sup>1</sup>

	pH	Number of Species	Individuals (#/m <sup>2</sup> )	Biomass (g/m <sup>2</sup> )	Shannon- Weaver Index (H')	Modified Simpson Index (S*)	Evenness Index (H' / H' max)
Cloud	4.71	28	5380	0.354	0.88	0.81	0.61
Open	4.84	30	2130	0.168	1.05	0.85	0.71
Merson-Cue	4.89	25	3720	0.364	0.85	0.75	0.61
Willie	4.96	24	1450	0.403	1.06	0.88	0.77
Brooklyn	5.01	26	1100	0.320	1.14	0.81	0.90
DeSa	5.05	23	3990	0.376	0.87	0.80	0.64
Deeler	5.09	23	2950	0.428	0.75	0.73	0.55
Magnolia	5.10	21	2590	0.557	0.75	0.76	0.57
Mewery	5.19	23	940	0.223	1.03	0.86	0.76
Johnson	5.20	23	980	0.335	1.02	0.85	0.75
Marie	5.72	17	2860	0.299	0.59	0.60	0.48
Altho	6.00	17	1240	0.080	0.69	0.68	0.56
Josephine	6.07	33	2130	0.596	1.85	0.56	0.71
Geneva	6.12	24	690	0.127	1.05	0.86	0.76
Etta	6.37	25	1220	0.331	1.12	0.90	0.80
Lacid	6.40	27	1940	0.728	1.04	0.86	0.73
June	6.64	37	2330	0.705	1.05	0.84	0.67
Francis	6.66	32	2490	0.632	0.99	0.86	0.66
Kingsley	6.68	22	1980	0.254	0.83	0.77	0.62
Lay	6.69	32	3960	0.457	0.80	0.53	0.73

Values are averages for the four sampling periods.

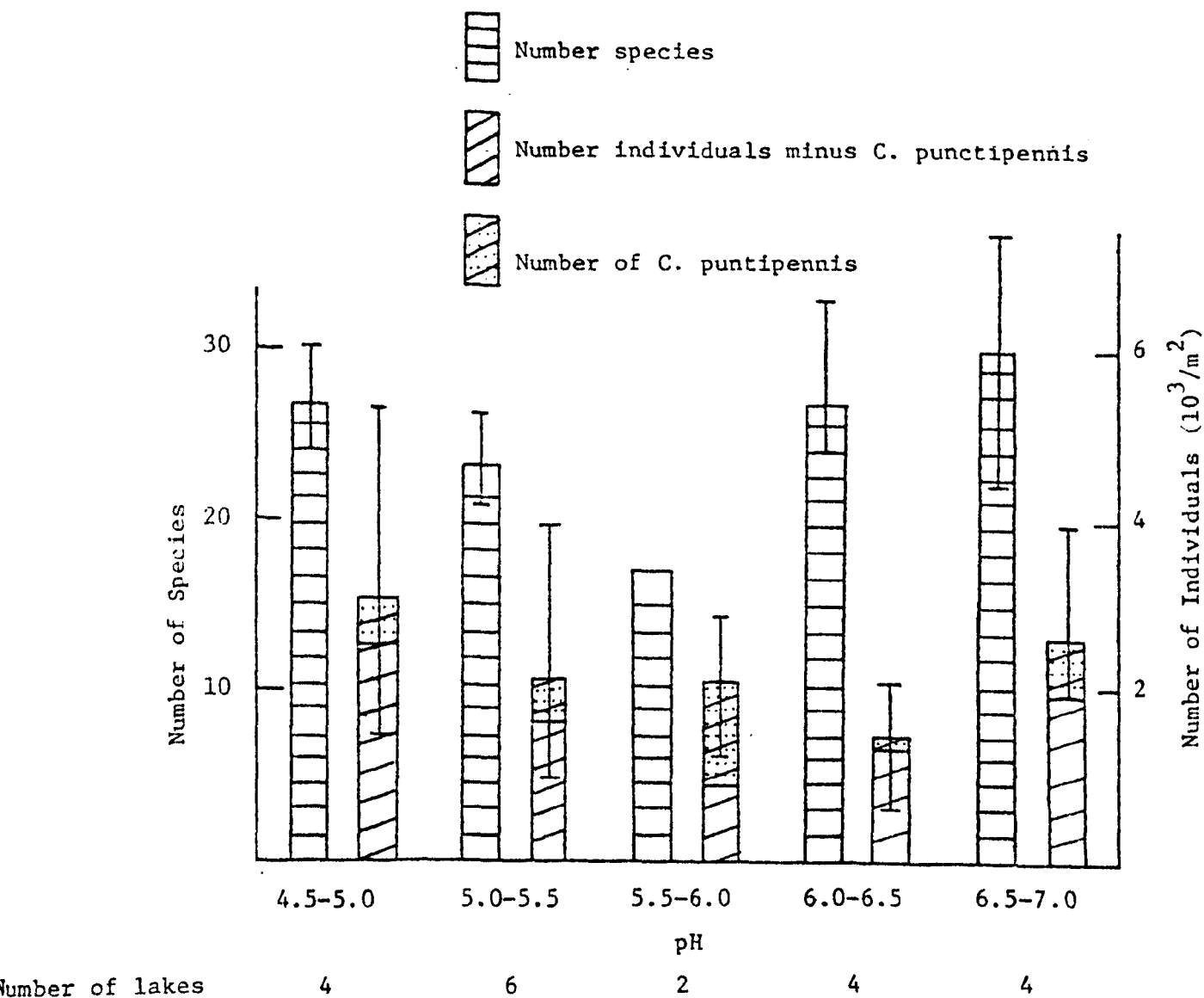


Figure 6-21. Mean number of species of benthic invertebrates and their mean population density for the 20 lakes grouped into five pH intervals.



benthic community structure has been well-established by Harp and Campbell (1967) and Bloom et al. (1972). The wide variation in species richness at all pH levels in this study may in part be attributed to interbasin variations in sediment characteristics. Based on the previously established productivity - pH relationship, organic deposition and thus sediment organic content may be expected to decrease with decreasing pH. Thus, species requiring a highly organic substrate for either deposit feeding or burrow formation may be excluded from lower pH lakes. The variations in the benthos response within a given pH interval is a reflection of the fact that the organic content of sediments is influenced by allochthonous organic inputs from the watershed, as well as autochthonous production.

Finally, both the quality and quantity of food may limit benthos distribution. Filter-feeding species may be eliminated from low pH lakes due to the generally lower algal concentrations in these lakes. In addition, bacteria, which are known to be an important dietary component for some benthic invertebrates, are in reduced concentrations in acidic habitats (Anderson et al. 1978).

#### Number of Individuals

A reduction in the total number of benthic individuals has been associated with increased acidity (Lackey 1938; Harp and Campbell 1967). Results from the present study (Table 6-9) indicate a high degree of variability among the 20 study lakes, with no clear reduction in the abundance of benthic invertebrates being associated with increased acidity. The mean number of benthic invertebrates in the 10 acidic lakes ( $\text{pH} < 5.6$ ) was  $2,520/\text{m}^2$ , with a range of 936 to  $5,380/\text{m}^2$ ; and nonacidic group ( $\text{pH} > 5.6$ ) had a mean of  $2,080/\text{m}^2$ , with a range of 692 to  $3,960/\text{m}^2$ .

When grouped into five pH-intervals, benthic invertebrate abundance displays a bimodal pattern with the most acidic lakes and the least acidic lakes containing the greatest number of individuals (Figure 6-21). The present results demonstrate a decline in abundance in moderately acidic lakes (pH 5.5-6.0), but do not delineate a linear reduction in benthic invertebrates with decreasing pH.

Larvae of the dipteran, Chaoborus punctipennis, were often collected in benthic samples and were counted as part of the benthic invertebrate assemblage in the present study. C. punctipennis is known to be associated with bottom sediments during the day and to migrate up through the water column at night (Roth 1968). Elimination of this species from our benthic counts decreased the total number of individuals at all pH levels but failed to change the general abundance-pH relationship discussed above.

#### Biomass of Benthic Invertebrates

Biomass of benthic invertebrates (ash-free dry weight) generally decreased with decreasing pH in the 20 Florida lakes (Table 6-9). Mean biomass for the 10 acidic lakes was  $0.32 \text{ g/m}^2$  and for the 10 nonacidic lakes was  $0.42 \text{ g/m}^2$ . The large variation in biomass of benthic invertebrates in the lakes (Figure 6-22) suggests that additional factors besides pH are influencing the distribution of the benthos.

#### Species Diversity

Species diversity was calculated separately for each of the 20 lakes as Shannon-Weiner ( $H'$ ), evenness, and Simpson ( $SI^*$ ) indices. The 10 acidic lakes had a mean value for  $\log H'$  of 0.94 and a range of 0.75 to 1.44, but the 10 nonacidic lakes had a slightly lower mean value for  $H'$  of 0.90 and a range of 0.59 to 1.12 (Table 6-9). Thus, no clear relationship between Shannon-Weiner

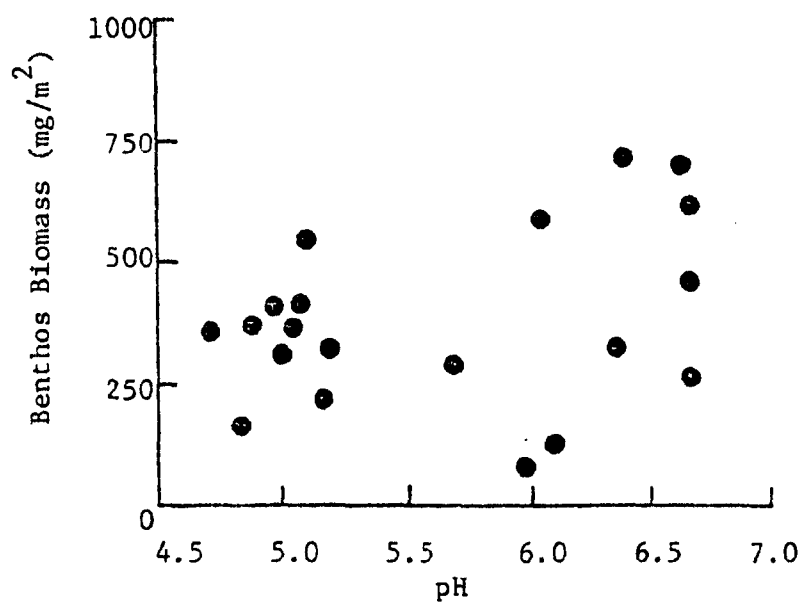


Figure 6-22. Mean biomass of benthos (ash-free dry weight) vs. pH the 20 survey lakes.

diversity and pH could be delineated.

Mean values for the modified Simpson's index (Table 6-9) were 0.82 (acidic lakes) and 0.86 (nonacidic lakes). Simpson's index is sensitive to dominance by a few species. The slightly higher value for SI\* from the 10 nonacidic lakes reflects a more even distribution of individuals among the various species. Overall, very little difference exists between the two lakes groups in reference to the three measures of diversity, and no strong relationship could be established between these indices and pH.

#### Community Composition

The relationship of individual species or groups of species to pH can provide useful data on the response of benthos to acidification. A group of acid tolerant species was found to dominate invertebrate assemblages at all pH levels: Limnodrilus hoffmeisteri, Hyalella azteca, Bezzia setulosa, Chaoborus punctipennis, Coelotanytus tricolor, Procladius sp., Stictochironomus devinctus, Cladotanytus sp., and Tanytarsus sp. Other species also occurred at all pH levels but were never present in large numbers (Table 6-10). Chironomid larvae were an important component in the benthic communities of all study lakes and accounted for nearly 50% of the number of total individuals as well as a majority of the species in the acidic lakes. Chironomids were found in all nonacidic lakes but accounted for a smaller portion of the individuals and species richness than in the acidic lakes. A replacement series of major invertebrate groups was noted along the pH gradient (Figure 6-23). Oligochaetes and amphipods increased in importance with increasing pH, but chironomids and molluscs decreased with increasing pH, with no individuals of the latter group found in lakes with a pH <6.0.

Decapods such as Palaemonetes paludosus were only found in lakes with

Table 6-10. Composite species list of Benthic invertebrates from 20 Florida lakes. Lakes listed in order of increasing pH.

Organism	McCloud	Coupen	Anderson-Cue	Galilee	Brooklyn	Rosa	Sheeler	Magnolia	Lowery	Johnson	Annie	Alto	Josephine	Geneva	Lotta	Placid	June	Francis	Kingsley	Clay
<i>ugesia tigrina</i>					X								X			X	X	X	X	X
<i>Limnodrilus hoffeisteri</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Umbriculus</i> sp.	X		X	X			X	X	X	X	X		X	X	X	X	X	X	X	X
<i>Ellobdella</i> sp.							X					X	X			X	X	X	X	X
<i>Ulinobdella</i> sp.												X	X							
<i>Isidium</i> sp.												X	X				X	X		
<i>Orbicula fluminea</i>															X		X	X		
<i>Capra</i> sp.																	X	X		
<i>Ustia</i> sp.																	X			
Unid. Plecopotera													X				X			X
<i>Madonotides</i> sp.																		X		X
<i>Nysa</i> sp.																	X	X		
<i>Umicola limosa</i>																	X	X		
<i>Uraulius deflectus</i>																	X			
<i>Uviparus intertexus</i>																	X			
<i>Ualella azteca</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Urangonyx</i> sp.				X					X				X							
<i>Uommarus</i> sp.													X							
<i>Ualaemonetes poludosus</i>																	X			
<i>Uimocythere</i> sp.																	X			
<i>Ueragenia</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Uomphus williamsoni</i>	X				X					X				X						X
<i>Uidymops</i> sp.													X							X
<i>Uogenius brevistylus</i>								X												
<i>Uelthemis</i> sp.	X												X							
<i>Uacromica</i> sp.	X																			
<i>Uympetrum</i> sp.																				X
<i>Ueptocella</i> sp.	X	X	X	X	X		X		X			X			X	X	X	X		
<i>Upsychomia</i> sp.				X																
Unid. Tricoptera				X					X					X	X		X	X		X
<i>Uyethira</i> sp.					X															
<i>Uydroptilidae</i>	X	X				X		X					X					X		
<i>Uezzia setulosa</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Uhaoborus punctipennis</i>	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Urocladius</i> sp.	X	X	X	X	X	X	X	X	X	X		X	X	X	X		X	X	X	X
<i>Urupus</i> sp.																				X
<i>Ublabesmyia porajanta</i>	X	X	X	X	X	X	X	X	X	X			X	X	X	X	X	X		X
<i>Uelotanytus tricolor</i>	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X
<i>Uelotanytus scapularia</i>																		X		
<i>Umatopynia</i> sp.		X			X		X				X			X						
<i>Uaralauterborniella</i> sp.	X		X	X	X	X		X	X	X			X			X		X		
<i>Uhironomus attenuatus</i>											X		X			X	X	X	X	X
<i>Uryptochironomus fulvus</i>		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Uarnischia viridulus</i>	X	X	X	X	X	X	X	X	X	X	X		X	X	X		X		X	X
<i>Uarachironomus</i>																				
<i>Uectinatellae</i>	X	X	X	X		X	X					X	X						X	X
<i>Ulypedilum halterale</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Ulypedilum scalaenum</i>													X	X			X			

Table 6-10. continued...

<i>Lyptotendipes senilis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Psectrochironomus devinctus</i>	X	X	X	X	X		X	X	X	X		X	X	X	X	X	X	X	X
<i>Lyptotendipes leueoscelis</i>		X	X			X		X	X			X		X	X	X	X	X	X
<i>Pseudochironomus</i> sp.	X	X	X	X	X	X	X	X	X			X		X	X		X	X	
<i>Stantaneura</i> sp.	X											X							
<i>Infeldia</i> sp.						X			X						X				X
<i>Paracladopelma</i> sp.														X		X			
<i>Podotanytarsus</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Tanytarsus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Onstempellina</i> sp.		X																	
<i>Corelia</i> sp.		X																	
<i>Podotanytarsus</i> sp.	X	X																	
<i>Psectroclodius</i> sp.	X	X						X				X			X				
<i>Lyptotendipes</i> sp.														X		X			
<i>Orthocladinae</i>												X		X				X	
<i>Chironomidae</i> pupa	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X
<i>Psectrotanytarsus</i> sp.					X					X									
<i>Pseudodiamesa pertnax</i>		X																	
<i>Orthocladus</i> sp.									X										
<i>Podotopus</i> sp.																			X
<i>Mittia</i> sp.					X	X								X					
<i>Alarucella</i> sp.		X													X				
<i>Ylloopus</i> sp.	X	X	X			X	X								X		X		
<i>Hydessus</i> sp.			X			X													

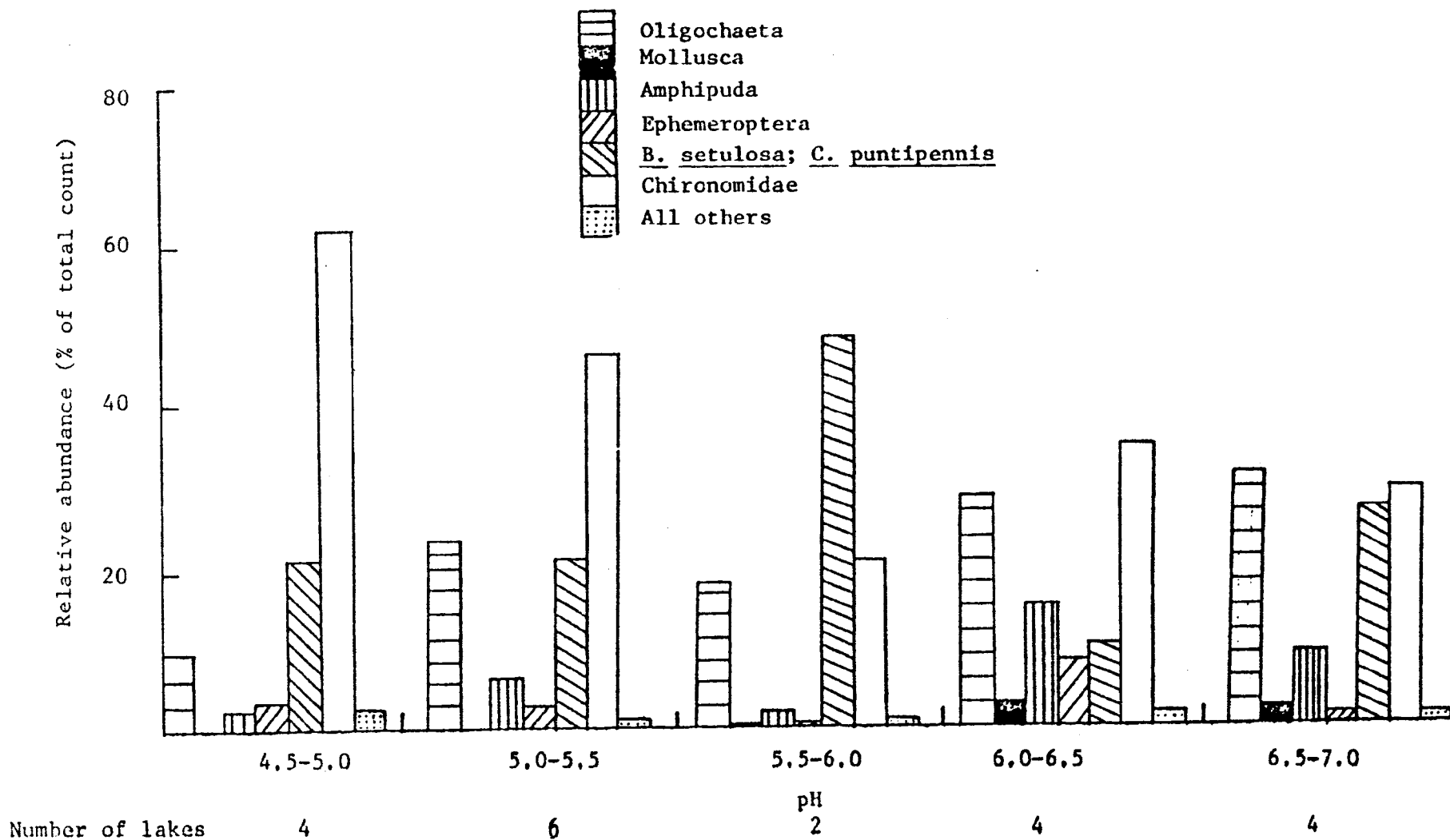


Figure 6-23. Percent contribution of selected groups of benthic invertebrates to the total number of benthic individuals in five pH intervals from 20 Florida lakes.

high pH. In most cases, species restricted to nonacidic lakes were found in low numbers when present. Conversely, several rare taxa were found only in acidic lakes: Macromia sp., Psychomia sp., Zavrelia sp. and Pseudodiamesa pertnax.

The benthic assemblages of all 20 Florida lakes were dominated by a group of species whose distribution appeared to be independent of pH. Individual species confined to either acidic or nonacidic lakes never constituted a major component of the benthos in any lake. Thus, changes in the partitioning of individuals among species rather than the wholesale replacement of species was the principal response of benthic invertebrates to increasing acidification.

#### Classification of Benthic Communities

Benthic data were classified by standard (Q-mode) analysis using Czekanowski's Similarity Index on log transformed quantitative data from the 20 study lakes. A Q-mode classification of quarterly quantitative benthic data (Figure 6-24) did not demonstrate the same high degree of seasonality displayed from a similar analysis of zooplankton data. The majority of lakes, both acidic and nonacidic, showed a stronger interbasin similarity than intrabasin similarity when considering all four quarters of data. Two major groups can be identified from the Q-mode analysis (Figure 6-24); group A is composed of nonacidic lakes, and group B is composed principally of acidic lakes. The remainder of the dendrogram consists of a large number of very small clusters of both acidic and nonacidic lakes linked to groups A and B at decreasing levels of similarity. Such a loose pattern of associa-



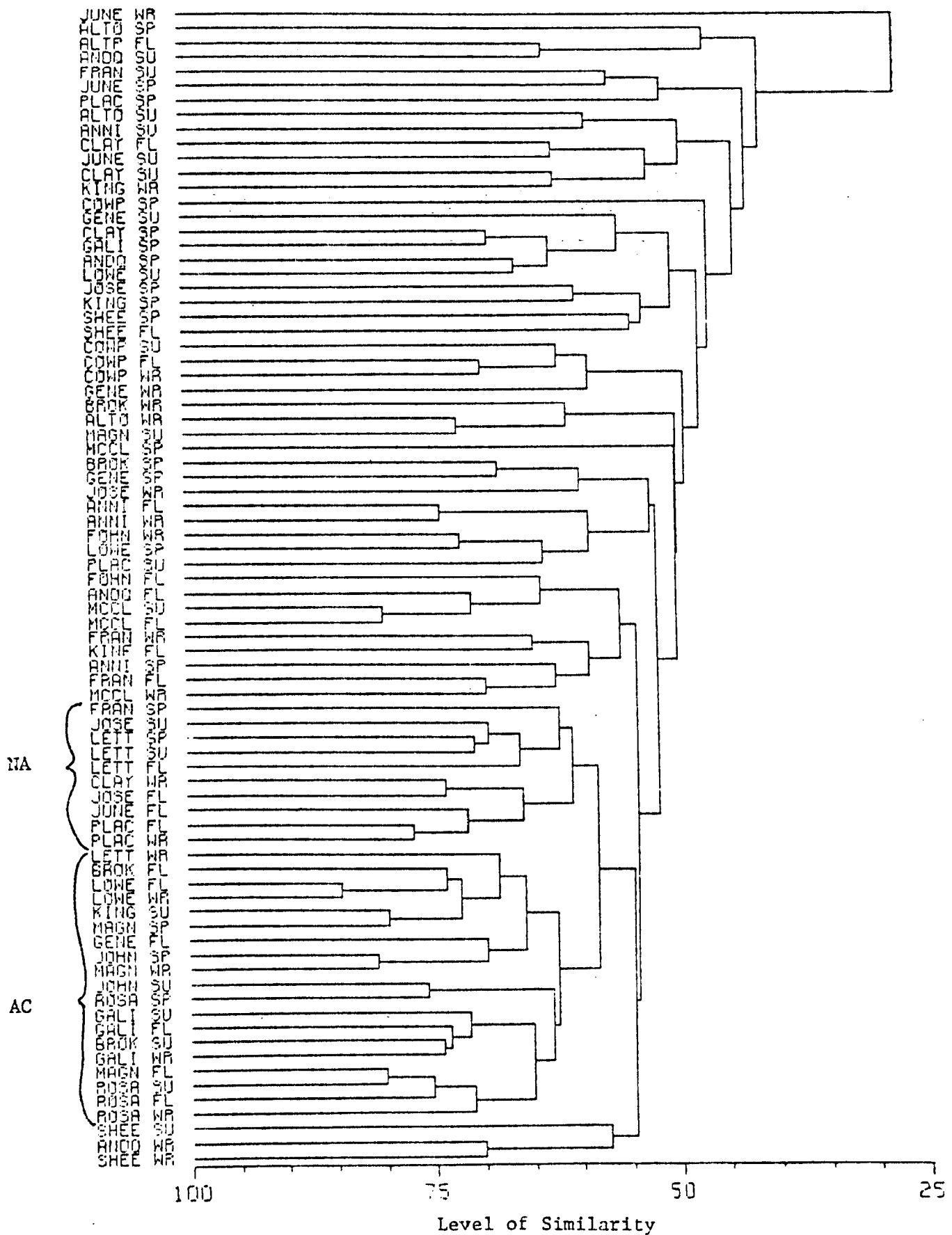


Figure 6-24. Dendrogram of the 20 lakes based on quantitative data for benthos. Names on the left represent lakes and season

tion suggests that the structure of the benthic community is controlled less by pH than by additional factors, including substrate heterogeneity.

Classification of the 20 study lakes using a Q-mode analysis of quantitative benthic data expressed as a yearly mean (4 quarters combined) per each lakes (Figure 6-25) identified two distinct clusters, one composed of acidic lakes (A) and one composed of nonacidic lakes (B). Six lakes, 2 acidic and 4 nonacidic, did not cluster within either group A or B. Two of these six lakes, Annie and Sheeler, are very oligotrophic and are considerably deeper than the other study lakes.

#### Ordination of Benthic Invertebrate Data

Principal coordinate analysis based on Gower's distance measure, unit variance standarization, and log normalized data resulted in a central lake group with a small number of lakes some distance away (Figure 6-26a). This three dimensional representation of the lakes plotted on the first three principal axes accounted for 37% of the variance in the data. Lake Cowpen (6) and June-in-Winter (12) show a high degree of dissimilarity from the remaining 18 lakes. Lake Cowpen (mean pH 4.84) contained the highest aluminum concentrations of the 20 study lakes (Figure 6-6). Tricopterans and two species of chironomids (Tanytarsus sp. and Pseudochironomus sp.) were higher in Cowpen than other lakes, but Chaoborus punctipennis, a major dominant in both the acidic and nonacidic lakes, was totally absent. Lake June-in-Winter (mean pH 6.64) contained the greatest number of total species as well as greatest number of species and abundance of molluscs.

The exact location of individual lakes in the central cluster of Figure 6-26a can not be defined because of the overlap of lakes. This problem can be overcome by examining the position of individual basins on axes two and three (Figures 6-26bc) relative to principal axis one. Two clusters are de-

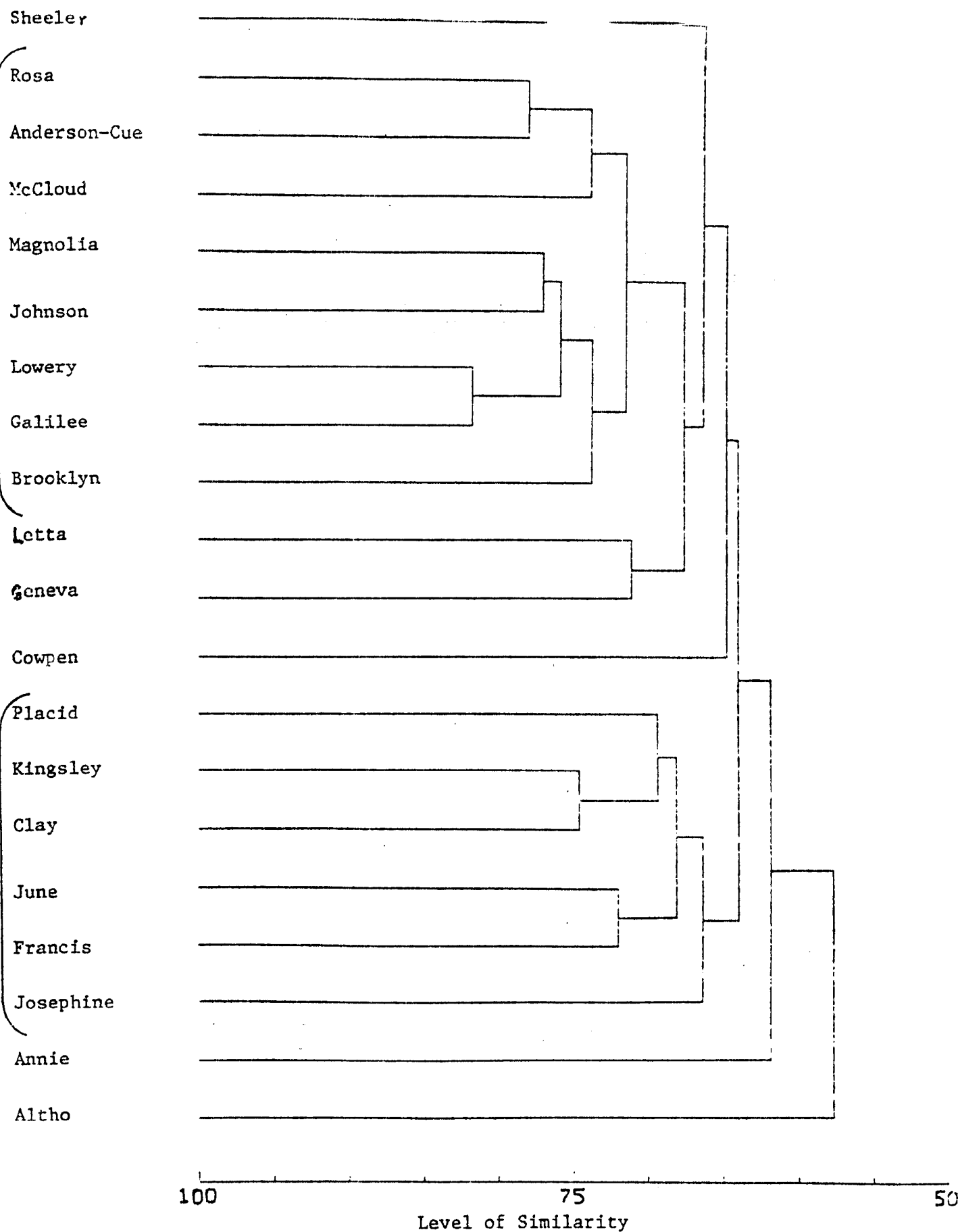


Figure 6-25. Dendrogram of the 20 lakes classified on the basis of mean annual data for benthos populations. AC is an acid group; NA a nonacid group of lakes.

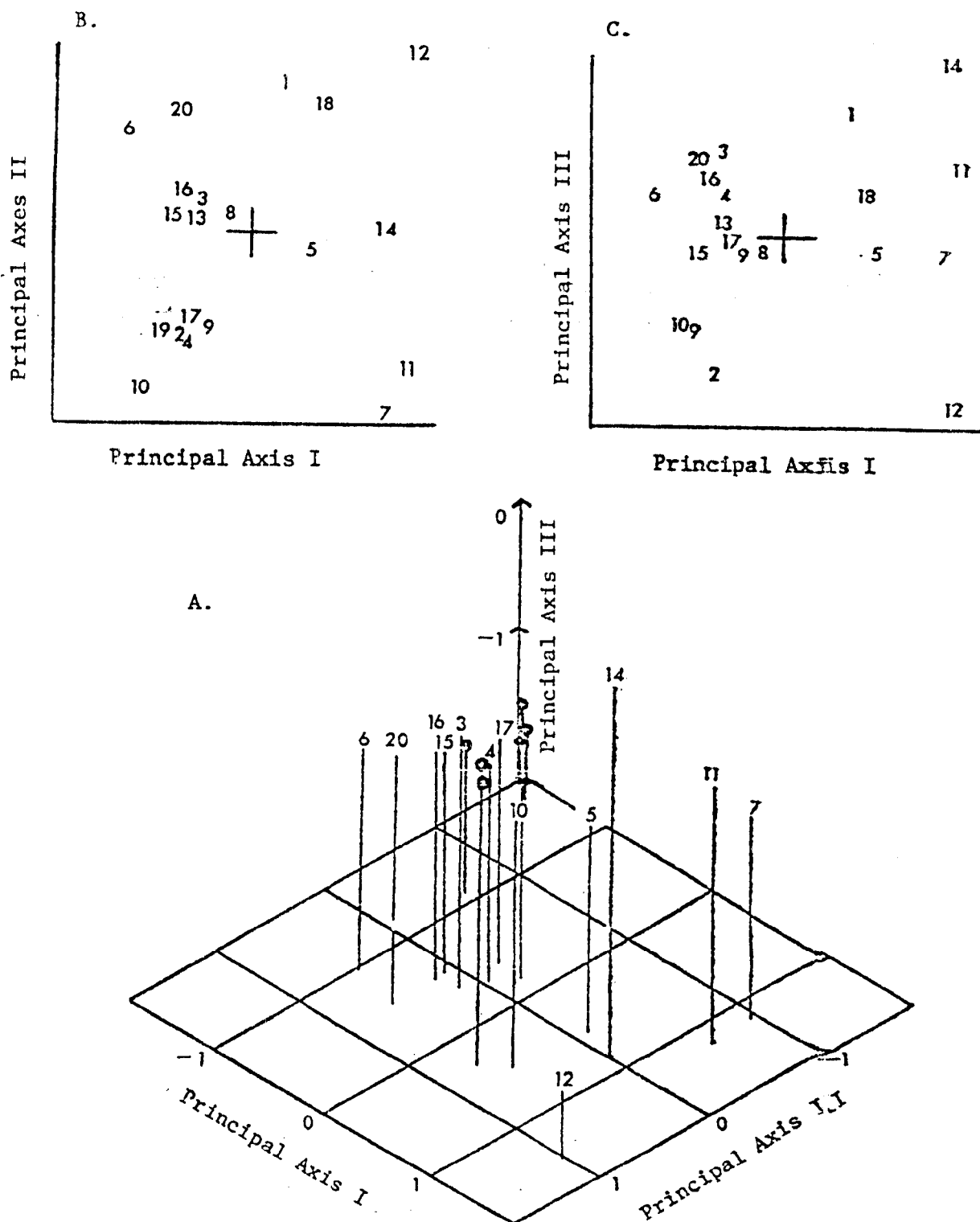


Figure 6-26. Principal coordinate analysis of study lakes based on benthic invertebrate community structure. A. Placement of lakes on first three principal axes. B and C. Placement of lakes on the first and second and first and third principal axes, respectively. For lake number code see Table 6-1. Black circles represent overlapping lakes.

fined from a combination of the first and second principal axes (Figure 6-26b), one composed of 6 nonacidic lakes (cluster A) and one composed of 9 acidic and 3 nonacidic lakes (Cluster B). This arrangement suggests a correlation between the composition of benthic communities and pH. The inclusion of three lakes with high pH and relatively low productivity i.e. Lake Geneva (14), Annie (11) Altho (12), in the acidic cluster also suggests a correlation between trophic state and the structure of benthic communities.

The position of the 20 study lakes on the first and third axes (Figure 6-26c) shows a high degree of similarity between the acidic and nonacidic cluster of lakes. No clear distinction is visible between the two groups of lakes with reference to their position along the third principal axes, suggesting that most of the variation in the benthic data from the 20 lakes that can be correlated with pH is explained along the first two principal axes.

In summary, both classification and ordination techniques demonstrated a general trend of greater similarity in the benthic communities of lakes with similar pH. These data do not indicate that a detrimental effect is being exerted by decreased pH on the benthic biota. More complete studies are needed to determine specific responses by the benthic invertebrates to increased acidity.

## FISH

Several preliminary studies on the fish populations in acidified Florida lakes also were undertaken as part of the present project. A qualitative survey of the fish fauna of Lake Sheeler (mean annual pH 5.09) was conducted with SCUBA during the summer of 1979. The narrow littoral zone was dominated by mosquito fish (Gambusia affinis) and secondarily by centrarchid fingerlings. The pelagic fauna, although somewhat sparse, was comprised of several species of centrarchids, including bream (Lepomis macrochirus) and largemouth bass (Micropterus salmoides), and one unidentified species of ictalurid catfish. Largemouth bass ranged in length from approximately 25 to 60 cm.

Adult largemouth bass were collected from Lakes McCloud (mean annual pH 4.71) and Anderson-Cue (mean annual pH 4.89) in July, 1979. A condition factor (K), relating body length (L, in mm) to body weight (W, in g) was calculated according to the formula:  $K = \frac{105 W}{L^3}$  (Nikolsky (1963)). Fish body weight per unit body length (and thus the condition factor, K) should increase in response to enhanced growth conditions. The mean K values for largemouth bass from McCloud and Anderson-Cue were 1.00 (n = 3) and 1.19 (n = 6), respectively. These values are in contrast to a K value of 2.17 calculated by Chew (1974) for largemouth bass in Lake Weir, Florida (mean annual pH 6.5), suggesting that the fitness of largemouth bass declines with lake acidification. This trend is not surprising given that aquatic productivity and thus the food supply of these secondary carnivores should decrease with decreasing pH. Consequently, fish populations may have to rely increasingly on allochthonous organic matter to sustain them (Yamamoto 1972).

The age of individual bass was determined from microscopic examination of scale annuli. The individual fish ranged in age from two to four years old; thus although Anderson-Cue Lake has been acidic (pH <5.0) for at least

the past 10 years (Table 6-2), reproduction of largemouth bass has continued. These data are in contrast to those of Beamish (1976) indicating that small-mouth bass (Micropterus dolomieu), a congeneric of largemouth bass, failed to reproduce in Ontario lakes with pH <5.5-6.0.

Cronan and Schofield (1979) attributed both the observed gill necrosis and the general impoverishment of the fish fauna in acidified Adirondack lakes to recent increases in aluminum mobilization within the watersheds as a result of acid precipitation. Some physical damage to fish has been associated with Al concentrations as low as 100 µg/L, but the most serious effects have been reported at Al levels above 200 µg/L. Wright and Snekvik (1978) suggested that increased calcium concentrations may ameliorate the deleterious effects of increased acidity on fish populations by reducing sodium loss from blood. Calcium concentrations generally declined with increasing acidity in the 700 Norwegian lakes they examined. Based on this survey, Wright and Snekvik concluded that fish could be expected in lakes with pH values >4.5-5.5 and calcium concentrations >1-4 mg/L.

Based on the findings of Cronan and Schofield (1979) for Adirondack fishes, we also examined the gills of the bass for signs of necrosis associated with lake acidification. No evidence of either gill necrosis or of other physical deformities were found in any specimen. The lack of a response may reflect differences in water chemistry between Florida lakes and north-temperate lakes of comparable pH, where responses were noted. If fish populations respond more to concentrations of heavy metals and cations than to pH directly, then observations of breeding populations of largemouth bass in Florida at pH values lower than those required by congenetics in temperate lakes may be explained. Fish reproduction should not be impaired by either the low aluminum concentrations (mean 58 µg/L) or the moderate calcium levels (mean 1.0 mg/L) found in acidic Florida lakes. However, it should be noted that

these are preliminary observations, and that further studies are needed on the distribution, fertility and growth of fish in acidic Florida lakes, as well as on the forms and levels of aluminum in the lakes. The effect of increased temperature on the response of fishes in subtropical Florida lakes to acidification also is unknown.



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# Analytical Methods for Chemical and Physical Parameters on Rain and Lake Samples.

Parameter	Method	Reference
pH	Orion Model 801 Ionalyzer in the lab. An Orion Model 401 Ionalyzer in the field.	
Conductivity	Beckman Model RC 16B2 conductivity bridge.	APHA (1976)
Dissolved Oxygen	YSI Model 51A Oxygen Meter, Hydrolab Monitor, or Winkler wet chemical technique.	APHA (1976)
Temperature	YSI Model 51A Oxygen Meter or Hydrolab Monitor.	
Color	Sample centrifuged and compared against standard chloroplatinate solution at 420 mm on a Bausch and Lomb Spectromic 88.	APHA (1976)
Turbidity	Hach Turbidimeter Model 2424 standardized with formazin suspensions.	APHA (1976)
Alkalinity	Titration with standard acid using color indicators.	APHA (1976)
Total Kjeldahl Nitrogen (TKN)	Manual semi-micro digestion followed by analysis of ammonium on neutralized samples by alkaline phenol method on AutoAnalyzer.	EPA (1974)

Parameter	Method	Reference
Ammonium	Alkaline phenol method on AutoAnalyzer.	EPA (1974)
Nitrate	Cadmium (wire) reduction method on AutoAnalyzer.	Stainton (1975)
Total Phosphorus	Sample digested with ammonium persulfate, and measured using the single reagent molybdenum blue test on an unfiltered sample.	APHA (1976)
Orthophosphate	Measured at 880 nm using the molybdenum blue test on a filtered sample.	APHA (1976)
Total Inorganic and Organic Carbon	Measured by combusting samples in a Beckman Model 915 TOC Analyzer with analysis in a Beckman Model 865 Infrared Analyzer. TC - IC = OC.	APHA (1976)
Silica	Molybdenum blue method on Technicon AutoAnalyzer. (Analogous to manual method in APHA 1975).	Technicon Method #186-72W
Sulfate	Methylthymol blue method on Technicon AutoAnalyzer.	APHA (1976)
Chloride	Ferricyanide method on Technicon AutoAnalyzer.	APHA (1976)
Aluminum	Eriochrome Cyanine R Method on Technicon AutoAnalyzer.	APHA (1976)
Fluoride	Orion Model 96-09 Specific Ion Electrode	APHA (1976)
Cations (Calcium, Magnesium, Sodium, Potassium)	Varian Model 1200 atomic absorption spectrophotometer.	EPA (1974)

## APPENDIX II

Volume-weighted mean concentrations and Annual Deposition Rates for each site during the project period.

position rates by site. (See end of appendix for explanation of symbols and units).

OBS	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	OP	TP	TKN
1	APOOKA WET	1978	103.0	4.37	17.7	0.244	0.094	0.029	0.166	0.113	0.250	1.61	0.360	0.005	0.010	0.231
2	BADIA HONDA KEY	1978	100.0	5.54	27.5	0.540	0.274	0.290	0.803	0.098	0.157	1.60	4.720	0.009	0.014	0.173
3	BELLE GLADE WET	1978	157.0	5.25	11.2	0.346	0.102	0.046	0.456	0.120	0.212	1.13	0.747	0.007	0.010	0.270
4	BROADBENT	1978	179.0	4.72	16.0	0.349	0.141	0.039	0.400	0.121	0.188	1.78	0.708	0.018	0.025	0.329
5	BROWN	1978	137.0	4.82	13.3	0.262	0.114	0.031	0.203	0.179	0.161	1.57	0.553	0.016	0.033	0.316
6	CLAR KEY BULK	1978	137.0	5.12	21.9	0.260	0.161	0.163	0.363	0.351	0.211	1.64	2.490	0.058	0.070	0.458
7	CHIMLEY	1978	145.0	4.63	28.8	0.245	0.216	0.036	0.287	0.415	0.353	2.37	0.453	0.039	0.044	0.495
8	CLEWISTON	1978	137.0	5.60	18.5	0.620	0.209	0.146	1.620	0.240	0.267	1.95	1.310	0.038	0.037	0.441
9	CORASOREN SWAMP BULK	1978	95.8	5.14	11.4	0.434	0.089	0.053	0.205	0.099	0.185	1.02	0.690	0.007	0.030	0.441
10	FORT MYERS	1978	147.0	5.84	16.6	0.453	0.252	0.137	1.280	0.137	0.182	1.77	0.982	0.032	0.046	0.458
11	GAINESVILLE BULK	1978	134.0	4.64	13.6	0.257	0.108	0.057	0.438	0.155	0.258	1.57	0.377	0.024	0.034	0.370
12	GAINESVILLE WET	1978	134.0	4.66	13.5	0.187	0.071	0.031	0.195	0.113	0.209	1.32	0.408	0.007	0.013	0.355
13	HASTINGS	1978	119.0	5.07	17.3	0.642	0.412	0.117	0.274	0.253	0.176	1.91	1.240	0.069	0.033	0.458
14	JASPER	1978	130.0	4.88	21.4	0.356	0.254	0.106	0.871	0.264	0.313	2.42	0.658	0.022	0.107	0.458
15	JAY	1978	202.0	4.58	19.6	0.282	0.089	0.044	0.253	0.214	0.232	2.07	0.481	0.012	0.030	0.457
16	LAKE ALFRED	1978	131.0	4.76	22.0	0.501	0.153	0.152	0.781	0.307	0.348	2.23	0.938	0.044	0.058	0.457
17	LAKE PLACID	1978	123.0	4.95	11.8	0.534	0.085	0.034	0.207	0.197	0.164	1.28	0.638	0.010	0.018	0.457
18	LISBON	1978	109.0	4.89	16.9	0.256	0.179	0.049	0.295	0.329	0.246	1.99	0.690	0.041	0.057	0.457
19	MACINTOSH FARMS	1978	108.0	5.75	17.4	0.602	0.196	0.075	0.980	0.244	0.221	1.37	1.240	0.026	0.038	0.457
20	MARTINLAND	1978	101.0	5.65	76.1	8.470	0.681	1.010	1.310	0.163	0.295	3.55	16.700	0.027	0.044	0.457
21	MIAMI	1978	100.0	5.52	18.1	0.932	0.262	0.135	0.399	0.137	0.199	1.62	1.870	0.018	0.033	0.457
22	STUART	1978	95.4	5.12	23.9	2.160	0.318	0.267	0.454	0.177	0.165	1.49	4.000	0.029	0.036	0.457

OBS	H	ORGN	ORGP	INORGN	TOTN	UEQH	EQHIMP	SES04	EXS04	SESEDP	EXSEDP	SOSEDP	NACDP
1	0.0002245153	0.100	0.005	0.363	0.471	26.9153	290.636	0.05100	1.54900	0.21960	3.2764	17.2880	2.1846
2	0.0003286940	0.090	0.005	0.255	0.335	2.8810	28.840	0.05500	0.96500	2.11667	2.167	16.0000	2.1846
3	0.000350544	0.105	0.003	0.332	0.484	5.7544	90.344	0.06650	1.04350	0.45268	4.610	17.7410	2.1846
4	0.000350544	0.210	0.007	0.299	0.517	19.0546	341.077	0.08725	1.69275	0.52059	10.1031	31.2620	2.1846
5	0.000351356	0.157	0.019	0.340	0.477	15.1354	207.358	0.05350	1.50450	0.27912	6.8705	21.5090	2.1846
6	0.000351356	0.137	0.012	0.562	0.699	7.5328	103.925	0.31500	1.32500	1.45550	6.0503	4.6800	2.1846
7	0.000351356	0.145	0.009	0.768	0.903	23.4423	343.257	0.05125	2.30875	0.26008	11.3339	4.6800	2.1846
8	0.000351356	0.214	0.019	0.507	0.761	3.3119	27.360	0.20500	1.74500	0.74483	4.402	4.6800	2.1846
9	0.000351356	0.105	0.011	0.284	0.339	7.2444	49.401	0.10500	0.91150	0.34848	1.707	4.7110	2.1846
10	0.000351356	0.199	0.014	0.319	0.518	1.4344	21.248	0.11325	1.55675	0.59192	1.991	2.6010	2.1846
11	0.000351356	0.215	0.010	0.413	0.628	14.4544	193.609	0.06675	1.30325	0.23315	7.145	21.0330	2.1846
12	0.000351356	0.143	0.035	0.322	0.465	21.0776	293.150	0.04675	1.27355	0.23262	4.973	17.7410	2.1846
13	0.000351356	0.212	0.020	0.459	0.671	8.5114	101.255	0.16080	1.73450	0.65565	10.777	32.7250	2.1846
14	0.000351356	0.234	0.017	0.577	0.821	13.1626	171.373	0.08900	2.87100	0.32567	1.4410	15.8200	2.1846
15	0.000351356	0.133	0.033	0.446	0.574	26.3027	321.314	0.07080	1.99950	0.47470	4.691	15.8200	2.1846
16	0.000351356	0.154	0.034	0.655	0.819	17.3700	227.652	0.12525	2.15475	0.54692	4.071	14.7450	2.1846
17	0.000351356	0.159	0.033	0.351	0.490	11.2202	132.008	0.08380	1.19650	0.34235	4.056	15.7440	2.1846
18	0.000351356	0.150	0.028	0.575	0.725	12.8925	140.419	0.06960	1.90100	0.32337	4.5070	21.6910	2.1846
19	0.000351356	0.180	0.032	0.465	0.653	1.7753	19.205	0.15050	1.21950	0.54180	4.3102	14.7450	2.1846
20	0.000351356	0.210	0.017	0.458	0.663	2.3387	22.611	2.11750	1.45250	7.12592	4.8227	35.8100	2.1846
21	0.000351356	0.243	0.015	0.336	0.584	3.0236	30.200	0.23300	1.35700	0.77667	4.6223	16.8200	2.1846
22	0.000351356	0.185	0.009	0.342	0.527	7.5858	72.360	0.54000	0.95000	1.71720	3.0210	14.2140	2.1846

OBS	KDEP	NOSEDP	CADSEDP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	TNDEP	ORGNDEP	ORGPDEP	INDEP
1	1.01580	0.5132	2.0093	1.22040	2.7000	6.048	0.05400	0.10800	2.38180	3.0868	1.1664	0.01400	0.01400
2	2.28000	2.5500	3.0000	0.98000	1.5700	47.200	0.07000	0.14000	1.78000	3.3500	0.6000	0.00000	0.00000
3	1.30140	0.7252	7.1972	1.80400	3.3264	11.728	0.10550	0.15700	4.27040	7.9980	0.0654	0.04710	0.04710
4	2.55120	0.4751	7.1600	1.98490	3.3652	12.675	0.32220	0.44750	9.08910	9.2543	0.0022	0.12500	0.12500
5	1.55120	0.4257	7.3811	2.45250	2.2057	7.562	0.19180	0.45210	4.32970	6.5369	0.6769	0.00000	0.00000
6	2.47770	0.0031	4.9731	4.00670	2.8907	34.113	0.79460	0.95900	6.68560	9.5763	0.8749	0.14440	0.14440
7	2.15000	0.0036	4.9731	4.00670	2.8907	6.614	0.51100	0.43440	8.03000	13.1633	0.9710	0.02340	0.02340
8	2.37810	0.0077	11.5040	2.61600	2.9103	16.459	0.41420	0.62130	5.38160	8.2749	0.7686	0.00710	0.00710
9	0.54102	0.0077	2.9219	0.94342	1.7723	8.506	0.08627	0.19160	1.93432	3.7266	0.0024	0.10539	0.10539
10	1.78440	0.0139	10.8150	2.01590	2.6754	14.455	0.47040	0.67620	4.93920	7.6146	0.4253	0.00000	0.00000
11	0.44720	0.0233	5.8592	2.07700	3.4372	7.732	0.32150	0.45560	4.95600	8.4152	0.6810	0.13400	0.13400
12	0.55140	0.4154	2.8130	1.51420	2.8006	5.467	0.09360	0.17420	3.43040	6.2010	0.9162	0.00040	0.00040
13	0.50250	1.13223	2.5505	3.35770	0.9744	14.756	0.77350	1.01150	3.97050	7.9849	0.2288	0.00000	0.00000
14	0.23500	1.13223	4.49200	4.0650	0.0650	8.554	1.95000	0.41700	4.00400	10.6730	1.1720	0.00000	0.00000
15	0.79720	0.0077	5.1105	4.34500	4.6664	8.716	0.44240	0.40400	4.00400	1.6748	0.1186	0.00000	0.00000
16	0.00430	0.0032	10.0011	4.02170	4.5503	12.268	0.57210	0.87060	4.17010	10.7089	1.484	0.00000	0.00000
17	0.00430	0.0032	2.4451	2.42310	0.0172	7.847	0.12000	0.22140	4.00780	6.0270	0.8667	0.00000	0.00000
18	0.55110	0.0032	3.7155	3.58610	2.6814	7.521	0.44690	0.75210	5.22110	7.9023	6.350	0.00000	0.00000
19	2.00300	0.8100	10.6704	2.55500	3.9368	13.392	0.26080	0.18840	4.66560	7.0524	0.0004	0.00000	0.00000
20	0.87610	10.2010	15.2510	1.64500	2.9795	163.670	0.27270	0.44440	3.76730	6.7450	1.210	0.17170	0.17170
21	0.50000	1.2500	8.9900	1.57000	1.9900	18.700	0.19000	0.33000	3.85000	5.8400	2.800	0.15000	0.15000
22	0.00372	2.1472	4.1404	1.68858	1.5741	38.160	0.27666	0.36252	3.45343	3.0276	7.649	0.02582	0.02582

A. Calendar Year 1978 cont....

Q35	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	OP	TP	TKN
23	TALLAHASSEE	1978	103	4.75	17.2	0.327	0.298	0.048	0.497	0.194	0.250	1.69	0.832	0.012	0.021	0.298
24	WALDO BULK	1978	104	4.56	19.8	0.591	0.272	0.073	0.286	0.115	0.220	2.24	0.842	0.018	0.035	0.477
25	WALDO THROUGHFALL	1978	100	4.80	29.5	1.550	0.733	0.350	1.450	0.156	0.259	3.32	3.220	0.022	0.038	0.568
Q35	H	GRN	DRCP	INORGN	TOTN	UEGH	EGHDEP	SES04	EXS04	SESDEP	EXSDEP	SO4DEP	NADEP			
23	0.0000173780	0.104	0.009	0.444	0.548	17.3780	231.128	0.08175	1.80825	0.36242	8.01637	25.137	4.3491			
24	0.0000275423	0.352	0.017	0.335	0.697	27.5423	369.067	0.14775	2.09225	0.65995	9.34538	30.016	7.9194			
25	0.0000158489	0.412	0.016	0.415	0.827	15.8489	158.489	0.38750	2.93250	1.29167	9.77500	33.200	15.5000			
Q35	KDEP	MGDEP	CADEP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	TNDEP	GRNDEP	DRCPDEP	INNDEP			
23	3.8304	0.6384	6.6101	2.5902	3.325	11.0656	0.1596	0.2793	3.9634	7.2884	1.3832	0.1197	5.9052			
24	3.6448	0.9782	3.8324	1.5410	2.948	11.2828	0.2412	0.4690	6.3918	9.3398	4.6508	0.2278	4.4890			
25	7.3300	3.5000	14.5000	1.5600	2.590	32.2000	0.2200	0.3900	5.6800	8.2700	4.1200	0.1600	4.1500			



B. Calendar year 1979. Volume-weighted average annual concentrations and deposition rates by site. (See end of appendix for explanation of symbols and units).

Q2S	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	GP	TP
1	APOPKA WET	1979	131	4.63	13.6	0.243	0.061	0.037	0.221	0.091	0.169	1.230	0.551	0.003	0.010
2	BALGA HONDA KEY	1979	103	6.17	52.9	4.200	0.858	0.595	2.040	0.102	0.186	2.320	7.530	0.006	0.012
3	BELLE GLADE WET	1979	138	5.49	11.9	0.618	0.050	0.087	0.714	0.205	0.180	1.090	1.250	0.003	0.014
4	BRADENTON	1979	136	4.77	17.5	0.719	0.144	0.100	0.800	0.142	0.252	1.970	1.250	0.016	0.033
5	BRADENTON	1979	138	4.62	14.1	0.350	0.058	0.042	0.302	0.080	0.189	1.210	0.581	0.003	0.009
6	CELAIR KEY BULK	1979	132	4.60	22.8	1.340	0.081	0.162	0.357	0.068	0.187	1.600	2.550	0.003	0.002
7	CELAIR KEY WET	1979	132	4.51	23.4	1.180	0.075	0.147	0.311	0.078	0.159	1.620	2.400	0.003	0.005
8	CHIMLEY	1979	174	4.76	10.4	0.229	0.080	0.033	0.102	0.178	0.137	1.150	0.467	0.005	0.014
9	CLINTON	1979	114	5.37	16.3	1.050	0.157	0.193	0.742	0.195	0.235	1.450	1.900	0.037	0.056
10	COCKSCREW SWAMP BULK	1979	159	5.18	19.6	0.672	0.128	0.124	0.658	0.151	0.235	1.670	1.500	0.030	0.038
11	COCKSCREW SWAMP WET	1979	159	4.93	7.8	0.161	0.036	0.020	0.142	0.088	0.125	0.496	1.040	0.017	0.023
12	FLAT MEERS	1979	134	5.43	14.2	0.471	0.133	0.125	1.180	0.098	0.162	1.410	0.676	0.006	0.013
13	GAINESVILLE BULK	1979	164	4.65	15.9	0.316	0.070	0.087	0.517	0.106	0.210	1.710	0.453	0.003	0.006
14	GAINESVILLE WET	1979	164	4.53	14.8	0.205	0.041	0.042	0.217	0.093	0.180	1.250	0.410	0.018	0.024
15	HAD TIGGS	1979	153	4.76	16.3	0.691	0.111	0.097	0.275	0.103	0.151	1.300	1.410	0.047	0.115
16	JACKSON	1979	156	5.13	19.3	0.389	0.225	0.083	0.759	0.316	0.201	2.130	0.634	0.015	0.039
17	JACKSONVILLE	1979	157	4.69	20.4	0.754	0.160	0.104	0.444	0.141	0.166	1.960	0.768	0.005	0.020
18	JAY	1979	135	4.70	16.1	0.455	0.058	0.073	0.438	0.142	0.175	1.670	0.819	0.016	0.033
19	LAKE ALFRED	1979	155	4.94	10.6	0.451	0.079	0.062	0.237	0.053	0.125	0.931	0.831	0.005	0.011
20	LAKE PLACID	1979	155	4.94	10.6	0.451	0.079	0.062	0.237	0.053	0.125	0.931	0.831	0.005	0.011
21	LITCH	1979	146	4.95	15.2	0.517	0.133	0.062	0.395	0.226	0.208	1.470	0.823	0.042	0.050
22	MACARTHUR FARMS	1979	155	5.22	14.9	0.697	0.115	0.095	0.676	0.313	0.179	1.270	1.330	0.020	0.038

Q2S	TKN	H	ORGN	DRCP	INDRGN	TOTN	UEGH	ECHDEP	SES04	EXS04	SESDP	EXSDP	SO4DEP
1	0.356	0.0000334403	0.245	0.007	0.260	0.525	23.4423	307.094	0.06075	1.16925	0.2653	5.1057	16.1130
2	0.000	0.0000000000	0.052	0.004	0.268	0.370	0.6761	6.964	1.05000	1.27600	3.6050	4.3603	23.8950
3	0.000	0.0000000000	0.078	0.011	0.065	0.453	3.2059	44.556	0.15450	0.93550	0.7107	4.3033	19.0420
4	0.000	0.0000000000	0.135	0.017	0.374	0.559	16.9824	230.961	0.17975	1.79025	0.8149	8.1158	26.7920
5	0.000	0.0000000000	0.131	0.006	0.267	0.400	23.9663	351.059	0.07000	1.14000	0.3220	9.2440	18.6450
6	0.000	0.0000000000	0.107	0.005	0.254	0.392	35.1109	331.569	0.03500	1.34500	1.4740	5.9180	22.1760
7	0.000	0.0000000000	0.107	0.002	0.254	0.371	30.9050	407.919	0.05500	1.32500	1.2960	6.6300	21.6840
8	0.000	0.0000000000	0.107	0.009	0.315	0.394	17.3780	302.377	0.05725	1.09275	0.3310	6.5679	20.0160
9	0.000	0.0000000000	0.107	0.019	0.351	0.458	4.2658	48.640	0.26550	1.16750	0.9475	4.4065	18.3880
10	0.000	0.0000000000	0.110	0.008	0.305	0.506	6.6059	105.050	0.21800	1.45200	1.1554	7.6956	26.5550
11	0.000	0.0000000000	0.108	0.004	0.213	0.371	11.7490	186.609	0.04025	0.45575	0.2163	2.4155	7.6640
12	0.000	0.0000000000	0.125	0.006	0.260	0.427	3.7154	49.704	0.12775	1.25725	0.9483	5.7497	18.6940
13	0.000	0.0000000000	0.167	0.006	0.260	0.442	22.3672	367.150	0.07900	1.63100	0.4319	6.9161	22.0440
14	0.000	0.0000000000	0.125	0.007	0.316	0.427	29.5121	483.998	0.05125	1.15375	0.2502	4.5522	20.5000
15	0.000	0.0000000000	0.124	0.003	0.273	0.377	27.3780	265.004	0.17275	1.12725	0.6310	9.2490	19.6400
16	0.000	0.0000000000	0.174	0.005	0.254	0.430	17.3780	265.004	0.09725	2.02275	0.4509	9.2151	35.5780
17	0.000	0.0000000000	0.171	0.068	0.517	0.688	7.4131	100.518	0.19100	1.75700	0.9996	9.2879	35.7280
18	0.000	0.0000000000	0.205	0.024	0.307	0.542	20.4174	320.553	0.10750	1.71250	0.8027	7.7687	45.7680
19	0.000	0.0000000000	0.077	0.014	0.343	0.420	25.3027	589.180	0.11375	1.55425	0.5157	7.0550	22.7120
20	0.000	0.0000000000	0.110	0.017	0.317	0.427	19.9526	271.356	0.08525	0.95675	0.3567	4.3555	14.4805
21	0.000	0.0000000000	0.115	0.005	0.178	0.294	11.4915	177.964	0.16775	0.82575	0.4280	6.5250	21.4620
22	0.000	0.0000000000	0.135	0.008	0.434	0.570	11.2202	163.915	0.12425	1.34075	0.9003	3.7647	19.5550

Q2S	NADEP	KDEP	MGDEP	CADEP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	INDEP	GRNDEP	DRCPDEP	INDRDEP
1	0.103	0.7471	0.4047	2.8951	1.1921	2.2159	7.213	0.0393	0.1310	4.6635	6.8775	3.4715	0.0417	3.4060
2	0.000	0.8074	0.1805	21.0120	1.0506	1.9159	77.557	0.0618	0.1236	3.8110	0.8445	0.0418	0.0418	3.7561
3	0.000	1.2420	1.2003	9.6332	2.0270	2.4840	17.250	0.0414	0.1932	3.9054	6.3894	1.0744	0.1918	3.9054
4	0.000	1.9384	1.5400	9.2480	1.5312	3.4272	17.544	0.2176	0.4488	4.1752	7.6024	2.2440	0.2312	3.9054
5	0.000	0.8743	0.8743	4.1676	1.1040	2.6082	8.018	0.0414	0.1242	2.9118	5.5200	1.8078	0.0228	3.7122
6	0.000	1.0642	2.1304	4.8444	0.8976	3.4684	33.660	0.0396	0.1056	2.7060	5.1743	1.6084	0.0660	3.7122
7	0.000	1.0423	1.9401	4.1052	0.9700	2.0938	31.660	0.0396	0.0660	2.7584	4.8972	1.8084	0.0264	3.0628
8	0.000	1.3920	1.9401	3.1543	0.9972	2.3533	8.126	0.0870	0.2436	4.4718	6.2556	1.3746	0.1556	5.4810
9	0.000	1.9700	2.2230	2.2230	0.9972	1.784	21.660	0.4218	0.5384	3.4128	5.2212	1.2198	0.0166	4.0014
10	0.000	0.0352	1.9715	10.4622	2.4009	3.7643	23.950	0.4770	0.6042	4.3089	8.0454	1.9060	0.1272	6.1024
11	0.000	0.5724	0.3160	1.3492	1.3492	1.9573	8.997	0.0795	0.1431	3.9114	5.8967	2.9122	0.0676	3.9267
12	0.000	1.7822	1.6864	15.8120	1.3132	1.708	13.935	0.2773	0.3082	3.5510	5.7218	2.0378	0.0604	4.8040
13	0.000	1.1480	1.4889	8.4789	1.7384	4.446	11.015	0.0494	0.2132	3.8548	7.2488	2.0654	0.1148	5.1604
14	0.000	0.8724	0.6068	3.5538	1.5322	3.920	21.429	0.0494	0.0504	3.5563	6.5108	2.0304	0.0496	4.4722
15	0.000	1.8700	1.8700	4.2075	1.5759	3.105	11.573	0.2754	0.3672	4.2587	5.5795	2.6528	0.0518	3.6352
16	0.000	0.0600	1.7104	10.5324	2.2975	7.556	23.853	0.2555	0.5120	5.4032	8.5094	3.0899	0.0760	4.8154
17	0.000	0.9120	1.5003	5.9708	2.2157	6.062	38.593	0.1374	0.4680	5.5776	9.4000	1.7440	0.0136	7.6632
18	0.000	1.9533	1.9533	6.7548	3.6528	8.304	17.405	0.1374	0.4488	3.4272	5.6072	1.4960	0.0310	4.3112
19	0.000	1.108	0.9748	1.9748	1.9312	2.360	11.138	0.0775	0.1708	4.6195	4.5570	1.7980	0.0950	2.7540
20	0.000	1.2345	0.9516	3.6755	0.8219	1.9375	12.690	0.0775	0.7300	8.2632	8.3220	1.9656	0.1168	6.3384
21	0.000	1.5418	0.9552	5.7670	2.2995	3.368	0.016	0.3100	0.5690	8.0755	10.8500	3.2240	0.2740	7.6260
22	0.000	1.7625	1.4550	10.4750	4.8515	2.7745	20.415							

B. Calendar year 1979 continued...

OBS	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	OP	TP
23	MARINELAND	1979	152	5.26	101.0	13.000	0.861	1.540	1.740	0.091	0.201	4.36	23.900	0.019	0.036
24	MIAMI	1979	110	5.38	16.7	1.260	0.085	0.184	0.759	0.097	0.140	1.24	2.580	0.009	0.018
25	STUART	1979	165	5.02	14.6	1.220	0.070	0.155	0.341	0.096	0.147	1.23	2.300	0.008	0.014
26	TALLAHASSEE	1979	204	4.71	12.7	0.286	0.082	0.052	0.338	0.063	0.135	1.31	0.586	0.006	0.012
27	WALDO BULK	1979	154	4.75	15.8	0.551	0.080	0.077	0.251	0.215	0.177	1.81	1.080	0.010	0.015
28	WALDO THROUGHFALL	1979	123	4.67	38.7	2.360	0.656	0.457	1.690	0.068	0.192	3.63	4.860	0.011	0.016
OBS	TKN	H	ORCN	ORGP	INORGN	TOTN	UEQH	EQHDEP	SES04	EXS04	SESDEP	EXSDEP	EC4DEP		
23	0.242	0.0000054954	0.151	0.017	0.292	0.443	5.4954	86.827	3.25000	1.11000	17.1167	5.8460	68.668		
24	0.233	0.0000011687	0.135	0.009	0.237	0.373	4.1687	45.856	0.31500	0.92500	1.1550	3.3917	15.650		
25	0.227	0.0000095499	0.131	0.006	0.243	0.374	9.5499	158.529	0.30500	0.92500	1.6877	5.1163	20.418		
26	0.213	0.0000194934	0.150	0.006	0.198	0.348	19.4984	397.768	0.07150	1.23850	0.4862	8.4218	28.724		
27	0.563	0.0000177828	0.153	0.003	0.392	0.545	17.7828	291.636	0.13775	1.67225	0.7530	9.1416	29.664		
28	0.343	0.0000213796	0.255	0.005	0.280	0.535	21.3796	262.969	0.59000	3.24000	2.4190	13.2840	47.109		
OBS	NADEP	KDEP	MGDEP	CADEP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	TNDEP	GRNDEP	ORPDEP	INNDEP	
23	205.400	13.5038	21.3320	27.4920	1.4378	3.1758	377.620	0.3002	0.5688	3.8236	6.9994	2.3858	0.2486	4.6136	
24	15.660	0.9250	2.0240	8.3490	1.0670	1.5400	28.360	0.0990	0.1950	2.5630	4.1050	1.4960	0.0550	2.6070	
25	20.252	1.4910	2.5730	5.6506	1.5936	2.4402	38.180	0.1328	0.2324	3.7582	6.2084	2.1748	0.0976	4.0358	
26	5.834	1.6723	1.0608	6.8952	1.2852	2.7540	11.954	0.1224	0.2448	4.3452	7.0992	3.0600	0.1224	4.0392	
27	9.036	1.3130	1.2523	4.1164	3.5260	2.9028	17.712	0.1640	0.2460	6.0352	8.9380	2.5092	0.0820	6.4268	
28	29.028	6.0386	5.6211	20.7870	1.0824	2.3616	59.778	0.1353	0.1968	4.2189	6.5805	3.1965	0.0615	3.4440	

C. Volume-weighted concentrations and total deposition over two year project period, 1978 and 1979. (See end of appendix for explanation of symbols).

Q35	SITE	DATE	RAIN	PH	CON	NA	K	MO	CA	NH4	N23	SO4	CL	OP	TP
1	POPPA NET	78879	239	4.21	15.3	0.243	0.075	0.034	0.206	0.101	0.304	1.39	0.555	0.004	0.010
2	SAHIA HONDA KEY	78879	203	5.35	28.8	0.230	0.250	0.306	0.868	0.098	0.159	1.64	0.870	0.003	0.014
3	WHELLE CLADE NET	78879	203	5.35	11.4	0.412	0.079	0.056	0.519	0.140	0.304	1.12	0.871	0.003	0.014
4	WHELETON	78879	203	4.74	16.7	0.516	0.143	0.056	0.527	0.135	0.317	1.85	0.970	0.003	0.014
5	WHELETON	78879	203	4.72	13.7	0.270	0.080	0.032	0.249	0.133	0.172	1.40	0.565	0.003	0.014
6	CHAD KEY BULK	78879	203	4.74	22.3	1.310	0.120	0.161	0.325	0.180	0.196	1.47	2.130	0.003	0.014
7	CHAD KEY NET	78879	203	4.51	23.4	1.180	0.079	0.157	0.311	0.075	0.159	1.42	2.460	0.003	0.014
8	CHAD KEY NET	78879	203	4.71	14.1	0.253	0.129	0.034	0.200	0.263	0.214	1.58	0.462	0.003	0.014
9	CHAD KEY NET	78879	203	5.47	17.4	0.533	0.187	0.170	0.309	0.217	0.211	1.67	1.710	0.003	0.014
10	CLEWISTON	78879	203	5.12	13.0	0.537	0.091	0.079	0.437	0.118	0.203	1.22	1.120	0.003	0.014
11	CORRECTION SHAMP BULK	78879	203	5.60	15.0	0.471	0.197	0.152	0.350	0.119	0.173	1.60	1.010	0.003	0.014
12	PORT HERS	78879	203	4.73	13.8	0.294	0.037	0.074	0.480	0.129	0.173	1.64	0.433	0.003	0.014
13	GAINESVILLE BULK	78879	203	4.59	14.2	0.197	0.054	0.037	0.207	0.102	0.174	1.57	0.433	0.003	0.014
14	GAINESVILLE NET	78879	203	4.83	16.8	0.568	0.254	0.106	0.374	0.183	0.163	1.57	1.230	0.003	0.014
15	HARTTOS	78879	203	5.03	17.4	0.370	0.205	0.075	0.798	0.298	0.210	2.42	0.642	0.003	0.014
16	JASPER	78879	203	4.58	16.6	0.371	0.094	0.053	0.253	0.189	0.195	1.92	0.654	0.003	0.014
17	LAKE ALFRED	78879	203	4.73	10.9	0.476	0.125	0.111	0.603	0.222	0.257	1.97	0.677	0.003	0.014
18	LAKE ALFRED	78879	203	4.25	11.1	0.368	0.082	0.050	0.324	0.118	0.142	1.69	0.745	0.003	0.014
19	LASSON	78879	203	4.91	16.3	0.410	0.153	0.054	0.331	0.292	0.233	1.81	0.757	0.003	0.014
20	MAGNANIM FARM	78879	203	5.44	16.3	0.444	0.155	0.054	0.331	0.274	0.203	1.34	0.757	0.003	0.014
21	MAGNANIM FARM	78879	203	5.40	16.3	10.400	0.778	1.300	0.630	0.184	0.244	3.99	0.640	0.003	0.014
22	MAGNANIM FARM	78879	210	5.44	17.4	1.110	0.169	0.192	0.823	0.116	0.128	1.42	2.430	0.003	0.014
Q35	TRN	H	GRN	DRGP	INDGRN	TOTN	ULOH	EDHUP	SECO4	EXSC4	SECOEP	EXSCOP	SECOEP	EXSCOP	NADEP
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	24.5471	592.68	0.05075	1.32925	0.4840	10.0897	33.221	1.603	0.003
2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.7542	55.91	0.67750	0.92850	4.4471	6.1434	33.221	1.603	0.003
3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	5.1986	151.29	0.10300	1.01700	1.0128	10.0897	33.221	1.603	0.003
4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	10.1970	573.21	0.10300	1.73100	1.0545	18.1735	33.221	1.603	0.003
5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	19.0544	524.60	0.06750	1.33250	0.2107	12.2141	33.221	1.603	0.003
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	18.1970	489.00	0.32750	1.34250	2.9365	12.0827	33.221	1.603	0.003
7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	39.4030	631.29	0.32750	1.32500	2.8450	11.0827	33.221	1.603	0.003
8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	17.4064	675.75	0.05675	1.52125	0.6267	12.0827	33.221	1.603	0.003
9	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.2884	79.54	0.23325	1.45475	1.7433	10.0897	33.221	1.603	0.003
10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	6.9183	176.42	0.14925	1.11075	1.2685	9.4414	33.221	1.603	0.003
11	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.5119	70.50	0.11775	1.48325	1.1037	13.0837	33.221	1.603	0.003
12	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	18.6809	354.90	0.07350	1.56650	0.7301	12.0827	33.221	1.603	0.003
13	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	25.7040	755.93	0.04925	1.23675	0.4892	12.0827	33.221	1.603	0.003
14	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	13.1624	358.57	0.16700	1.42300	1.5141	12.0827	33.221	1.603	0.003
15	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	9.5385	243.25	0.09450	2.33350	0.6379	20.0814	33.221	1.603	0.003
16	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	26.3037	1120.49	0.05775	1.08725	1.3170	25.9169	33.221	1.603	0.003
17	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	18.6809	397.18	0.11750	1.85050	1.0635	14.4844	33.221	1.603	0.003
18	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	11.2402	311.92	0.07700	0.99300	0.8967	9.4414	33.221	1.603	0.003
19	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	12.3037	413.73	0.10225	1.70675	0.8778	14.4844	33.221	1.603	0.003
20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	3.6308	95.49	0.16100	1.17900	1.4114	10.0897	33.221	1.603	0.003
21	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	103.11	272300	1.25500	25.5289	1.4114	25.5289	33.221	1.603	0.003
22	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.6308	70.25	0.27750	1.14250	1.9435	7.6775	33.221	1.603	0.003
Q35	KDEP	INDEP	CADEP	NH4DEP	NOSDEP	CLDEP	OPDEP	TPDEP	TKNDEP	INDEP	GRNDEP	OPDEP	INDEP	TPDEP	NADEP
1	79.75	0.8126	4.9234	2.4139	4.0756	13.244	0.0956	0.2390	7.1461	12.0217	4.7352	0.1438	7.1461	12.0217	4.7352
2	27.70	0.8110	17.6204	1.9894	2.0777	98.841	0.1827	0.2842	6.8411	1.2248	0.1438	0.1438	6.8411	1.2248	0.1438
3	3.41	0.8120	1.2103	1.1390	0.0180	23.474	0.1770	0.2545	8.1123	14.1306	3.4052	0.1438	8.1123	14.1306	3.4052
4	1.00	0.8120	0.0000	0.0000	0.0000	19.545	0.1770	0.2545	8.1123	14.1306	3.4052	0.1438	8.1123	14.1306	3.4052
5	0.0000	0.8120	16.8005	0.9375	0.0000	19.545	0.1770	0.2545	8.1123	14.1306	3.4052	0.1438	8.1123	14.1306	3.4052
6	0.0000	0.8120	0.0000	0.0000	0.0000	67.738	0.6725	0.6777	0.5723	13.7097	0.0000	0.0000	0.5723	13.7097	0.0000
7	0.0000	0.8120	8.3559	0.0175	4.2771	64.560	0.0007	0.1343	5.7028	9.9747	0.0000	0.0000	5.7028	9.9747	0.0000
8	0.0000	0.8120	6.6830	0.4160	0.8860	14.794	0.5120	0.0040	11.5300	10.4000	0.1350	0.0000	11.5300	10.4000	0.1350
9	0.0000	0.8120	20.0730	0.8591	4.7052	29.133	0.0251	1.2408	9.8754	13.5007	0.0000	0.0000	9.8754	13.5007	0.0000
10	0.0000	0.8120	11.1435	0.0000	5.1765	28.560	0.4335	0.6885	5.8935	11.0150	0.0000	0.0000	5.8935	11.0150	0.0000
11	0.0000	0.8120	34.5630	0.3459	4.0613	28.381	0.7025	0.6835	0.5143	13.0756	0.0000	0.0000	0.5143	13.0756	0.0000
12	0.0000	0.8120	14.3040	0.8442	6.9135	18.774	0.4172	0.6854	8.7910	15.7045	4.9458	0.0000	8.7910	15.7045	4.9458
13	0.0000	0.8120	6.1686	0.0396	5.7812	12.963	0.1490	0.2882	7.0050	12.7842	3.9444	0.0000	7.0050	12.7842	3.9444
14	0.0000	0.8120	7.4828	1.136	4.4536	36.175	1.0800	1.4415	10.3632	14.7948	5.4476	0.0000	10.3632	14.7948	5.4476
15	0.0000	0.8120	21.2268	9.9348	6.3540	17.077	1.2738	3.0218	12.1404	19.5441	5.2125	0.0000	12.1404	19.5441	5.2125
16	0.0000	0.8120	12.0888	8.6314	8.3370	27.680	0.3603	0.6500	12.2688	20.5738	4.2194	0.0000	12.2688	20.5738	4.2194
17	0.0000	0.8120	16.1835	9.9274	6.9153	22.412	0.2010	1.3350	9.5668	15.4739	3.6312	0.0000	9.5668	15.4739	3.6312
18	0.0000	0.8120	6.2072	9.9804	3.9475	20.711	0.1946	0.3890	4.8432	10.5915	3.0638	0.0000	4.8432	10.5915	3.0638
19	0.0000	0.8120	8.4405	7.4460	3.9415	10.792	1.0425	1.5810	11.1435	17.0850	3.8775	0.0000	11.1435	17.0850	3.8775
20	0.0000	0.8120	22.4075	7.2062	5.3589	33.654	0.6112	1.1572	12.0818	17.7252	5.1611	0.0000	12.0818	17.7252	5.1611
21	0.0000	0.8120	42.2170	5.2116	6.3196	539.540	0.3527	1.0191	7.8813	14.1414	4.5102	0.0000	7.8813	14.1414	4.5102
22	0.0000	0.8120	17.5250	4.3360	5.5260	47.040	0.2700	0.5250	7.4050	9.9350	3.4690	0.0000	7.4050	9.9350	3.4690

C. Project period (1978-79) continued...

GDS	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SQ4	CL	DP	TP	TKIN
23	STUART	78/79	281	3.05	18.2	1.580	0.178	0.198	0.377	0.127	0.154	1.33	2.950	0.016	0.024	0.279
24	TALLAHASSEE	78/79	237	4.73	14.6	0.304	0.171	0.050	0.407	0.120	0.185	1.55	0.692	0.002	0.015	0.250
25	WALDO PULX	78/79	298	4.65	17.4	0.567	0.159	0.075	0.265	0.174	0.145	1.99	0.993	0.013	0.022	0.412
26	WALDO THROUGHFALL	78/79	223	4.71	33.5	1.790	0.534	0.400	1.550	0.120	0.226	3.60	3.810	0.015	0.027	0.433
GDS	H	DRCH	DRCP	INDRCH	TOTN	UEQH	EQHDEP	SES04	EXS04	SESDEP	EXSDEP	SG4DEP	NADep			
23	0.0000059125	0.152	0.008	0.281	0.433	8.9125	230.616	0.39500	0.93500	3.43650	8.1345	34.713	41.2300			
24	0.0000125069	0.130	0.008	0.305	0.405	19.5209	441.315	0.07600	1.48400	0.60040	11.7236	32.972	7.8043			
25	0.0000218775	0.238	0.010	0.369	0.607	21.8775	651.953	0.14175	1.04025	1.40805	18.3593	54.332	15.8938			
26	0.000194984	0.318	0.011	0.546	0.654	19.4984	434.815	0.44750	3.15250	3.32642	23.4356	60.280	39.9170			
GDS	KDEP	MODEP	CADEP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	TNDEP	ORGDEP	ORGPDEP	INNDEP			
23	4.6458	5.1678	9.8397	3.3147	4.0194	77.2560	0.4176	0.6264	7.2819	11.3013	3.9572	0.2053	7.3341			
24	4.0527	1.1850	9.5459	2.8440	4.3045	16.4004	0.1096	0.3792	5.9250	10.3095	3.0810	0.1896	7.2365			
25	4.7382	2.2356	7.8976	5.1852	5.9110	29.2934	0.3874	0.4854	12.2776	18.0886	7.0924	0.1960	10.4962			
26	14.1382	9.9200	34.5650	2.6760	5.0398	84.9630	0.3520	0.6021	9.7674	14.8072	7.0414	0.2453	7.7159			

1, 1978 to April 30, 1979. (See end of appendix for explanation of symbols and units).

035	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	OP	TP
1	APOKA WET	78-79	123	4.60	16.6	0.319	0.076	0.049	0.255	0.090	0.206	1.58	0.624	0.004	0.007
2	BANTA HONDA KEY	78-79	108	5.45	25.9	0.260	0.430	0.248	0.802	0.083	0.129	1.45	4.180	0.010	0.016
3	BELLE GLADE WET	78-79	137	5.21	11.9	0.435	0.108	0.060	0.511	0.109	0.203	1.14	0.890	0.006	0.009
4	BRADENTON	78-79	156	4.70	17.0	0.514	0.122	0.062	0.508	0.109	0.200	1.68	0.574	0.010	0.017
5	BRONSON	78-79	136	4.74	13.8	0.340	0.121	0.044	0.318	0.144	0.152	1.41	0.610	0.013	0.022
6	CRANK KEY BULK	78-79	139	5.04	21.8	1.550	0.183	0.180	0.343	0.097	0.134	1.55	2.610	0.001	0.004
7	CRANK KEY WET	78-79	139	4.74	20.1	1.410	0.103	0.165	0.343	0.275	0.335	1.94	0.515	0.002	0.042
8	CUMLEY	78-79	151	4.76	16.3	0.278	0.173	0.043	0.275	0.247	0.250	1.66	2.070	0.044	0.064
9	CLEMENTSON	78-79	128	5.61	20.2	1.160	0.241	0.221	1.080	0.085	0.191	1.15	1.270	0.009	0.019
10	CORNUSOREN SWAMP BULK	78-79	110	5.15	12.8	0.605	0.087	0.084	0.443	0.121	0.162	1.64	1.030	0.034	0.045
11	FOOT MYERS	78-79	151	5.79	15.6	0.506	0.256	0.125	1.120	0.161	0.237	1.77	0.687	0.024	0.032
12	GAINESVILLE BULK	78-79	145	4.75	15.9	0.362	0.109	0.079	0.560	0.110	0.190	1.34	0.467	0.007	0.011
13	GAINESVILLE WET	78-79	145	4.63	14.4	0.243	0.076	0.042	0.254	0.248	0.162	1.76	1.350	0.062	0.072
14	HASTINGS	78-79	122	5.00	17.5	0.740	0.292	0.124	0.339	0.136	0.227	2.36	1.870	0.027	0.037
15	JACKSONVILLE	78-79	122	4.74	22.9	1.000	0.147	0.143	0.670	0.202	0.247	2.43	0.661	0.065	0.079
16	JASPER	78-79	159	4.97	18.5	0.371	0.209	0.094	1.040	0.176	0.195	1.76	0.629	0.031	0.014
17	JAY	78-79	207	4.62	17.7	0.364	0.107	0.051	0.309	0.276	0.217	2.04	1.042	0.031	0.050
18	LAKE ALFRED	78-79	153	4.74	21.1	0.585	0.144	0.139	0.817	0.217	0.140	1.17	0.763	0.029	0.017
19	LAKE PLACID	78-79	135	4.95	11.7	0.441	0.076	0.045	0.252	0.168	0.234	1.87	0.746	0.030	0.049
20	LISBON	78-79	136	4.80	17.2	0.493	0.152	0.052	0.404	0.229	0.204	1.33	1.560	0.022	0.030
21	MARANTHUR FARMS	78-79	108	5.71	17.8	0.803	0.173	0.100	1.010	0.103	0.248	3.54	17.600	0.025	0.039
22	MARTINLAND	78-79	125	5.53	78.2	9.020	0.626	1.050	1.640	0.103	0.248	3.54	17.600	0.025	0.039
035	TKN	H	ORGN	ORGP	INORCN	TOTN	UEQH	EQHDEP	SES04	EXS04	SE3DEP	EX3DEP	SE4DEP	EX4DEP	SE4DEP
1	0.159	0.0000251137	0.079	0.003	0.256	0.375	25.1189	313.984	0.07975	1.50025	0.33289	6.2510	19.750		
2	0.170	0.0000035481	0.087	0.006	0.212	0.299	3.5431	38.320	0.56500	0.88500	2.03400	3.1860	19.680		
3	0.267	0.0000061660	0.158	0.003	0.312	0.470	6.1660	84.474	0.10875	1.03125	0.49662	4.7094	19.618		
4	0.250	0.000199536	0.151	0.007	0.309	0.460	19.9526	311.261	0.12850	1.73150	0.64880	9.1078	19.628		
5	0.316	0.000161770	0.172	0.009	0.296	0.468	18.1970	247.479	0.06500	1.02500	0.58833	6.0067	19.176		
6	0.332	0.000591701	0.160	0.006	0.402	0.562	9.1201	126.770	0.38750	1.17250	1.75533	9.4326	19.684		
7	0.339	0.000918170	0.143	0.003	0.231	0.373	18.1970	252.938	0.05350	1.19750	1.65033	9.5484	21.540		
8	0.430	0.000173750	0.095	0.020	0.592	0.687	17.3780	262.408	0.06950	1.87050	0.31966	9.4143	19.694		
9	0.440	0.000004547	0.193	0.010	0.497	0.690	2.4547	31.420	0.25000	1.57000	0.62799	6.6967	19.680		
10	0.419	0.000697978	0.134	0.011	0.303	0.406	1.6218	26.111	0.12600	1.51350	0.67500	8.8587	19.680		
11	0.324	0.000018213	0.203	0.008	0.398	0.559	17.7028	257.851	0.09050	1.57950	0.43744	6.1830	19.680		
12	0.322	0.0009177528	0.161	0.004	0.300	0.430	23.4423	339.913	0.06075	1.27925	0.29264	6.1830	19.680		
13	0.440	0.0006334423	0.130	0.010	0.410	0.667	10.0000	122.000	0.18500	1.57500	0.75233	9.4326	19.680		
14	0.505	0.000100000	0.257	0.010	0.345	0.675	18.1970	222.004	0.27000	2.09000	1.05800	10.8293	19.680		
15	0.468	0.000161770	0.312	0.014	0.449	0.604	10.7152	148.941	0.09275	2.33725	0.43774	11.3161	19.680		
16	0.367	0.0000197152	0.155	0.014	0.449	0.604	18.1970	222.004	0.09100	1.66900	0.62799	8.3915	19.680		
17	0.266	0.000000533	0.090	0.003	0.371	0.461	23.9883	496.558	0.14650	1.87350	0.64948	8.3915	19.680		
18	0.432	0.000181770	0.156	0.019	0.493	0.641	11.2202	151.472	0.11025	1.05975	0.44612	7.7165	19.680		
19	0.301	0.000117302	0.133	0.008	0.308	0.448	15.8469	215.545	0.12325	1.74675	0.35673	7.7165	19.680		
20	0.414	0.000158189	0.122	0.019	0.326	0.599	1.9498	21.058	0.20075	1.12925	0.72270	4.0653	19.680		
21	0.355	0.0000019498	0.166	0.018	0.453	0.556	2.9512	36.090	0.25500	1.26500	0.39580	5.3542	19.680		
22	0.263	0.0000029512	0.185	0.014	0.351	0.556	2.9512	36.090	0.25500	1.26500	0.39580	5.3542	19.680		
035	NADEP	KDEP	MGDEP	CADEP	NH4DEP	NO3DEP	CLDEP	OPDEP	TPDEP	TKNDEP	INDEP	ORGNDEP	ORGPDEP	INDEP	INDEP
1	3.987	0.9500	0.6125	3.1975	1.1250	2.5750	7.800	0.0500	0.0975	2.1125	4.6875	0.9875	0.0375	3.7000	
2	4.408	0.8500	0.5784	8.5616	0.8924	1.3732	45.144	0.1080	0.1728	1.8360	3.2892	0.5596	0.0648	2.2560	
3	5.059	1.4771	0.6670	7.0007	1.4933	7.8111	12.193	0.0822	0.1333	3.6579	6.4390	0.2164	0.0411	4.2744	
4	5.018	0.8032	0.9572	7.9248	1.7004	12.000	15.194	0.1560	0.2452	4.0560	7.1760	2.3536	0.1092	4.6504	
5	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
6	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
7	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
8	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
9	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
10	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
11	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
12	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
13	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
14	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
15	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
16	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
17	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
18	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
19	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
20	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
21	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	
22	6.624	1.8435	0.5984	4.2976	1.9884	2.0672	18.296	0.1768	0.2992	4.2976	6.3648	2.3392	0.1024	4.6504	

D. Project period (May 1978-April 1979) continued....

CBS	SITE	DATE	RAIN	PH	CON	NA	K	MG	CA	NH4	NO3	SO4	CL	OP	TP
23	MIAMI	7/8-79	112	5.46	19.1	1.260	0.263	0.157	0.952	0.116	0.167	1.58	2.350	0.020	0.008
24	STUART	7/8-79	117	5.16	21.4	2.240	0.276	0.281	0.474	0.141	0.169	1.52	4.150	0.025	0.009
25	TALLAHASSEE	7/8-79	141	4.76	15.0	0.350	0.262	0.057	0.436	0.159	0.194	1.67	0.742	0.013	0.004
26	WALDO BULK	7/8-79	139	4.62	18.1	0.588	0.198	0.077	0.297	0.144	0.202	2.15	0.992	0.014	0.005
27	WALDO THROUGHFALL	7/8-79	105	4.73	29.9	1.570	0.593	0.329	1.340	0.121	0.219	3.18	3.250	0.017	0.006
OBS	TKN	H	ORGN	ORGP	INORGN	TOTN	UEGH	EQHDEP	SES04	EXS04	SESDEP	EXSDEP	SO4DEP		
23	0.387	0.0000334674	0.271	0.018	0.283	0.554	3.4674	38.835	0.3150	1.2650	1.17600	4.72267	17.695		
24	0.322	0.000027103	0.181	0.008	0.310	0.491	6.9103	80.944	0.5600	0.9600	2.18500	3.74400	17.784		
25	0.259	0.0000173700	0.130	0.010	0.353	0.493	17.3780	245.030	0.0875	1.5625	0.41125	7.43775	23.547		
26	0.380	0.000023953	0.236	0.011	0.346	0.582	23.9803	333.438	0.1470	2.0030	0.68110	9.23057	29.855		
27	0.463	0.0000156209	0.342	0.013	0.340	0.602	10.6209	195.519	0.3925	2.7875	1.37375	9.75625	32.390		
OBS	NADEP	KDEP	NO3DEP	CLDEP	NH4DEP	NO3DEP	CLDEP	ORDEP	TPDEP	TKNDEP	TNDEP	CRONCEP	ORGPDEP	INKDEP	
23	14.1120	2.9455	1.7584	10.6524	1.2992	1.8704	26.6560	0.2240	0.4256	4.3344	6.2048	3.0332	0.2016	3.1696	
24	25.2050	3.2292	2.2377	5.5458	1.6497	1.9773	49.0230	0.2574	0.3510	3.7674	5.7447	2.1177	0.0906	3.6270	
25	4.9350	3.6942	0.6037	6.1476	2.2419	2.7354	10.4522	0.1833	0.3243	4.0749	6.6103	1.8330	0.1410	4.9773	
26	8.1732	2.7522	1.0703	4.1203	2.0016	2.8078	15.7888	0.1946	0.3475	5.2820	8.0698	3.2304	0.1529	4.6094	
27	15.4950	5.2255	3.4545	14.0700	1.2705	2.2995	34.1250	0.1785	0.3150	4.8615	7.1610	3.5910	0.1365	3.5700	

# APPENDIX KEY

RAIN	=	Rainfall (cm)
PH	=	-Log [ $a_{H^+}$ ] (unitless)
CON	=	Specific conductance ( $\mu^S/cm$ @25%)
NA	=	Sodium (mg/L)
K	=	Potassium (mg/L)
MG	=	Magnesium (mg/L)
CA	=	Calcium (mg/L)
NH4	=	Ammonium nitrogen (mg/L)
NO3	=	Nitrate nitrogen (mg/L)
SO4	=	Sulfate (mg/L)
CL	=	Chloride (mg/L)
OP	=	Ortho-phosphorus (mg/L)
TP	=	Total phosphorus (mg/L)
TKN	=	Total Kjeldahl nitrogen (mg/L)
H	=	Hydrogen ion (g/L)
ORGN	=	Organic nitrogen (mg/L)
ORGP	=	Organic phosphorus (mg/L)
INORGN	=	Inorganic nitrogen (mg/L)
TOTN	=	Total nitrogen (mg/L)
UEQH	=	Microequivalents hydrogen ion ( $\mu eq/L$ )
EQHDEP	=	Hydrogen deposition (g/ha-yr)
SESO4	=	Sea (Marine-derived) sulfate (mg/L)
EXSO4	=	Excess (non-marine) sulfate (mg/L)
SESDep	=	Sea sulfate-sulfur deposition (kg/ha-yr)
EXSDep	=	Excess sulfate-sulfur deposition (kg/ha-yr)
SO4DEP	=	Sulfate deposition (kg/ha-yr)
NADEP	=	Sodium deposition (kg/ha-yr)
KDEP	=	Potassium deposition (kg/ha-yr)
MGDEP	=	Magnesium deposition (kg/ha-yr)
CADEP	=	Calcium deposition (kg/ha-yr)
NH4DEP	=	Ammonium nitrogen deposition (kg/ha-yr)
NO3DEP	=	Nitrate nitrogen deposition (kg/ha-yr)
CLDEP	=	Chloride deposition (kg/ha-yr)
OPDEP	=	Ortho-phosphorus deposition (kg/ha-yr)
TPDEP	=	Total phosphorus deposition (kg/ha-yr)

TKNDEP = Total kjeldahl nitrogen deposition (kg/ha-yr)  
TNDEP = Total nitrogen deposition (kg/ha-yr)  
ORGNDEP = Organic nitrogen deposition (kg/ha-yr)  
ORGPDEP = Organic phosphorus deposition (kg/ha-yr)  
INNDEP = Inorganic nitrogen deposition (kg/ha-yr)