Reports

Acid Precipitation and Sulfate Deposition in Florida

Abstract. *The acidity of rainfall in Florida has increased markedly in the past 25 years, and the average sulfate and nitrate concentrations have increased by factors of 1.6 and 4.5, respectively, over the period. Annual average* pH *values below 4.7 now occur over the northern three quarters of the state. Summer rainfall has average* pH *values 0.2 to 0.3 unit lower than winter rainfall, and sulfate concentrations at most sites are higher in summer. The annual deposition of H^+ (about 300 to 500 equivalents per hectare) in northern Florida is a third to a half of the deposition in the heavily impacted northeastern United States; comparable figures for excess sulfate (derived from sulfur dioxide) are 7 to 11 kilograms of sulfur per hectare or 50 to 90 percent of the sulfate deposition rates at Hubbard Brook, New Hampshire.*

Acid precipitation is a well-documented problem in Scandinavia (*1, 2*) and the northeastern United States (*3, 4*), and its progression southward and westward in recent years has been demonstrated (*5*). However, data are sparse on the geographical and seasonal variations in rainfall acidity outside of the northeastern United States. We present here results for Florida, based on a statewide precipitation sampling network. Rainfall has been collected biweekly or more frequently at 24 sites since the fall of 1977, and the samples have been analyzed for *p*H, conductivity, major ions, and other chemical parameters (*6*). Sites range across the panhandle and down the peninsula to the lower Keys and include several transects across the state (Fig. 1A). Bulk precipitation samplers (*7*) were used at 20 sites, and wet-dry collectors were used to obtain more detailed information at four sites. Rain was sampled on an event basis in Gainesville.

Results for the first year during which the entire network was sampled (May 1978 to April 1979) are described here. Acid precipitation occurs widely over northern and central Florida (Fig. 1A). The lowest (volume-weighted) average *p*H (4.60) during 1978–1979 occurred at Lake Apopka, 20 km northwest of Orlando; the highest value (5.80), slightly above geochemical neutrality, occurred at Fort Myers. The lowest *p*H observed in a bulk precipitation sample was 3.76 (at Jay, 21 to 31 August 1978), and the two most acidic rain events in Gainesville had a *p*H of 3.93 (15 September 1978 and 7 February 1979).

The *p*H isopleths (Fig. 1A) suggest that neutralization of bulk precipitation occurs along the Atlantic and Gulf coasts, apparently by reaction with marine-derived bases. However, recent data obtained with a wet-dry collector located about 100 m from the Gulf coast at Cedar Key (100 km southwest of Gainesville) indicates that rainfall itself is as acidic there as it is inland at Gainesville. Thus dry fall apparently accounts for the neutralization of rain in the bulk collec-

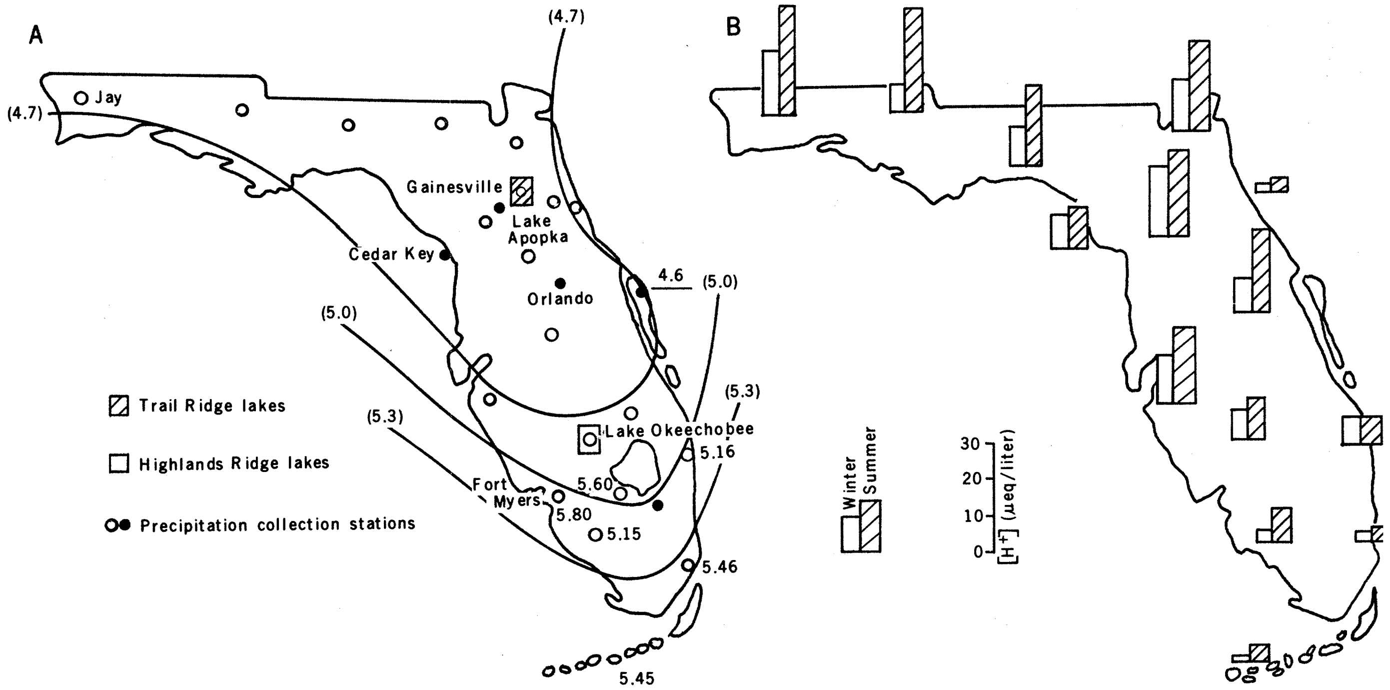

Fig. 1. (A) Isopleths for the *p*H of rainfall in Florida over the year May 1978 to April 1979; (open circles) bulk precipitation sampling sites; (closed circles) wet-dry precipitation sampling sites. Values next to selected sites represent volume-weighted annual *p*H. High *p*H values at Fort Myers (5.90) and Clewiston (east of Fort Myers) (5.60) are believed to reflect local effects rather than regional characteristics (*6*). The Cape Canaveral site is not in our network; the underlined value is from (*14*). Blocked areas show lake regions surveyed for the effects of acid rainfall on chemical and biological conditions (*6*). (B) Volume-weighted [H^+] in winter (November through April) and summer (May through October) rainfall. For clarity, results are not shown for some sites located close to other sites. The winter-summer legend shows statewide mean values (over all 24 sites) for the two seasons.

0036-8075/80/0530-1027$00.50/0

Table 1. Comparison of parameters related to the acidity of Florida rainfall in 1955-1956 (*9*) and 1978-1979.

Location	Weighted mean concentration (μeq/liter)					
	H^+		Excess SO_4^{2-}		NO_3^-	
	1956	1979*	1956	1979	1956	1979
Pensacola-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
West Palm Beach-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		4.5	

*The data for 1979 are for bulk precipitation (rainfall collectors open at all times), whereas the 1956 data are for rainfall only (collectors open to the atmosphere only during rain events). Adjacent wet-only (W) and bulk (B) collectors at Gainesville have yielded the following volume-weighted concentrations (in microequivalents per liter): excess SO_4^{2-}, 35.1 (B) and 26.6 (W), B/W = 1.3; NO_3^-, 16.9 (B) and 13.6 (W), B/W = 1.24. Thus differences in collector type do not wholly explain the increases in concentrations. †Proton concentration inferred from the anion-cation balance.

tors at coastal sites. Although all but four of the 24 sampling sites had *p*H values less than 5.0 in individual samples, the isopleths indicate that rainfall in south Florida (south of Lake Okeechobee) is only slightly below geochemical neutrality on an annual basis.

The volume-weighted mean *p*H of summer rain (May through October) is 0.2 to 0.3 unit lower at most sites than that of winter rain (November through April). Over the entire state the mean winter [H^+] was 9.0 μeq/liter (*p*H 5.05), whereas the summer mean was 14.9 μeq/liter (*p*H 4.85) (Fig. 1B). This trend may reflect seasonally higher rates of power generation in Florida during summer. Alternatively, the lower *p*H in summer may reflect differences in the efficiency of scavenging by convective showers (which occur in summer) compared to frontal events (which occur in winter). Because 65 percent of the annual rainfall occurs during the summer months, the seasonal differences in the deposition of H^+ are even more pronounced than the concentration differences.

Ionic balances indicate that H_2SO_4 and HNO_3 account for nearly all the acidity of Florida rainfall, with H_2SO_4 2.0 to 2.5 times as important as HNO_3. The statewide distribution of NO_3^- is relatively isotropic (*8*) and exhibits only small seasonal differentials. These trends suggest that HNO_3 contributes a diffuse background of H^+ to precipitation, but it probably does not account for the seasonal or geographic trends.

Sulfate, on the other hand, followed similar spatial and temporal trends (Fig. 2A), as H^+ did in 1978-1979. The major exceptions to the high summer-low winter pattern occurred at coastal sites, where rough winter surf resulted in high concentrations of sea-salt sulfur. In general, sea-salt [SO_4^{2-}] was higher in winter rain than in summer rain throughout the peninsula. Deposition of excess sulfur (that is, total sulfur minus sea-salt sulfur) averaged 7.9 kg/ha^{-1} year^{-1} for the northern sites (N = 14) in 1978-1979, as compared to 5.1 kg ha^{-1} year^{-1} for the southern sites (N = 10). These differences are significant at the 0.01 level according to the *t*-test. Excess sulfur (derived from SO_2) easily is the most important sulfur component at all but the most maritime sites; deposition of sea-salt sulfur was surprisingly low except at sites located within 1 km of the ocean.

Correlation of H^+ with excess SO_4^{2-} for data from 52 rain events sampled at Gainesville yielded a high r^2 (.79), where r is the correlation coefficient, but a similar correlation on the volume-weighted annual average values from the more heterogeneous statewide network yield-

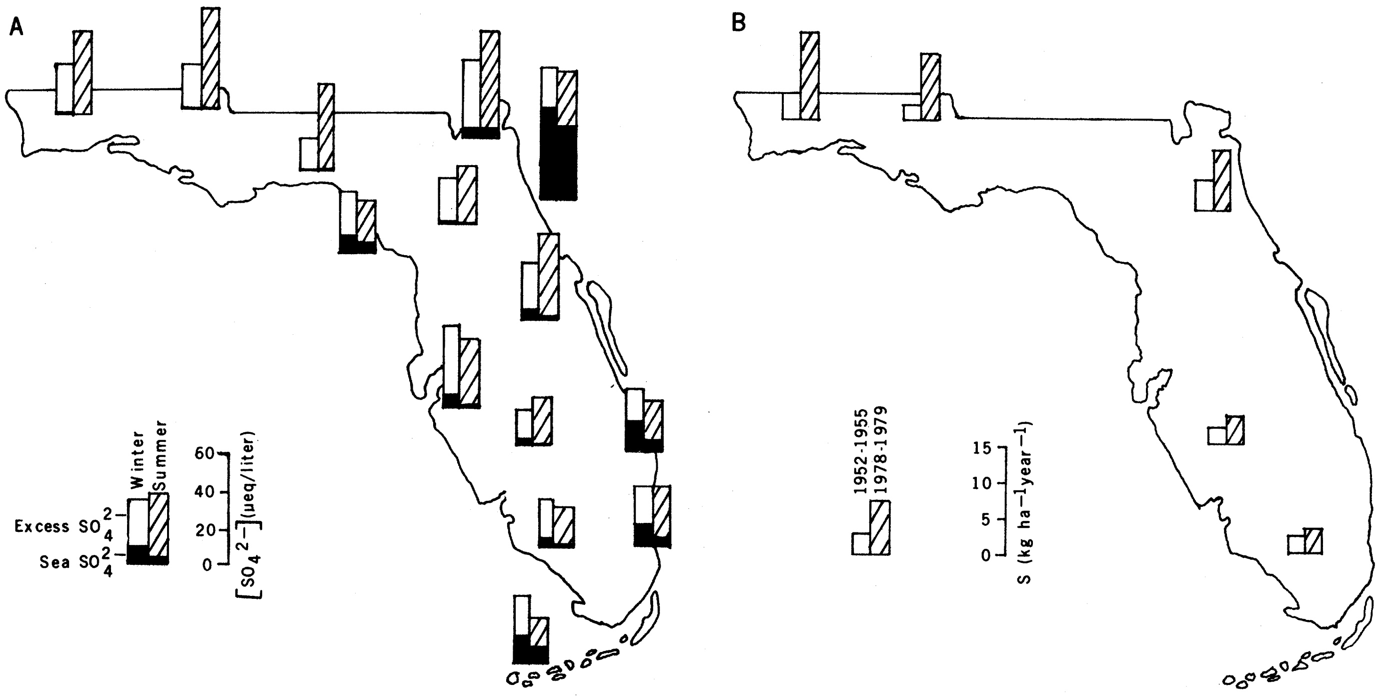

Fig. 2. (A) Volume-weighted [SO_4^{2-}] sulfur in winter (November through April) and summer (May through October) rainfall; solid bars, sea-salt sulfur; open bars, excess SO_4^{2-} sulfur. Some sites are not shown for clarity. The SO_4^{2-} legend shows grand means for the two seasons over all 24 sites. (B) Annual deposition of total sulfur (in kilograms per hectare) in bulk precipitation at five sites sampled from 1952 to 1955 (*10*) and at five sites from the present study that are close to the earlier sites. The legend for the two time periods shows the mean deposition rates over the five sites for each time period.

ed a much lower r^2 (.25). Multiple regressions of H^+ versus excess SO_4^{2-} and other parameters taken one at a time (for example, NO_3^- or NH_4^+) did not improve the correlation, but regression of H^+ versus excess SO_4^{2-} and Ca^{2+} yielded the equation

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

$R^2 = .75$, where the subscript xs stands for nonmarine-derived material. This two-variable model thus implies that the acidity of Florida rainfall can be accounted for in large part in terms of the interaction between H_2SO_4 and terrestrially derived basic calcium salts.

Historical pH data are lacking for Florida rainfall. However, pH values calculated by the ionic balance method (*2*) from Junge's data (*9*) for five locations in Florida indicate that rainfall at these sites had pH values above 5.6 in the mid-1950's (Table 1). Large increases have occurred in the concentrations of excess SO_4^{2-} and especially of NO_3^- in Florida rainfall since the mid-1950's. The average increase in the sum of these two ions over the state (23.5 μeq/liter) is more than adequate to account for the average increase in H^+ (14.8 to 17.3 μeq/liter). Moreover, present deposition values for SO_4^{2-} are up to four times higher (Fig. 2B) than values obtained at several sites in the early 1950's (*10*). The largest increases in the deposition of SO_4^{2-} have occurred in the northern part of the state. If fluxes of sea sulfur and biogenic sulfur have remained constant, the differences represent a substantial increase in anthropogenic excess SO_4^{2-}.

Although the degree of acidity in Florida rainfall is not as great as that presently occurring in the northeastern United States, our findings are of serious concern for several reasons. Because Florida receives 50 to 75 percent more rainfall annually than most of the Northeast, the differences in the annual deposition of H^+ and SO_4^{2-} are smaller than the pH-concentration data suggest. For example, 206 cm of rainfall resulted in the deposition of 500 eq of H^+ per hectare and 11.5 kg of sulfur per hectare at Jay in the period May 1978 to April 1979; analogous values for the same period at Lake Apopka are 136 cm of rain, 342 eq of H^+ per hectare, and 6.8 kg of sulfur per hectare. In comparison, precipitation at Hubbard Brook, New Hampshire, deposited an average of 970 eq of H^+ per hectare (*4*) and 12.7 kg of sulfur per hectare (*11*) over the 10-year period 1964-1965 to 1973-1974. Thus northern Florida receives about one third to one half the H^+ deposition and 50 to 90 percent of the excess SO_4^{2-} deposition of the heavily impacted Northeast.

Florida's highly weathered, sandy soils characteristically have low cation-exchange capacities (*12*). Thus soils in Florida are unable to provide much buffering capacity. Numerous soft-water lakes occur in the sandhill region of north and central Florida, and these lakes obtain most of their water directly from rainfall and from subsurface seepage through the sandy soils. Annual average pH values in a group of 12 such lakes (Trail Ridge lakes) located about 40 km east of Gainesville (Fig. 1A) are now 0.3 to 0.9 unit lower than the average pH values measured in the late 1950's and late 1960's (*6*). For example, Lake Brooklyn (Clay County) had a pH of 5.5 ($N = 6$) during 1957-1960, a pH of 5.0 ($N = 6$) during 1967-1972, and a pH of 4.9 ($N = 7$) during 1977-1979. In comparison, no significant long-term trends in pH have been observed in a group of eight soft-water lakes in Highlands County, south central Florida (Fig. 1A), in an area near the present southern limit of acid precipitation.

Because Florida's population still is expanding rapidly, the demands for electric power are increasing more rapidly in Florida than in most other states. Like most of the rest of the United States, Florida is shifting to coal as the energy source for new electric power-generating capacity. At present, six coal-fired plants [total capacity, 2086 MW (electric)] are operating in peninsular Florida, but 15 additional plants with a generating capacity of 6884 MW (electric) are planned for this region by 1987 (*13*). The effects of the added emissions on the acidity of Florida rainfall, and the consequent effects on Florida's vulnerable aquatic and terrestrial ecosystems, should be carefully examined in the coming years.

PATRICK L. BREZONIK
ERIC S. EDGERTON
CHARLES D. HENDRY

Department of Environmental Engineering Sciences, University of Florida, Gainesville 32611

References and Notes

1. F. H. Braekke, Ed., *Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway* (SNSF Project, 1432 Aas, Norwegian Forest Research Institute, Agricultural University of Norway, Norway, 1976).
2. L. Granat, *Tellus* **24**, 550 (1972).
3. C. V. Cogbill and G. E. Likens, *Water Resour. Res.* **10**, 1133 (1974); L. S. Dochinger and T. A. Seliga, Eds., *Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem* (Department of Agriculture, Washington, D.C., 1976).
4. G. E. Likens, *Chem. Eng. News* **54** (No. 48), 29 (1976).
5. ——, R. F. Wright, J. N. Galloway, T. J. Butler, *Sci. Am.* **241** (No. 4), 43 (1979).
6. P. L. Brezonik, C. D. Hendry, E. S. Edgerton, R. Schulze, T. L. Crisman, in preparation.
7. G. E. Likens, "The chemistry of precipitation in the central Finger Lakes region" (Technical Report 50, Water Resources and Marine Sciences Center, Cornell University, Ithaca, N.Y., 1972).
8. C. D. Hendry, E. S. Edgerton, P. L. Brezonik, paper presented at the 178th annual meeting of the American Chemical Society, Washington, D.C., September 1979.
9. C. E. Junge, *Trans. Am. Geophys. Union* **39**, 241 (1958); —— and R. T. Werby, *J. Meteorol.* **15**, 417 (1958).
10. H. V. Jordan, C. E. Bardsley, Jr., L. E. Ensminger, J. A. Lutz, "Sulfur content of rainwater and atmosphere in southern states" (Technical Bulletin 1196, Department of Agriculture, Washington, D.C., 1959).
11. G. E. Likens, F. H. Bormann, R. S. Pierce, J. S. Eaton, N. M. Johnson, *Biogeochemistry of a Forested Ecosystem* (Springer-Verlag, New York, 1977), p. 101.
12. Many agricultural and forest soils in Florida have cation-exchange capacities of 2 to 3 meq per 100 g; soils from New York and Pennsylvania generally have cation-exchange capacities of at least 18 to 20 meq per 100 g (B. Volk, personal communication).
13. W. E. Bolch and M. J. Ohanian, personal communication; Southeast Electric Reliability Council Report, Birmingham, Ala., 1 April 1978.
14. B. Madsen, personal communication.
15. We thank all those who have assisted us in maintaining precipitation collectors at distant sites. This work was supported by grant R805560 from the Environmental Protection Agency.

4 December 1979; revised 19 February 1980

Nickel Carbonyl: Decomposition in Air and Related Kinetic Studies

Abstract. *Nickel carbonyl [Ni(CO)$_4$] is a toxic gas used in the manufacture of metallic nickel which has been shown to be carcinogenic and teratogenic in laboratory studies. Its decomposition in air proceeds at a rate that is strongly dependent on the concentration of carbon monoxide (CO). In the absence of CO, the lifetime in air at 296°K and at atmospheric pressure is 60 ± 5 seconds. A mechanism consisting of equilibrium unimolecular decomposition to Ni(CO)$_3$ and CO, followed by reaction of the Ni(CO)$_3$ with molecular oxygen, is consistent with the observations.*

Nickel carbonyl [$Ni(CO)_4$] is used industrially in the Mond process for the manufacture of nickel, in nickel plating, and as an industrial catalyst (*1*). Although highly toxic, its effects on man remain somewhat controversial (*1-3*).

A knowledge of reactions of gaseous $Ni(CO)_4$ with other species that may be

0036-8075/80/0530-1029$00.50/0