HYDROGEN ION INPUT TO THE HUBBARD BROOK EXPERIMENTAL FOREST, NEW HAMPSHIRE, DURING THE LAST DECADE[1]

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ABSTRACT

Being downwind of eastern and midwestern industrial centers, the Hubbard Brook Experimental Forest offers a prime location to monitor long-term trends in atmospheric chemistry. Continuous measurements of precipitation chemistry during the last 10 years provide a measure of recent changes in precipitation inputs of hydrogen ion. The weighted average pH of precipitation during 1964-65 to 1973-74 was 4.14, with a minimum annual value of 4.03 in 1970-71 and a maximum annual value of 4.21 in 1973-74. The sum of all cations except hydrogen ion decreased from 51 μeq/ℓ in 1964-65 to 23 μeq/ℓ in 1973-74 providing a significant drop in neutralizing capacity during this period. Based upon regression analysis, the input in equivalents of hydrogen ion and nitrate increased by 1.4-fold and 2.3-fold respectively, from 1964-65 to 1973-74. Input of all other ions either decreased or showed no trend. Based upon a stoichiometric formation process in which a sea-salt, anionic component is subtracted from the total anions in precipitation, $SO_4^=$ contribution to acidity dropped from 83% to 66%, whereas NO_3^- increased from 15% to 30% during 1964-65 to 1973-74. The increased annual input

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of hydrogen ion at Hubbard Brook during the past 10 years is highly correlated with the increased input of nitrate in precipitation.

INTRODUCTION

Precipitation chemistry has been monitored at the Hubbard Brook Experimental Forest in New Hampshire since 1963. To our knowledge this is the longest comprehensive record of precipitation chemistry in the United States. The Hubbard Brook Experimental Forest, within the White Mountain National Forest, is downwind of eastern and midwestern industrial centers and as such offers a prime location to monitor changes in regional precipitation chemistry. Bulk precipitation samples are collected on a storm or weekly basis rather than the more commonly used monthly interval. Considering the problems of contamination and biogeochemical transformations that may occur in the reservoir of a precipitation collector in the field, our experience has shown that sampling intervals of a week or less are highly desirable, if not necessary, to obtain accurate data on precipitation chemistry. In areas where dry deposition is more prevalent, sampling of individual precipitation events may be the only alternative to obtain reliable precipitation chemistry.

PRECIPITATION CHEMISTRY AT HUBBARD BROOK

Sulfate and hydrogen ions dominate the precipitation falling on the forested watersheds at Hubbard Brook (Likens et al. 1976). On an equivalent basis sulfate is 2.5 times more important than the next most abundant anion, NO_3, and hydrogen ion is 5.9 times more abundant than the next most abundant cation, NH_4^+. For an 11-year period the total negative equivalent value is 94.9% of the total positive value (Table 1). The determination of hydrogen ion is probably our principal analytical error in the equivalent balance. Hydrogen ion concentration was estimated from measurements of pH and errors on the order of ±0.05 pH unit would be sufficient to explain the discrepancy in the cation-anion balance. However, considering that these long-term averages include the various sampling and analytical errors over an 8- to 11-year span, the agreement is quite good.

One of the more significant findings from these studies of precipitation chemistry was that the rain and snow at Hubbard Brook was highly acid (Likens et al. 1972 , Likens and Bormann 1974). Essentially, the incident precipitation at Hubbard Brook may be characterized as a contaminated solution of sulfuric and nitric acids at a pH of about 4.

Table 1. Weighted annual mean concentration in bulk precipitation for the Hubbard Brook Experimental Forest during 1963-1974.

Substance	Precipitation	
	(mg/ℓ)	(μeq/ℓ)
Ca^{++}	0.16	7.98
Mg^{++}	0.04	3.29
K^{+}	0.07	1.79
Na^{+}	0.12	5.22
NH_4^{+}	0.22[a]	12.2
H^{+}	0.073[ab]	72.4
$SO_4^{=}$	2.9[a]	60.3
NO_3^{-}	1.47[a]	23.7
Cl^{-}	0.47[c]	13.3
$PO_4^{\equiv}$	0.008[d]	0.25
HCO_3^{-}	∿0.006[e]	0.1
TOTAL	5.54	(+) 102.9 (-) 97.7

[a] 1964-1974

[b] calculated from pH measurements on weekly samples

[c] 1965-1974

[d] 1972-1974

[e] calculated from H^{+}-HCO_3^{-} equilibrium

The average annual weighted pH during the period from 1964-65 to 1973-74 ranged between 4.03 and 4.21 (Figure 1). The lowest value reported for a storm at Hubbard Brook was pH 3.0. Such precipitation is decidedly abnormal chemically since the lowest pH value for pure water in equilibrium with CO_2 in a pollution-free atmosphere should be about 5.7 (Barrett and Brodin 1955). Furthermore much of the dissolved and particulate material normally present in precipitation would tend to increase the pH. In other words, the precipitation at Hubbard Brook has a hydrogen ion concentration 50 to 500 times greater than expected.

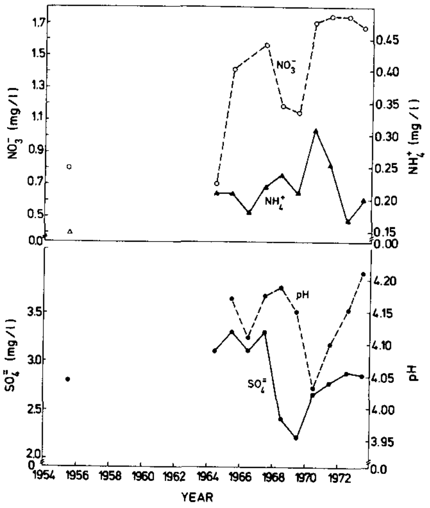

Figure 1. Annual weighted mean concentrations in precipitation for the Hubbard Brook Experimental Forest during 1955-1974. The values for 1955-56 were extrapolated from isopleth maps given by Junge (1958) and Junge and Werby (1958). Note that the ordinate has been compressed.

HYDROGEN ION INPUT

Acid precipitation apparently is a recent phenomenon (Likens 1972, Cogbill 1975, Likens and Bormann 1975), but has been falling on much of the eastern United States since at least the early 1950's (Cogbill and Likens 1974, Likens and Bormann 1974). The record at Hubbard Brook, although relatively short, provides some information on trends during the last 10 years. There was a downward trend in annual pH values between 1964-65 and 1970-71 followed by an upward trend until 1973-74, but no overall trend (1964-1974) is statistically significant (Figure 1). Likewise, concentrations for $SO_4^=$ and NH_4^+ vary from year to year, but there are no statistically significant trends for the period. In contrast, annual NO_3^- concentrations currently are about 2.3-fold greater than they were in 1955-56, or in 1964-65 (Figure 1). The sum of all cations except hydrogen ion ($\Sigma M^+ - H^+$) decreased from 51 μeq/ℓ in 1964-65 to 23 μeq/ℓ in 1973-74, which represented a 55% reduction in this $\Sigma M^+ - H^+$ component in precipitation during the period.

Even though the annual hydrogen ion concentrations are variable, the annual input (concentration times volume) in precipitation increased by 1.4-fold during the period 1964-65 to 1973-74 (Figure 2). In 1973-74 more than 1.1 equivalents X $10^3 H^+$/ha-yr were deposited on forested ecosystems at Hubbard Brook in precipitation. This increased input in hydrogen ion was in sharp contrast to the annual input of all other ions except nitrate (Table 2). Based upon a regression analysis, annual nitrate input increased by 2.3-fold during the decade, and it should be noted that there was no significant increase in annual sulfate input during the period.

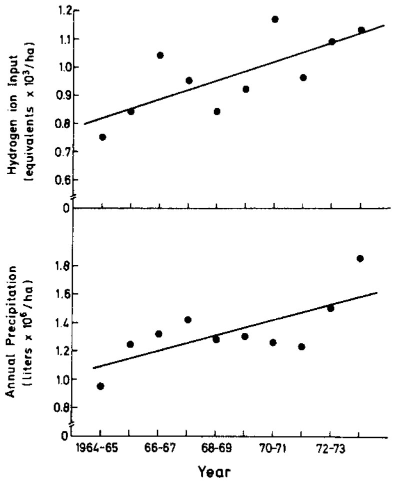

Figure 2. Annual hydrogen ion and precipitation input in precipitation for the Hubbard Brook Experimental Forest. The regression line for hydrogen ion is $Y = 0.033X + 0.819$ where Y is the H^+ input in equivalents X 10^3 per hectare and X is the year. The significant correlation coefficient is 0.74. Note that the ordinate has been compressed.

The increased annual input of hydrogen ion is partially explained by the significant increase in amount of annual precipitation during the 10-yr period (Table 2), but data for individual years show that factors other than increased precipitation are important (Figure 2). In fact hydrogen ion input is only weakly related to annual precipitation input (Figure 3). Thus other factors are operative in regulating

Table 2. Regression analysis of annual precipitation input on year for the Hubbard Brook Experimental Forest.

Substance	Slope	Correlation Coefficient	Time Period
Ca^{++}	-0.174^{**}	-0.83	1963-74
Mg^{++}	-0.046^{*}	-0.66	1963-74
K^{+}	-0.126^{*}	-0.66	1963-74
Na^{+}	-0.003	-0.02	1963-74
NH_4^{+}	0.110	0.57	1964-74
H^{+}	0.033^{*}	0.74	1964-74
$SO_4^{=}$	0.279	0.32	1964-74
NO_3^{-}	0.388^{**}	0.78	1964-74
Cl^{-}	0.300	0.22	1967-74
Water	4.96^{*}	0.72	1963-74

*probability of a larger F-value < 0.05

**probability of a larger F-value < 0.01

the annual input of hydrogen ion, and consequently annual weighted concentrations (pH) alone do not accurately reflect trends in total annual input.

The input of nitrate and sulfate also are directly related to the amount of annual precipitation (Figure 4). There is more variability in the sulfate relationship to precipitation than for nitrate, and in fact without the very wet and very dry years the relationship would not be meaningful (Figure 4). We were fortunate to have rather extreme variation in the hydrologic data during the 10-yr period. This spread from dry to wet years provided a clearer view of the relationships involved. In contrast to hydrogen ion, sulfate and nitrate, the input of all cations (summed) except hydrogen ion is not related to amount of annual precipitation (Figure 3). A plot of the ratio of inputs of hydrogen ion to the sum of all other cations by year shows a highly significant correlation (Figure 5). This relationship compares the relative input of hydrogen ion to all other cations independently of amount of annual precipitation.

Surprisingly the input of hydrogen ion is not significantly related to sulfate input over the 10-yr period (Figure 6). Even though sulfuric acid is the dominant acid in precipitation at Hubbard Brook (Table I), the annual input of sulfate has not significantly increased during the period whereas the annual input of hydrogen ion has (Table 2).

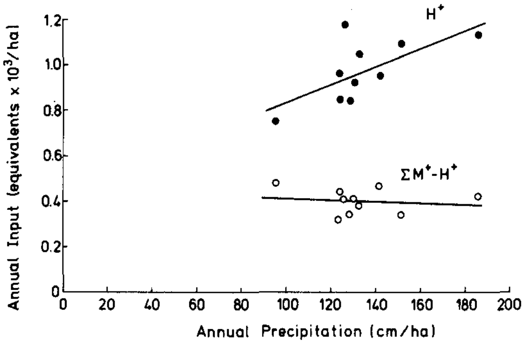

Figure 3. Relationship between annual input of hydrogen ion and all other cations except hydrogen ion ($\Sigma M^+ - H^+$) and precipitation input for the Hubbard Brook Experimental Forest during 1964-1974. The H^+ regression line is $Y = 0.004X + 0.437$, where Y is the annual hydrogen ion input in equivalents X 10^3 per hectare and X is the annual precipitation in cm per hectare; the correlation coefficient is 0.67 and the probability of a larger F-value is < 0.05. The slope of the regression line for $\Sigma M^+ - H^+$ is not significantly different from zero.

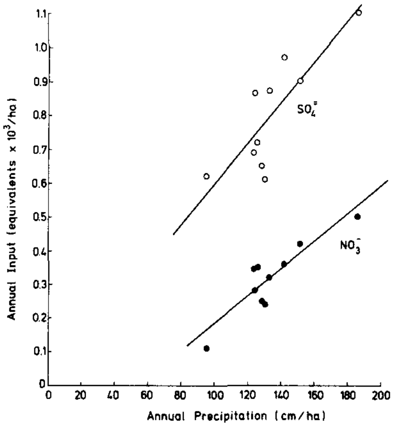

Figure 4. Relationship between annual input of sulfate or nitrate and annual input of precipitation. The sulfate regression line is highly significant (correlation coefficient, 0.81) and the nitrate regression line is very highly significant (correlation coefficient, 0.90).

In contrast, the annual hydrogen ion input is highly correlated with the annual nitrate input during the past decade at Hubbard Brook (Figure 7). The 1:1 relationship between annual inputs of hydrogen ion and nitrate is a powerful argument that nitric acid is the crucial variable in explaining the increased input of hydrogen ion during the past 10 years.

Precipitation chemistry has changed both qualitatively and quantitatively at Hubbard Brook during the past decade. Absolute concentrations have varied (Figure 1), and relative proportions of the component chemicals have changed (Figure 8). Based on a stoichiometric formation process in which the sea-salt, anionic component is subtracted from the total anions in precipitation (Cogbill and Likens 1974), the sulfate contribution to acidity dropped from 83% to 66% and nitrate increased from 15% to 30% from 1964-65 to 1973-74. Annual inputs reflect these changes in complex ways. In an attempt to resolve the relative importance of the various factors controlling the annual hydrogen ion inputs, a step-wise, multiple regression analysis was done to relate the annual hydrogen ion input to a variety of independent variables. An analysis of five independent variables indicated that

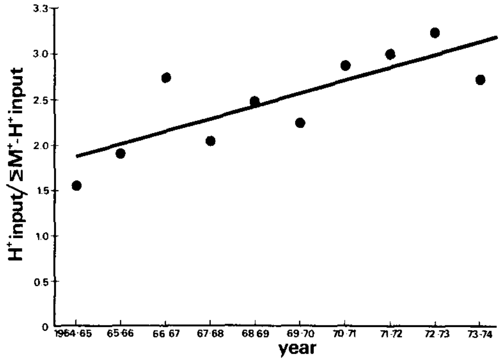

Figure 5. Relationship between cation inputs in precipitation and year. The regression line is highly significant (correlation coefficient, 0.80).

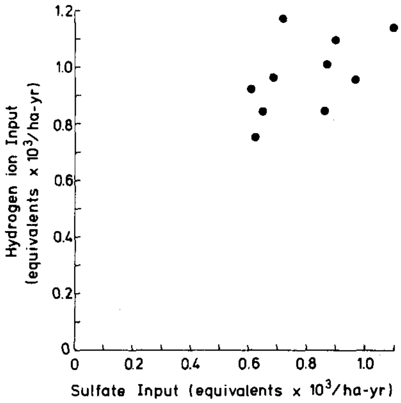

Figure 6. Relationship between the annual hydrogen ion input and the annual sulfate input during the period 1964-65 to 1973-74. The slope of a regression line fitted to these data was not significantly different from zero.

86% of the variability in annual hydrogen ion input during the decade was related to annual nitrate input. Six percent of the variability was due to annual sulfate input, 5% to the input of the sum of all cations minus hydrogen ion, 2% to year and < 0.01% to the annual amount of precipitation.

Thus although sulfuric acid dominates the precipitation at Hubbard Brook and has for a decade, the increased annual input of hydrogen ion during the past 10 years apparently has been due to an increase in the annual nitric acid input to this rural forested ecosystem.

An explanation for the increased concentration of nitrate in precipitation and the subsequent input of nitric acid for Hubbard Brook can only be surmised. Changes in nitrate concentrations in precipitation correlate well with increased emissions of nitrogen oxides (Figure 9) om combustion of fossil fuels, and to a regional spread of these materials (e.g. Likens 1972, Likens and Bormann 1974). However, there may be other factors operating to produce these changes. Data from the Hubbard Brook Experimental Forest suggest that acids in precipitation may result from a complex array of environmental factors, which affect both sulfuric and nitric acids and their proportions. This would seem to be a critical area for further research, since air quality standards and control measures relative to sulfur and nitrogen oxides often are considered independently.

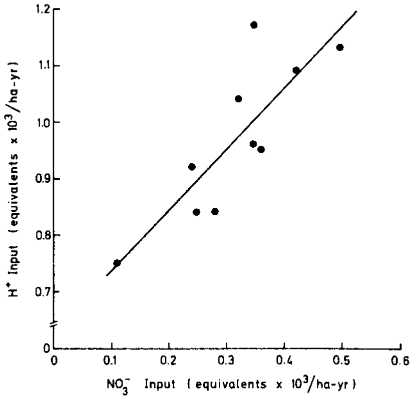

Figure 7. Relationship between the annual hydrogen ion input and the annual nitrate input during the period 1964-65 to 1973-74. The regression line: $Y = 1.07X + 0.631$, where Y is annual input of hydrogen ion in equivalents X 10^3/ha-yr and X is annual nitrate input in equivalents X 10^3/ha-yr, is highly significant (correlation coefficient of 0.84, and probability of a larger F-value is < 0.01).

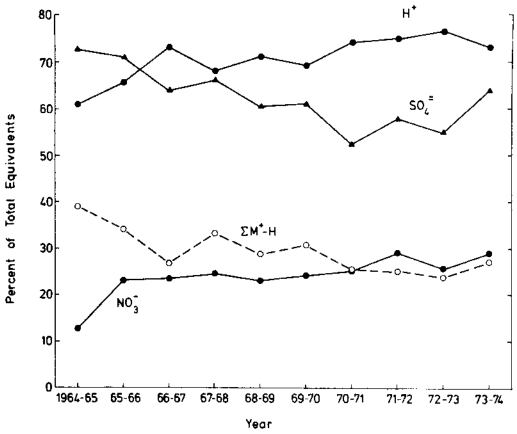

Figure 8. Variation in ionic composition of precipitation for the Hubbard Brook Experimental Forest during 1964-65 to 1973-74.

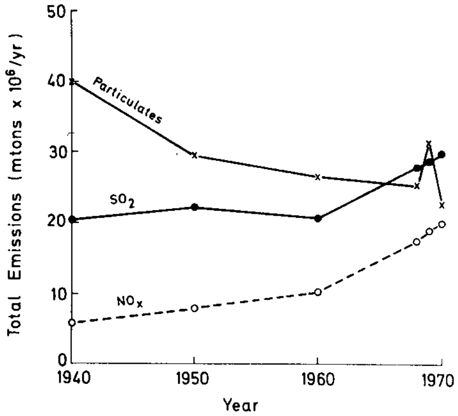

Figure 9. Total emissions of particulates, SO_2 and NO_x for the United States during 1940 to 1970 (from U. S. Environmental Protection Agency 1973).

ECOLOGICAL EFFECTS

The biogeochemical effects of excess acidity and its increased input during the past decade on forests, streams and the lake within the Hubbard Brook Valley are currently under study. The geochemical effects at present seem to be minimal (Johnson et al. 1972), but we do not know what the geochemical conditions were some 20-35 years ago when the precipitation first became more acid. The biological effects on forest dynamics are potentially significant (e.g. Whittaker et al. 1974), but data on forest dynamics are difficult to interpret and further analysis and study are required (Cogbill 1975).

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