

EFFECTS OF ACID PRECIPITATION ON NUTRIENT CYCLING IN TERRESTRIAL  
ECOSYSTEMS OF SOUTHERN APPALACHIAN AND PIEDMONT WATERSHEDS  
(Task Force Project T-20)

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IMPORTANCE

At the Coweeta Hydrologic Laboratory, a 1,600-ha experimental forest maintained by the Forest Service in the Blue Ridge Mountains of North Carolina, the effects of man's use of the forest on the quality and quantity of streamflow has been under study for 50 years. Because future productivity of the terrestrial and aquatic ecosystems are dependent on management practices applied to the landscape, detailed studies of mineral cycling on selected undisturbed and managed watersheds was begun 15 years ago. Atmospheric deposition is a major source of nutrients for forests, but chemical composition of precipitation, particularly its high acid content, can adversely impact terrestrial and aquatic ecosystems. Therefore, a network was established to quantify and monitor long term atmospheric input to the basin. Studies were begun to quantify the nutrient budgets for selected watersheds, to describe the cycling of nutrients through the system, and to determine changes in cycle produced by management, natural disturbances, or changes in atmospheric input. In perspective, acid deposition is one component of a larger research effort to define the nutrient budget of forested ecosystems in order to properly manage them. Description of recent acid precipitation research follows.

HYPOTHESES

- (1) How does atmospheric deposition vary between locations within the basin, between months, and between years? Is there a time trend?
- (2) How is precipitation chemistry altered as it passes through the canopy, litter, and into soil?
- (3) What is the fate of anions and cations in the soil system?

## TECHNICAL APPROACH

Rainfall input is measured at 12 sites within the Coweeta basin. At eight of these, samplers are installed to collect weekly bulk precipitation samples for chemical analysis. Samples are analyzed for pH, NO<sub>3</sub>-N, NH<sub>4</sub>-N, PO<sub>4</sub>-P, Cl, SiO<sub>2</sub>, SO<sub>4</sub>, Ca, Mg, K, and Na as described by Swank and Douglass (1977). These same parameters are also measured on weekly grab samples from each gaged watershed in the basin. Annual budgets are calculated by multiplying concentrations by volumes and subtracting output from input. Analysis of variance and regression techniques were applied to determine whether input varied between locations, months, or years and whether any time trend in H<sup>+</sup> concentration was apparent for the 10 years of record.

Changes in bulk precipitation chemistry as water moved through canopy, litter, and soil were examined for a mixed hardwood forest at Coweeta and a pitch pine (*Pinus rigida* Mill.) stand 13 km away in Franklin, North Carolina. The number of throughfall and lysimeter collectors varied between stands. Instrumentation and methods used in the two stands are described by Best and Monk (1976) and Swank and Swank (in press) and chemical analytical methods are described by Swank and Douglass (1977). Differences in mean concentrations of nutrients passing through successive compartments were determined by t-test.

Input-output SO<sub>4</sub> budgets of undisturbed watersheds in the Coweeta basin show large accumulations of elemental S varying from 5.9 to 8.9 kg ha<sup>-1</sup> year<sup>-1</sup> (Swank and Douglass, 1977). Soil samples collected from the A<sub>1</sub>, B<sub>1</sub>, and C horizons were analyzed and found to have large adsorption capacity of S (Johnson, et al., 1980). Because of high input of SO<sub>4</sub> and a finite adsorptive capacity of soils, soil samples from four watersheds were collected to study the transformation of S within the soil system. Carrier-free Na<sub>2</sub> <sup>35</sup>SO<sub>4</sub> was added to samples which were incubated and extracted to yield soluble, adsorbed, and non-salt extractable (organic) forms of S (Fitzgerald, et al., in press).

## RESULTS

Precipitation Acidity

Mean annual H<sup>+</sup> concentration of bulk precipitation at the eight locations within the Coweeta basin did not differ significantly (Table 1) with elevation or with any identifiable topographic or geomorphic characteristic. The mean annual concentration was 31.99 μ eq l<sup>-1</sup> with a standard deviation of 2.2 μ eq l<sup>-1</sup>. Expressed as pH, the range in mean annual concentration was from 4.46 to 4.54, or 0.08 pH units.

Table 1. Mean annual  $H^+$  concentration of bulk precipitation (1973-1982).

<u>Gage</u>	<u>Concentration</u> <u>(<math>\mu</math> eq <math>l^{-1}</math>)</u>	<u>pH</u>
5	32.7	4.49
6	35.0	4.46
13	34.3	4.46
20	30.8	4.51
31	30.1	4.52
41	31.1	4.51
55	28.6	4.54
96	33.3	4.48
$\bar{X} \pm S$	31.99 $\pm$ 2.20	

The average weighted monthly  $H^+$  concentration of bulk precipitation for the 10-year period differed significantly between months (Figure 1). Lowest concentrations occurred in fall and winter except for February, which, along with May through September, had highest concentrations of  $H^+$ . The observed pH extreme values for weekly samples were 6.30 and 3.35. Less than 4 percent of the months during the 10-year period had mean bulk precipitation more acid than pH 4.0.

Acidity of bulk precipitation differed significantly between years with 1977 being the year of least acidity and 1978 the year of greatest acidity, both years being drier than normal (Figure 2).

With a 10-year record of pH replicated at eight locations within a relatively small geographic area, we can say that there is no evident time trend toward either increasing or decreasing acidity of rainfall. It is obvious from Figure 2 that a much larger period will be required before any conclusive time trends for acidity of bulk precipitation can be established.

#### Acidity Changes in Hydrologic Compartments

As precipitation passes through the forest canopy,  $H^+$  ion concentration changes (Table 2). Hydrogen<sup>+</sup> concentration varied because measurements were made at different times and locations. In the pitch pine stand, throughfall was significantly less acid than rain, water leaching through the litter was significantly less acid than throughfall, but soil water was significantly more acid at 25 cm depth than water passing through the litter. A similar pattern of changes were observed as water passed through these compartments of the hardwood stand, except that the progressive neutralization of acidity of rain continued from canopy into the soil. Changes in  $NO_3-N$  in water passing through successive layers of the pitch pine and hardwood forest were similar to those of  $H^+$  concentration. However,  $SO_4$  concentration tended to increase as water passed through canopy and litter but were variable in soil depending on forest type. For detailed discussion of ion dynamics, see Swank and Swank (in press).

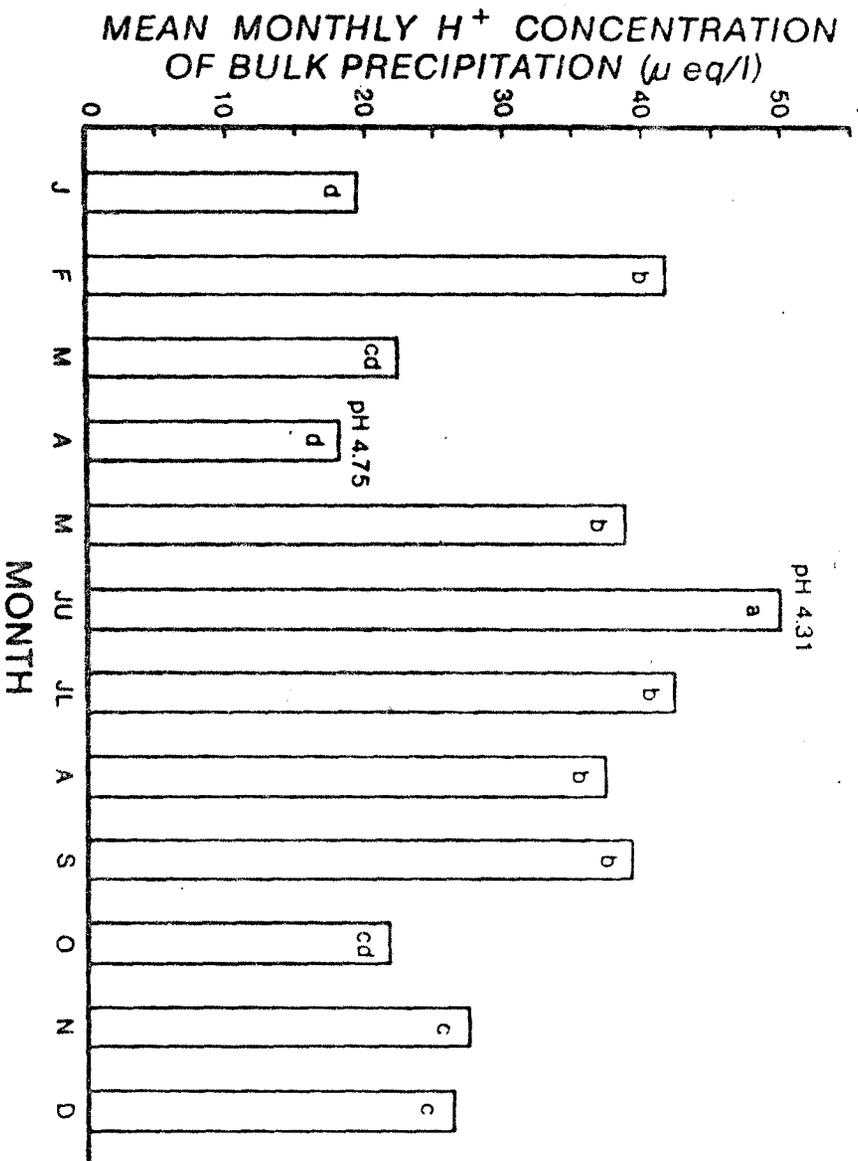


Figure 1. Average weighted monthly  $H^+$  concentration of bulk precipitation, 1973-1982. Months with the same letter are not significantly different.

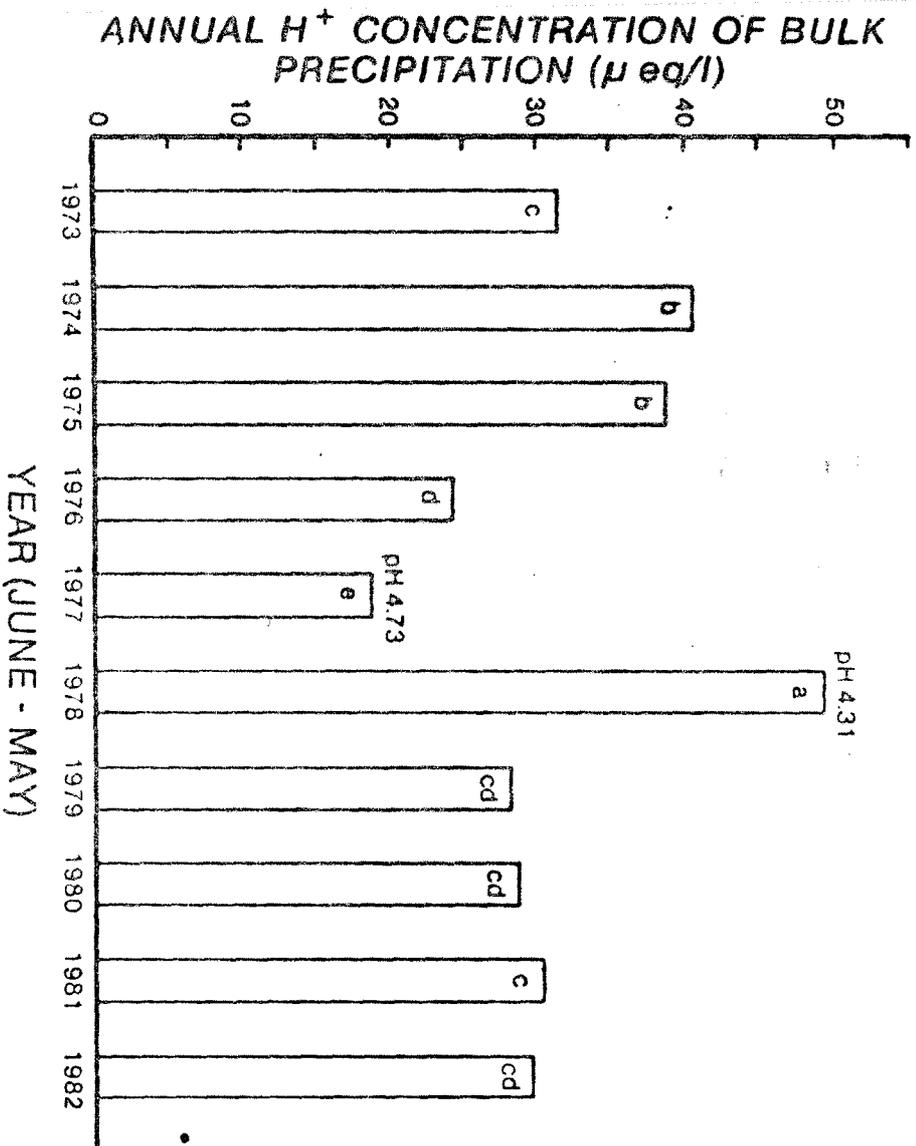


Figure 2. Average weighted annual H<sup>+</sup> concentration of precipitation, 1973-1982. Years with the same letter are not significantly different.

Table 2. Comparison of mean annual  $H^+$  ion concentration and pH in hydrologic compartments of mixed hardwood and pitch pine forests (t-test between successive compartments, \*p < 0.05; \*\*p < 0.01).

<u>Compartment</u>	<u><math>H^+</math> Concentration (<math>\mu</math> eq <math>l^{-1}</math>)</u>	<u>pH</u>
A. Pitch Pine		
Precipitation	98.2	4.01
Throughfall	52.9*	4.28
Litter water	5.6**	5.26
Soil water (25 cm)	17.4**	4.76
B. Mixed Hardwoods		
Precipitation	17.1	4.77
Throughfall	5.1*	5.30
Litter water	4.6	5.34
Soil water (25 cm)	1.0*	6.01

#### Metabolic Fate of Inorganic S

Soils studied were from an old-growth hardwood, two recently clearcut hardwoods, and a 26-year-old white pine forest. All soils were found to rapidly incorporate  $^{35}SO_4$  into non-salt extractable S. A substantial portion of the added  $^{35}SO_4$  was adsorbed by these soils but was completely released by the analytical procedure used (Fitzgerald, et al., in press). Although some differences existed between soils, 10 to 20 percent of the labeled inorganic  $SO_4$  added to the soils was transformed into non-salt extractable ester and carbon-bonded forms of S. Results support other evidence (Johnson, et al., 1980) that S accumulation is related to  $SO_4$  adsorption and that conversion of S into non-salt extractable organic forms may also play an important role in  $SO_4$  accumulation in these soils.

#### DISCUSSION

These results indicate a clear need for continued long term monitoring of atmospheric deposition to detect changing patterns of acidity, if any, and to provide basic data on nutrient cycling studies. Analyses of all nutrient input data and correlation of input and export concentrations and amounts are incomplete at this time. Reasons for the large changes in  $H^+$  concentrations as precipitation passes through various compartments and ultimately drops to nearly neutral levels in streamflow requires additional study, as does the linkage between  $H^+$  and the nitrate and sulfate dynamics in the soil system.

## CONCLUSIONS

1. Ten years of weekly measurements of  $H^+$  in bulk precipitation at eight locations in the Coweeta basin indicate:
  - a. No significant difference between locations,
  - b. Significant differences in  $H^+$  concentration between months,
  - c. No apparent trend toward increasing or decreasing acidity.
2. Hydrogen<sup>+</sup> concentration of precipitation decreases as it passes through the canopy and litter of pitch pine and mixed hardwood forests. Hydrogen<sup>+</sup> concentration in soil beneath the litter continues to decline beneath hardwoods but increases somewhat beneath pitch pine.
3. The large sulfate accumulations in Coweeta soils are due to both adsorption and conversion into organic forms with adsorption apparently most important.

## REFERENCES

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#### DELIVERABLES

- (1) Data set of bulk precipitation and streamflow chemistry for the Coweeta basin from 1972 to present.
- (2) See Swank and Swank, in press, and Fitzgerald, et al., in press. Both should appear in print in 1983.

#### RELATIONSHIP TO OTHER WORK

This work is part of the Forest Service effort at the Coweeta Hydrologic Laboratory; another part is contained in the Aquatic Task Force Reports. In addition, research at the Coweeta Hydrologic Laboratory bearing on the acid rain questions is sponsored by National Science Foundation under the Long-Term Ecological Research (LTER) program. Work on the fate of sulfate on Coweeta watersheds by J. W. Fitzgerald and supported by a National Science Foundation grant is related, as is the study of acid rain effects on whole tree harvesting (see D. W. Johnson, this meeting) supported by Department of Energy and Environmental Protection Agency. In addition, cooperative testing by Electric Power Research Institute of the ILWAS model on a watershed is underway at Coweeta.

#### ACTIVITIES

See Fitzgerald, et al. (in press) and Swank and Swank (in press). The latter was presented at the Symposium on Catchment Experiments in Fluvial Geomorphology in Exeter, England.

#### SUPPORT

Forest Service, \$45,000, continuing; Environmental Protection Agency, \$15,000, 1982.

#### PERSONNEL

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