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Project Summary

Acidity, Nutrients, and Minerals in Atmospheric Precipitation Over Florida: Deposition Patterns, Mechanisms and Ecological Effects

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A monitoring network of 21 bulk and 4 wet/dry collectors located throughout Florida was operated to determine spatial and temporal trends in atmospheric deposition of acidity, nutrients, and minerals. During an intensive study year, May 4, 1978 to April, 1979, nitrogen (N) and phosphorus (P) deposition via bulk precipitation averaged 0.77 and 0.050 g/m^2-yr, respectively. Highest deposition rates occurred in agricultural areas and lowest deposition rates occurred in coastal and forested areas. Nutrient concentrations were higher during summer (convective) rains than in winter (frontal) events. Wet-only input accounted for most of the deposition of inorganic N, but dryfall was more important for organic N and especially for total phosphorus (TP). Inorganic forms accounted for most of the N and P in rainfall. Statewide deposition rates of N and P were below the loading rates associated with eutrophication, but the average N loading from bulk precipitation approached the mesotrophic criterion of Vollenweider, and N and P loadings exceeded mesotrophic loading criteria at a few agricultural sites.

The acidity of Florida rainfall has increased markedly in the past 25 years, and concentrations of nitrate and sulfate have risen correspondingly. Annual average pH values of less than 4.7 occur over the northern two-thirds of the state. Summer rain averaged 0.2-0.3 pH units lower than winter rain, and excess sulfate levels were higher at most sites during summer. Sulfuric acid accounted for about 70% of the observed acidity, and nitric acid accounted for the remainder. 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 eq./ha over interior northern Florida, or about one-third to one-half the deposition rate for H^+ over the northeastern United States.

Levels of pH in some softwater lakes of north Florida have declined by up to 0.5 units over the past 20 years; no changes were observed in similar lakes of south-central Florida. Chlorophyll *a* and TP decreased with pH in a survey of 20 softwater lakes. Aluminum levels increased with decreasing pH, but observed maximum levels (100-150 μg/L) probably are not high enough to cause fish toxicity. The major change in phytoplankton populations was a replacement of blue-green algae by green algae in acidic lakes. Species diversity and abundance also declined with decreasing pH, but the data exhibited much scatter. Some trends were noted in zooplankton and benthic invertebrates

along a pH gradient, but both composition and abundance changes 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.

This Project Summary was developed by EPA's Environmental Research Laboratory, Corvallis, OR, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Although the chemistry of rainfall has been studied for over a century, 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. Much less information is available on levels of "rock-bound" nutrients (e.g., phosphorus) in rainfall. Moreover, information in the literature exhibits a wide variation in concentrations both spatially and temporally in rainfall. Causes for this variability have not been explained.

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. Previous studies on acid rainfall 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 of the United States, the Southeast, for example. Edaphic conditions in that region, especially in Florida, suggest a high susceptibility for deleterious ecological effects; and demographic patterns suggest that the Southeast may experience increasingly acidic precipitation in the future.

Most of the project results 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 dryfall 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 in pristine areas; and transects were established to evaluate north-south and east-west (coastal-inland) gradients in deposition patterns (Figure 1). The network provided valuable information on nutrient and mineral deposition patterns, and yielded the first comprehensive analysis of the acid rainfall problem in the state of Florida.

The second field effort involved a sampling program on 20 softwater lakes in north-central and south-central Florida. Routine limnological measurements and complete chemical and biotic analyses were done on each lake to evaluate the effects of acidification. Phytoplankton, zooplankton and benthic invertebrate communities were analyzed for species diversity and abundance. The results of the project are summarized according to the three major phases of the project: (1) atmospheric deposition of nutrients; (2) the spatial and temporal distribution of rainfall acidity in Florida, and (3) the effects of acidification on chemical and biological conditions in soft-water lakes of Florida.

Atmospheric Loadings of Nutrients

Bulk precipitation is an important source of nitrogen for both terrestrial and aquatic systems. Average annual loadings of total nitrogen (TN) for the 21 bulk sampling sites ranged from 0.3 to 1.3 g/m^2-yr during the two-year study period, with a statewide mean of 0.72 g/m^2-yr (Figure 2). About 70% of the nitrogen was inorganic (ammonium and nitrate) and thus was readily available to plants. Deposition rates were highest in rural agricultural areas (0.88 g/m^2-yr) and lowest along the coast (0.58 g/m^2-yr). In comparison with critical loading rates for lake eutrophication, the annual deposition of TN at all 24 collection sites (Figure 2 was below the values associated with eutrophic conditions (assuming nitrogen was the limiting nutrient). The statewide average deposition rate was about 75% of the "permissible" loading for shallow lakes suggested by Vollenweider (1968),

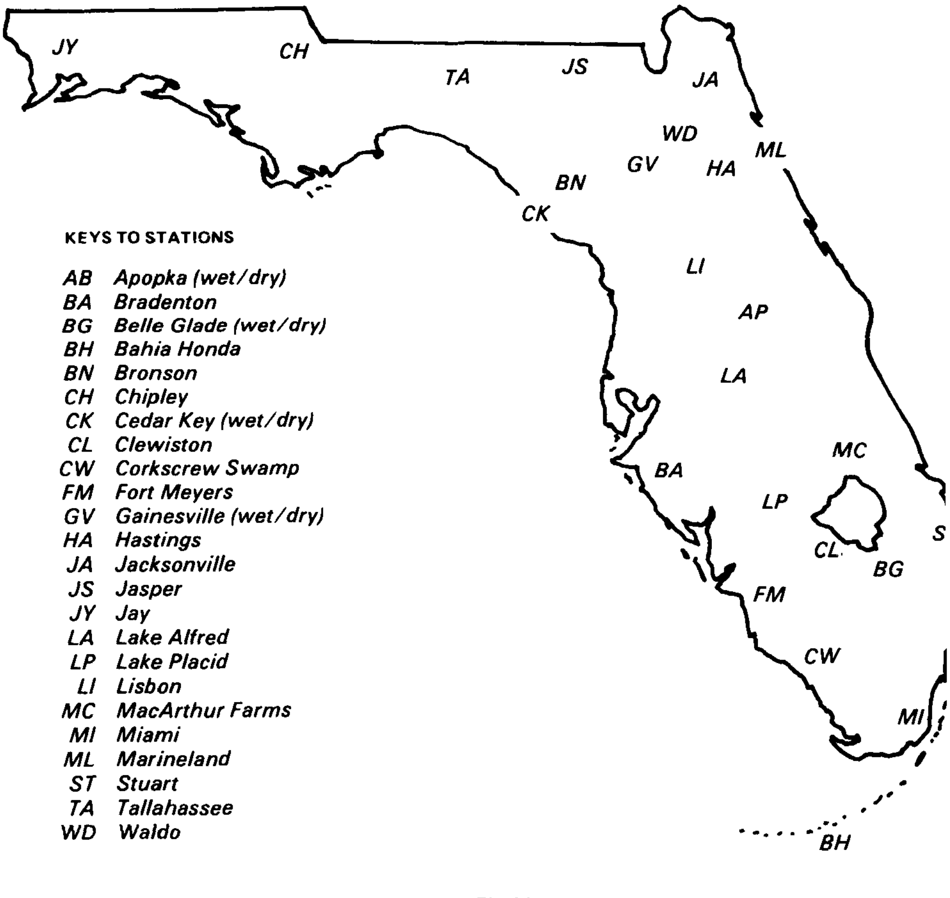

Figure 1. Location of sampling stations in the Florida Atmospheric Deposition Network (FADN).

deposition at several agricultural locations slightly exceeded the permissible criterion but none approached the eutrophic loading criterion.

Bulk precipitation has significant levels of total phosphorus (TP); the statewide two-year average was 33 µg/L, and the mean deposition rate was 48 mg P/m²-yr. Land use had an important effect on atmospheric deposition rates for TP. Rural (non-agricultural) and coastal sites had the lowest rates (27 and 31 mg P/m²-yr, respectively), and agricultural sites had the highest permissible loading rate for the lakes that are most vulnerable to eutrophication, i.e. shallow lakes with long hydraulic residence times. Figure 2 compares annual bulk deposition rates of TP for the rainfall network sites to the phosphorus loading criteria proposed by Vollenweider (1975); according to whom the critical (i.e., eutrophication-causing) loading rate is a function of the areal water loading rate, q_s. For most Florida lakes q_s is in the range of 1-5 m/yr. Based on Vollenweider's loading criteria appropriate to this range of q_s, bulk precipitation in Florida supplies only 12-16% of the loading required to induce eutrophic conditions.

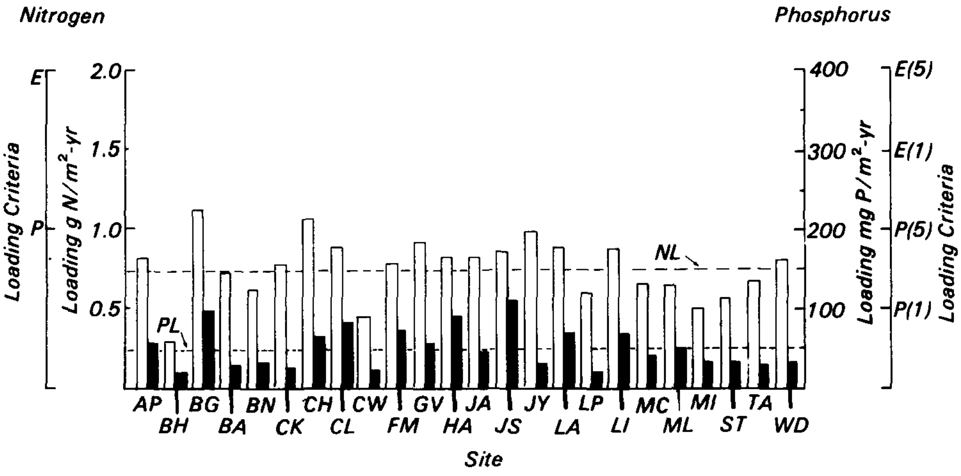

Figure 2. *Loadings of TN (open bars) and TP (closed bars) by bulk precipitation at each FADN site. Statewide average loadings shown by dashed lines. Permissible loading criteria (P) and excessive loading criteria (E; i.e., inducing eutrophy) for TP are for two values of areal water loading (q_s = 1 and 5 m/yr), as given by Vollenweider (1975). Loading criteria for TN are from Vollenweider (1968) for lakes with mean depth < 5 m.*

Average concentrations of TP in summer rainfall were about 1.5 times as high as those in winter rainfall. Whereas most of the atmospheric deposition of inorganic N and TN occurs via rainfall rather than dryfall, the opposite is true for phosphorus. At the four sites with wet-only/dryfall collectors, wet deposition accounted for an average of only 20% of the TP. Thus, most of the phosphorus in bulk precipitation is dryfall, presumably of large wind-blown particles of dust and soil that are not transported large distances.

Average concentrations of total sulfate in rainfall ranged from about 0.2 to 1.2 mg/L (as S); about two-thirds of the total deposition of sulfate was by rainfall. Deposition rates (Figure 3) ranged from 3 to 23 kg S/ha-yr (for all sites over the two-year study), indicating that the atmosphere is a significant source of sulfur to soils in Florida. Except at sites very close (a few km) to the coast, most of the sulfate in Florida rain is excess SO_4^{2-} i.e., sulfate derived from SO_2. Sea salt aerosols contributed only about 0.5 kg/ha-yr of sulfate-S to bulk deposition at inland

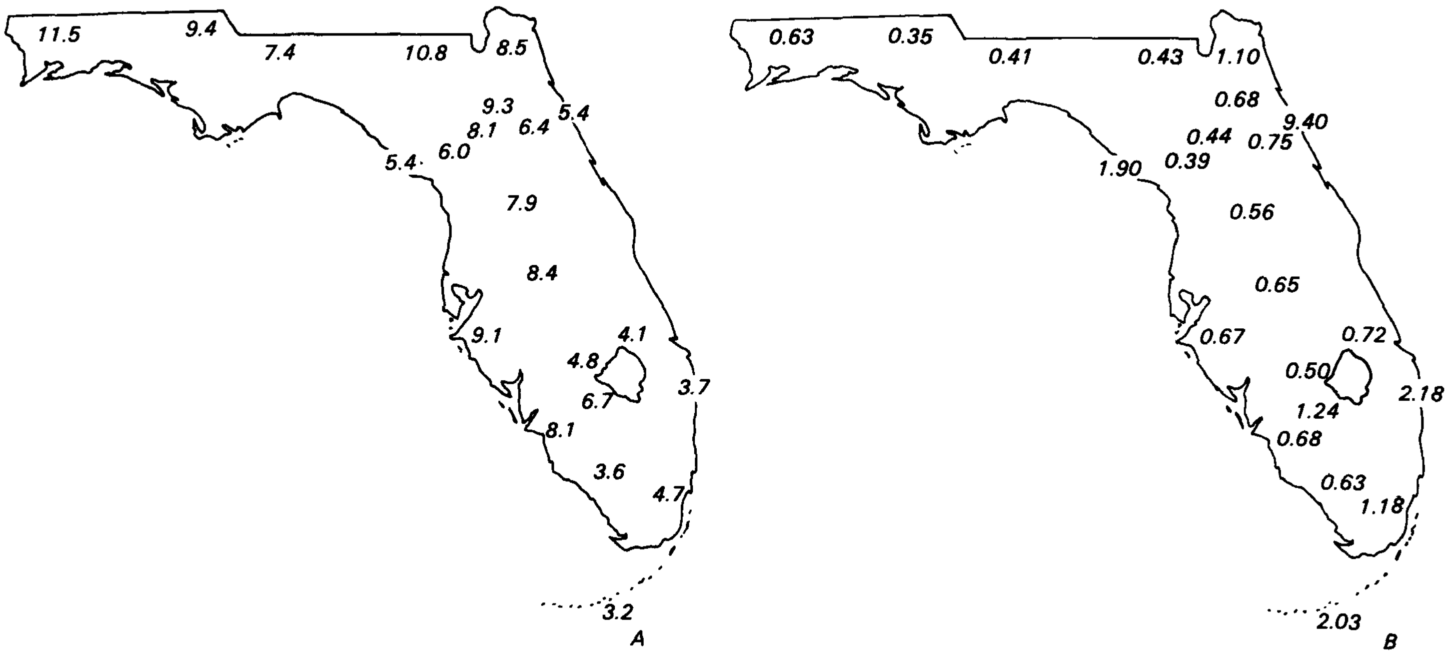

Figure 3. *Annual deposition (kg/ha) of (A) excess sulfate-S and (B) sea-salt sulfate-S across Florida for period May 1978- April 1979.*

sites. Because formation of excess sulfate from SO_2 in the atmosphere concomitantly results in stoichiometric production of hydrogen ion ($SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$), the occurrence of excess sulfate in Florida rainfall also has important implications regarding the acidity of the rain.

Acidity of Precipitation

Rainfall throughout Florida is acidic (Figure 4), with average values for all but a few stations in south Florida being less than geochemical neutrality (pH~5.7). Single events as low as pH 3.9 were 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 1978). A definite geographic pattern exists for acid deposition in bulk precipitation around the state; mean annual pH values (volume-weighted) for 1978-1979 were around 4.6-4.7 throughout the panhandle and the northern two-thirds of the peninsula. Mean annual values south of Lake Okeechobee were around 5.0 or above.

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.

A seasonal pattern was found in precipitation acidity throughout the state with summertime pH averaging 0.2-0.3 units lower than wintertime values. Possible reasons for the difference include (1) increased summertime emissions of SO_2 and NO_x (caused in part by seasonal demands for air conditioning); (2) greater thunderstorm activity in summer, resulting in greater fixation of 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 these factors.

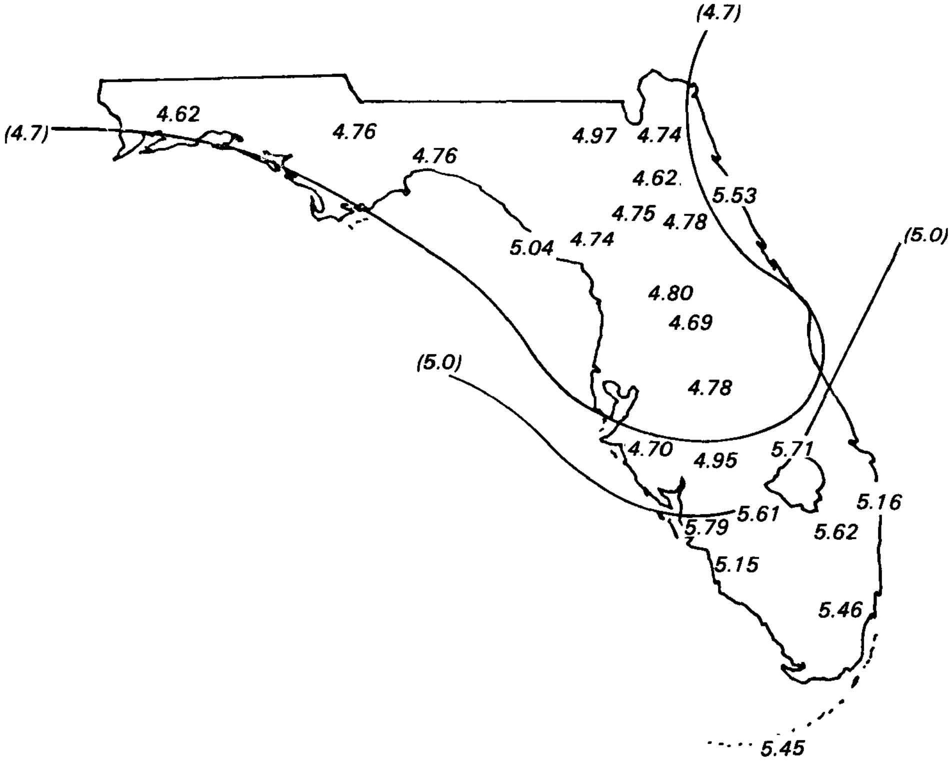

Figure 4. *Volume-weighted mean pH of precipitation throughout Florida, May 1978-April 1979.*

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.

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 with $[H^+]$ as the dependent variable and $[SO_4^{2-}]_{xs}$ and $[Ca^{2+}]_{xs}$ as independent variables explained about 75% of the variance in hydrogen ion concentration over the statewide network: $[H^+] = 6.1 + 0.54[SO_4^{2-}]_{xs} - 0.35[Ca^{2+}]_{xs}$, where 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 neutralized by terrestrial calcium carbonate.

Bulk precipitation throughout northern and central Florida deposited 250-500 equiv H^+/ha-yr during 1978-1979, which is 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 northern Florida and ~13 kg/ha-yr in the northeastern U.S. (the 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. Although historical data are lacking on the pH of Florida rainfall, calculated values for rainfall pH during the mid-1950's indicate wet-only precipitation was not acidic at that time (Table 1). Moreover, present values of sulfate deposition in northern Florida are up to four times higher than values for the early 1950's. Scattered information for the pH of rainfall at Gainesville from 1973 to the present, however, do not show any long-term trends.

Table 1. *Comparison of Parameters Related to the Acidity of Florida Rainfall in 1955-56 and 1978-79*

	Weighted-Mean Concentration ($\mu eq/L$)					
Location	H^+		*Excess-*SO_4^{2-}		NO_3^-	
	1956	*1978-9†*	*1956**	*1978-9†*	*1956**	*1978-9†*
Mobile	<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*
1978-9/1956	*>8.4*		*1.6††*		*4.5††*	

* *Data from Junge and Werby (1958) and Junge (1958); proton concentration inferred via anion/cation balance.*

† *This study; May 1978-April 1979.*

†† *Present data are for bulk precipitation; 1956 data are for rainfall-only. Adjacent wet-only (W) and bulk (B) collectors at Gainesville in this study yielded the following volume-weighted average 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. Differences in collector type thus do not wholly explain the increases in concentrations.*

Effects of Acid Precipitation on Florida Lakes

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 for 13 such lakes in northern Florida and 7 soft-water lakes in south-central Florida, pH has decreased by up to about 0.5 units in some of the northern soft-water lakes, whereas no temporal trends could be discerned for the southern group. Corresponding decreases in alkalinity and increases in sulfate concentration were observed in the northern lakes. 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. The 20 lakes surveyed 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.

A general trend of increasing aluminum with decreasing pH was found in the 20 Florida lakes (Figure 5). However, maximum values (100-150 μg/L) were below the levels associated with fish toxicity; this may explain the occurrence of largemouth bass and several other common game fish species in lakes with pH values below 5.0. Aluminum concentrations are generally low in Florida's sandy soils, but further studies are needed to evaluate the impact of acid precipitation on leaching of aluminum from these soils to Florida's soft-water lakes.

A general trend of increasing chlorophyll *a* concentration with increasing pH was found. However, total phosphate concentration also tended to rise with pH (Figure 6). 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.

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 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. (Figure 7). 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.

Similar trends were found in the zooplankton; i.e., slight decreases in the numbers of species and individuals with pH, but the trends 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. Some of the observed changes in zooplankton community structure may not have been directly related to changes in pH but rather to changes in overall trophic conditions that varied somewhat along the pH gradient. Acidic lakes tended to be less productive, were more nutrient-depauperate, and had low standing crops of phytoplankton. Whether these trends were caused by or merely correlated with pH cannot be determined from the survey data, and further experimental studies are needed to evaluate this matter.

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

Overall, pH appears to have relatively small effects (in the range 4.7-6.8) on community structure in soft-water Florida lakes that otherwise have similar chemical composition. More dramatic effects may occur, of course, under more acidic conditions (pH < 4.7), and significant changes may occur in community metabolism, productivity, and nutrient cycling processes within the pH range of the lakes included in the survey. Further studies on the biological effects of acidification on Florida lakes should be directed at these processes.

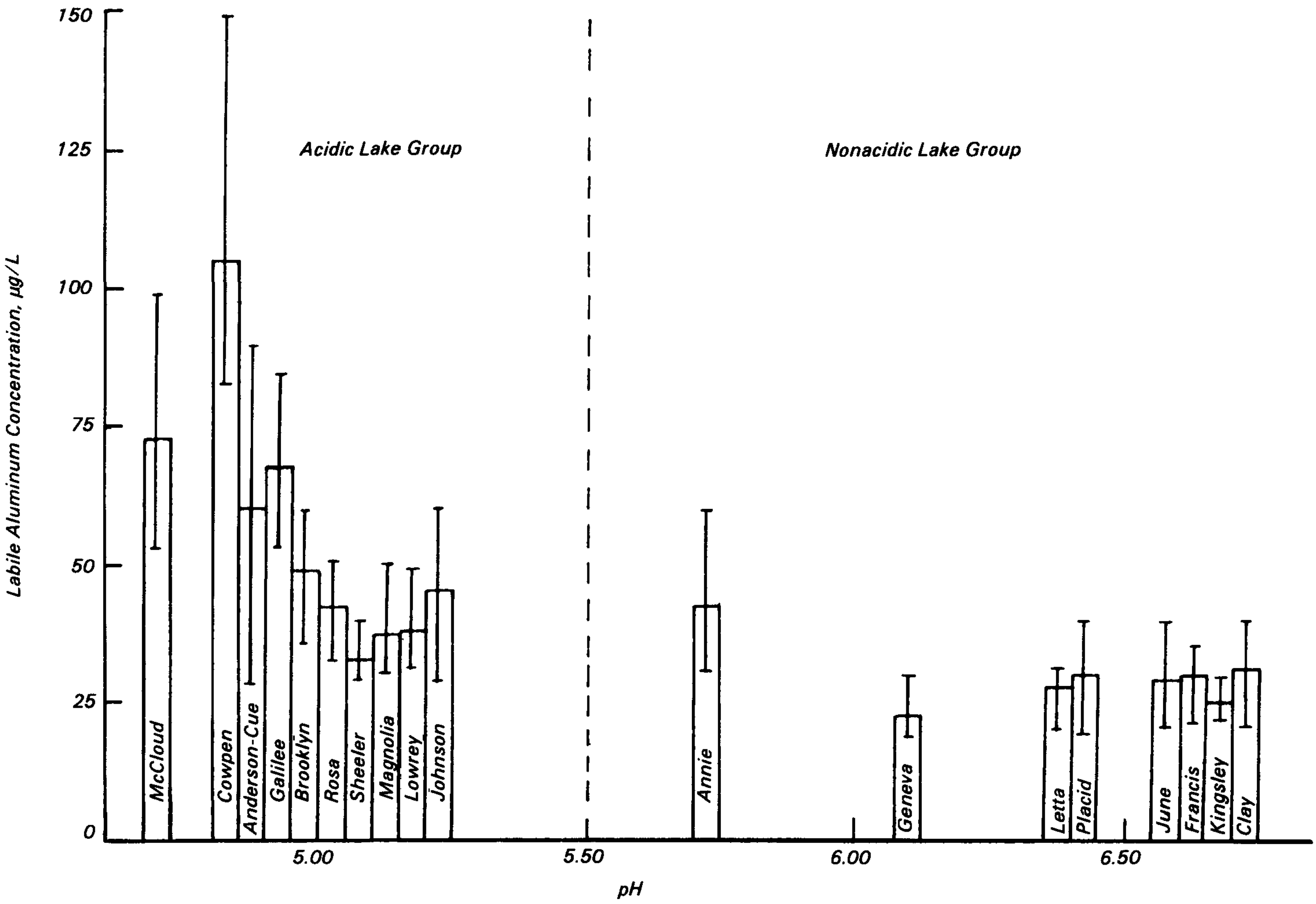

Figure 5. Average and range of labile aluminum in the 20 survey lakes vs. pH.

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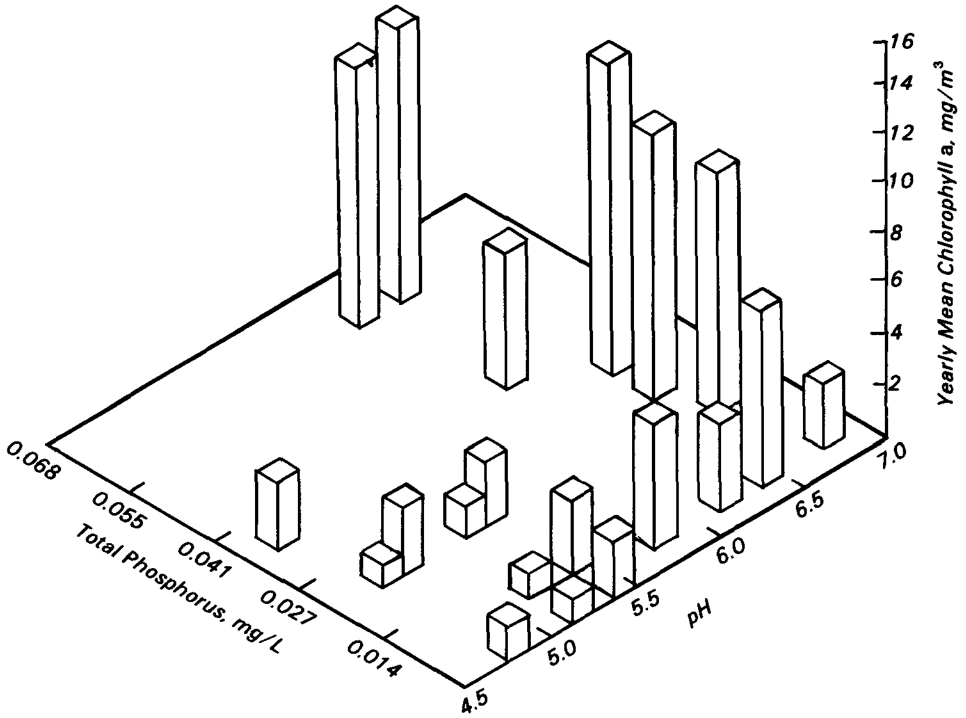

Figure 6. *Three-dimensional plot of chlorophyll* a *as function of pH and TP in the 20 survey lakes.*

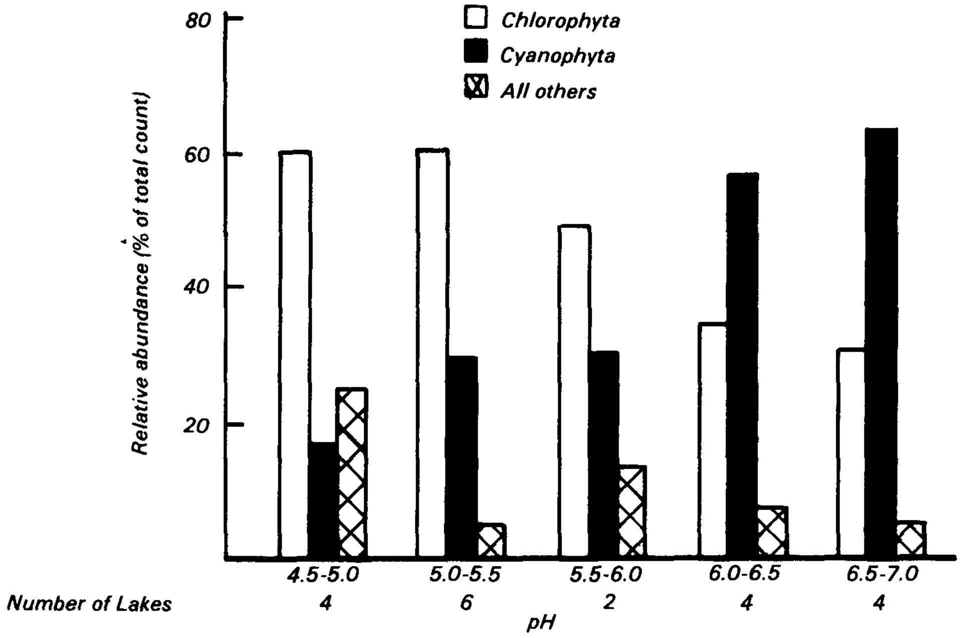

Figure 7. *Relative abundance of major phytoplankton taxa in the lakes grouped within five pH intervals.*

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***Charles F. Powers** is the EPA Project Officer (see below).*

The complete report, entitled "Acidity, Nutrients, and Minerals in Atmospheric Precipitation Over Florida: Deposition Patterns, Mechanisms and Ecological Effects," (Order No. PB 83-165 837; Cost: $16.00, subject to change) will be available only from:

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