SEASONAL PATTERNS IN ACIDITY OF PRECIPITATION AND THEIR IMPLICATIONS FOR FOREST STREAM ECOSYSTEMS

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ABSTRACT

Data collected since 1965 at a network of 9 stations in the northeastern United States show that precipitation is most acid in the growing season (May-September) and least acid in winter (December-February). For the Hubbard Brook station in New Hampshire, where the mean hydrogen ion content of precipitation ranges between 46 μeq/l in winter and 102 μeq/l in summer, the seasonal pattern in acidity correlates closely with seasonal differences in sulfur deposition from the atmosphere. As summer precipitation passes through the forest canopy, hydrogen ion concentrations are lowered by an average of 90 percent, primarily as a result of exchange with other cations. In winter the hydrogen ion content of incident precipitation is lowered from a mean of 50 μeq/l to a mean of 25 μeq/l during storage in the snowpack.

Information about the chemistry of precipitation in the northeastern United States has accumulated in recent years to the point where it is now possible to look for trends or patterns. By coupling any discovered patterns with current knowledge of the forest-stream ecosystem, we can more accurately evaluate the ecologic role of precipitation chemistry. In this study, we have attempted to determine seasonal patterns in the acidity of precipitation in the Northeast, and to discuss their implications for the forest-stream ecosystem.

If we assume that the chemistry and acidity of precipitation are the result of in-cloud scavenging and of washout, some reasons for expecting seasonal patterns are obvious. For example, the origins and tracks of major storms often differ by seasons. In turn, the sources of chemicals and the amounts of them that occur in precipitation may be expected to vary with season.

Also, chemicals entering the atmosphere as a result of industrial emissions, residential heating, combustion engines, and other activities may be related to the season. Dusts and organic materials may have greater impacts on the chemistry of precipitation at certain times of the year because of seasonal activities such as farming and construction or the presence of wind-borne pollen or snow cover. And seasonal temperature patterns may have an effect simply by determining whether precipitation occurs as rain or as snow.

The receiving surface also has seasonal patterns that are important to the chemistry of precipitation. For example, growth activities take place in spring and summer, so the potential of precipitation chemistry for stimulation or damage may be greatest during these seasons. Also, the intercepting surface of forests, especially deciduous hardwoods, changes with the seasons and affects the chemistry of precipitation reaching the forest floor. Soil moisture patterns are seasonal and can affect the length of time that precipitation is stored in the soil and the extent to which its original chemical composition is changed before it becomes streamflow. Nutrient ions in the forest canopy, forest floor, and soil may be more susceptible to exchange or leaching during certain seasons, depending on biologic activity.

METHODS

We analyzed data from nine stations in the Northeast for seasonal patterns in acidity of precipitation. Eight of the stations are part of a U.S. Geological Survey (USGS) network located in New York and Pennsylvania (Pearson and Fisher 1971); the ninth station is at the Hubbard Brook Experimental Forest in central New Hampshire and is operated by the U.S. Forest Service in cooperation with Cornell and Yale Universities. The USGS locations were used only to determine the existence and extent of seasonal patterns in acidity; Hubbard Brook was studied in greater detail for causes and implications of seasonal patterns.

The USGS network began operating in the autumn of 1965, and our study includes data collected through December 1973 (U.S. Department of Interior, 1965-1974). Precipitation samples are composites for monthly periods from collectors which are continuously open to the atmosphere. The collectors were described by Gambell and Fisher (1966); they consist of a straight-sided glass funnel through which precipitation drains into a polyethylene reservoir. A fritted glass disc is attached at the bottom of the funnel for filtration, and the funnel and reservoir are housed in an insulated chest. Techniques for the chemical analysis of precipitation samples are described in Pearson and Fisher (1971).

We began determining the chemistry of precipitation at Hubbard Brook in 1963, but we include here only the data collected from

June 1965 through June 1974, the period comparable to available USGS data. Precipitation samples are collected weekly from a polyethylene collector consisting of an uncovered funnel, tubing, and reservoir in summer and plastic trash cans in winter (Likens et al. 1967). The entire system is meticulously cleaned and re-installed each week. In addition to the precipitation data, our paper incorporates information from other Hubbard Brook studies concerning the chemistry of throughfall and stemflow (Eaton et al. 1973), the snowpack (Hornbeck and Likens 1974a and b), and streamflow. The analytical procedures for all samples collected at Hubbard Brook are those given by Likens et al. (1967) and Fisher et al. (1968) with the exception that automated colorimetric analysis has been used for anion and ammonium determination since 1972 (Likens 1972). Hydrogen ion concentrations for both Hubbard Brook and the USGS stations are calculated from measured pH values determined with glass electrodes and electronic pH meters.

We have based much of this paper on the means of monthly values that have been weighted proportionally for amount of precipitation. We determined coefficients of variation together with the means and found that Hubbard Brook consistently had lower coefficients of variation than the USGS stations. For example, the monthly coefficients of variation for hydrogen ion concentration in Hubbard Brook precipitation ranged from a low of 23 percent for July to a maximum of 58 percent for October. As examples from the USGS data, monthly coefficients of variation ranged from 75 to 163 percent for Albany, N. Y.,; 31 to 100 percent for Rock Hill, N. Y.; and 37 to 74 percent for Athens, Pa.

There are several possible explanations for the differences in coefficients of variation between Hubbard Brook and the USGS stations. Samples are collected at weekly intervals at Hubbard Brook as opposed to monthly intervals at USGS stations. Variations caused by contamination and aging should be less over the shorter sampling interval used at Hubbard Brook. Higher variations in the USGS data might also be a result of the glass funnels and filters used in the collectors. Glass is known to be more active chemically than polyethylene, so variation may be greater for those collectors than for samples collected in a system made completely of polyethylene. These factors would tend to raise the pH values of the USGS samples, thus giving a conservative estimate of precipitation acidity.

SEASONAL PATTERNS IN ACIDITY OF PRECIPITATION

A comparison of monthly means for each of the nine stations suggests some patterns in acidity of precipitation. With the exceptions of Albany, Hinckley, and Mays Point stations, acidity in terms of hydrogen ion concentration is generally maximal in summer months, intermediate in spring and fall, and minimal in winter (fig. 1). Maximum hydrogen ion concentrations most often occurred in June, July, or

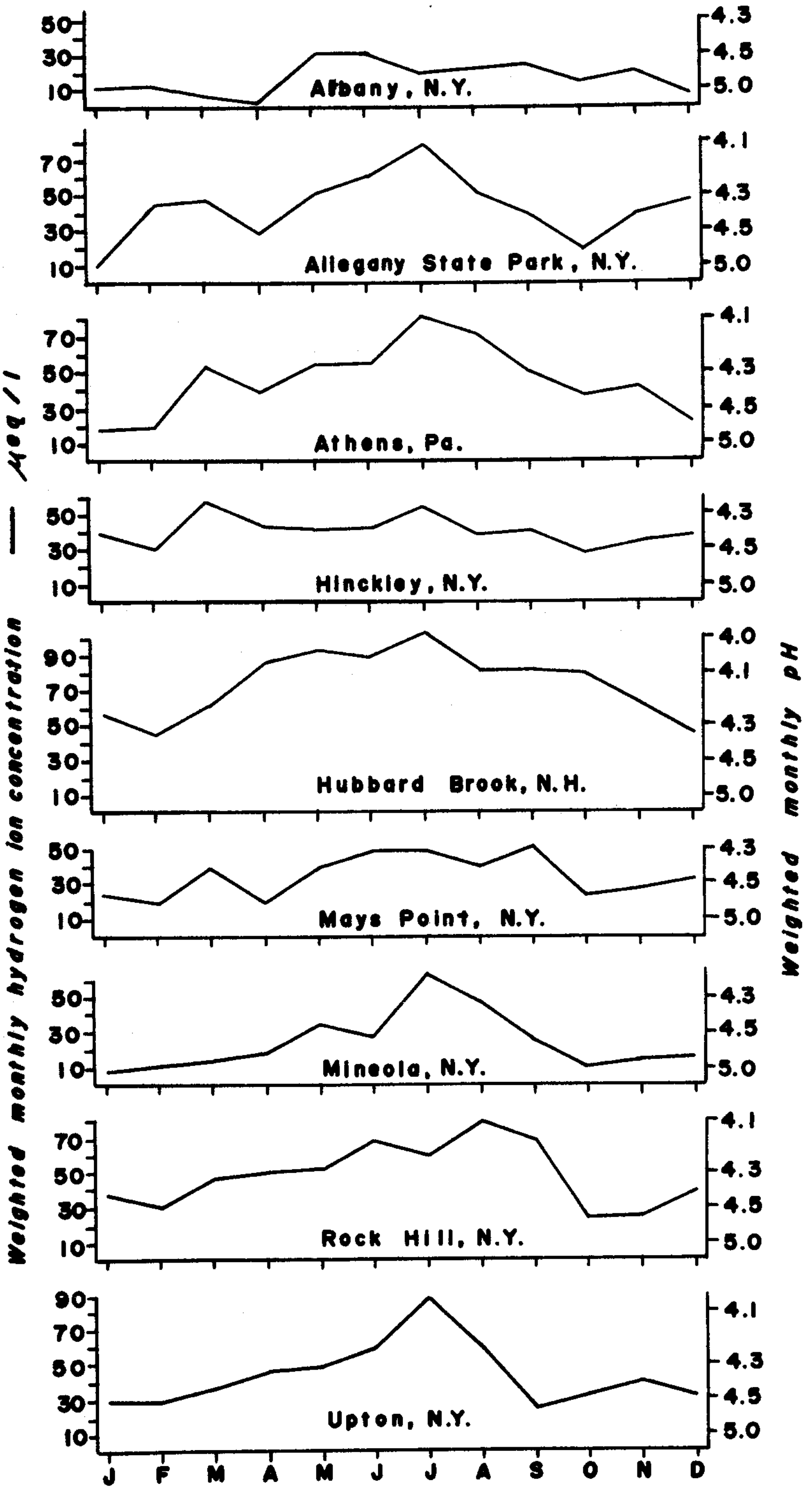

Figure 1.--Weighted hydrogen ion concentration and pH of precipitation. The curves are based on 8 or more years of data for each location.

August. Minimum values most often occurred in January or February.

The levels and ranges of acidity varied considerably among stations (fig. 2). Albany, N. Y., had the lowest hydrogen ion concentration,

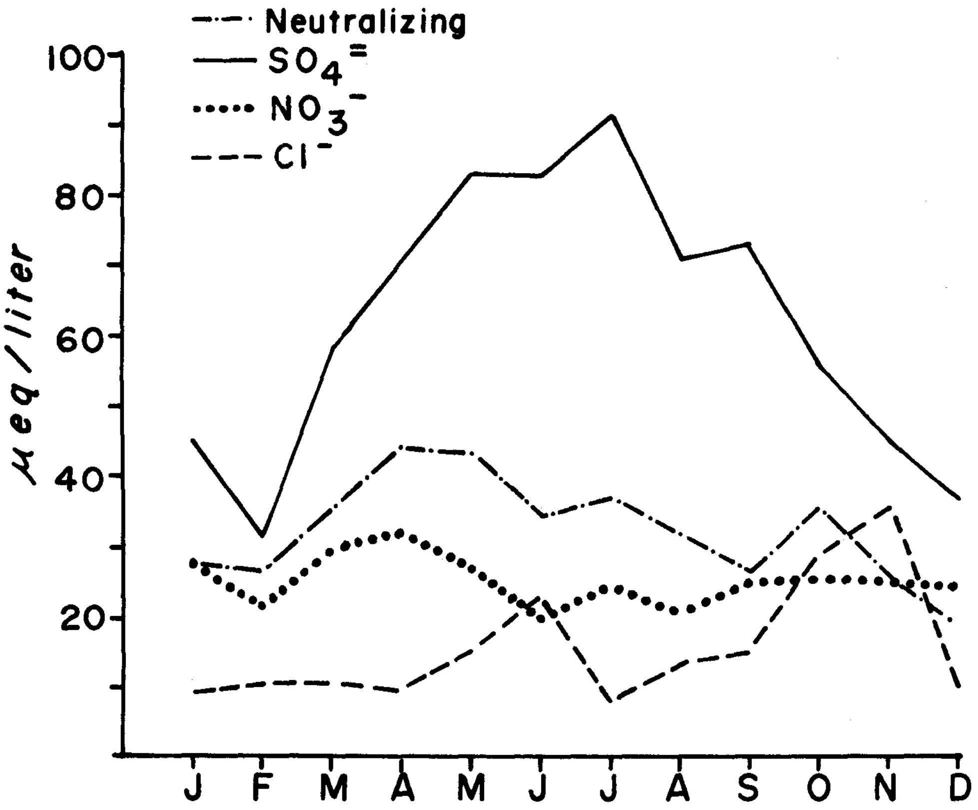

Figure 2. Neutralization and acid-forming components in Hubbard Brook precipitation. These data are weighted means for 9 years of record.

with average monthly values ranging from 2 to 30 μeq/l. Hubbard Brook had the highest levels, ranging from an average of 45 μeq/l in February to over 100 μeq/l in July. Four stations - Allegany State Park, Athens, Hubbard Brook, and Upton - had maximum and minimum values that were separated by at least 55 μeq/l.

The differences in levels and ranges between stations may be due in part to location. Hubbard Brook is the most isolated and is surrounded by vast areas of forest, while the USGS stations are located closer to agricultural, urban, and industrial activities. Thus the chances of neutralization by dusts and other materials may be least at Hubbard Brook, and quite variable at the other stations.

The apparent seasonal patterns in acidity of precipitation at most of the stations suggest that a sine curve is a useful first approximation for modeling the acidity of precipitation over the course of a year. The phase constant appears to be similar for most of the stations, but the amplitude is variable. Testing potential biologic impacts by using different phases and amplitudes for the curve could be an interesting experiment to perform with such a model.

EXPLANATION OF SEASONAL PATTERNS

Chemical data for precipitation at Hubbard Brook were analyzed in greater detail for possible explanations of seasonal patterns in acidity. Total neutralization and acid-forming components found in Hubbard Brook precipitation were calculated on an equivalent basis and plotted as monthly means for a 9-year period (fig. 2). The total neutralization component includes the sum of calcium, magnesium, potassium, sodium, and ammonium ions.

The chloride, nitrate, and neutralization components show some month-to-month variation, but no strong seasonal patterns. In contrast, the sulfate component shows a strong seasonal pattern practically identical to that for hydrogen ion concentration (fig. 1). This close relationship between hydrogen and sulfate is strong evidence that the seasonal pattern in acidity is almost solely the result of seasonal differences in sulfur deposition from the atmosphere.

The primary sources for sulfur found in precipitation are combustion of fossil fuels and natural processes such as forest fires, volcanic eruptions, and biologic reduction of sulfate. The combustion of fossil fuels is considered to be a particularly important source in the northeastern United States (Likens 1972; Likens and Bormann 1974; Pearson and Fisher 1971). The seasonal pattern is puzzling in this regard. Because of their use in heating, it would seem that maximum combustion of fossil fuels would be in winter. Yet the maximum sulfur in precipitation occurs in midsummer. As one possible explanation, Fisher et al. (1968) have suggested that snow may be less efficient than rain in capturing sulfur compounds from the atmosphere. Another possibility may be that greater electric power generation in summer more than compensates for the reduced heating. In any case, the apparent importance of sulfur on a seasonal basis and in the overall chemical composition and acidity of precipitation suggest that future research should further quantify its sources and explain its seasonal patterns.

IMPLICATIONS FOR THE FOREST-STREAM ECOSYSTEM

The seasonal patterns in acidity have some obvious implications for the forest-stream ecosystem. For example, maximum acidity occurs during the season when plants are actively growing and the potential for biologic impacts may be at a maximum. An important concern is the impact that higher summer acidities may have on the leaching of nutrients from foliage and soils.

A study showing the importance of hydrogen ion exchange as a mechanism for leaching cations from above-ground vegetation was conducted at Hubbard Brook during June through October 1969 (Eaton et al. 1973). For the study period, the precipitation had a weighted mean hydrogen ion concentration of 87 µeq/l (table 1). On the other hand, throughfall or precipitation that passed through the canopy had a weighted mean hydrogen ion concentration of 10 µeq/l. Thus about 90 percent of the hydrogen ions were left in the forest canopy as the precipitation passed through on the way to the forest floor.

Table 1.--Hydrogen ion content of precipitation above and below the forest canopy at Hubbard Brook Experimental Forest. Mean monthly values for June to October 1969

Month	Above canopy			Below canopy		
	pH	Concentration	Total content	pH	Concentration	Total content
		µeq/l	meq/ha x 10^{-5}		µeq/l	meq/ha x 10^{-5}
June	4.12	76	0.71	4.85	14	0.11
July	3.93	117	2.37	4.89	13	.23
August	4.16	69	1.01	5.52	3	.04
September	4.15	71	.34	4.72	19	.07
October	4.18	66	.42	5.70	2	.01
Weighted mean	4.06	87	.97	5.01	10	.09
Total	--	--	4.85	--	--	0.46

Budgetary information showed that hydrogen ions made up 4.85 × 10^{-5} meq/ha or 74 percent of the total cation input in precipitation and only 0.46 × 10^{-5} meq/ha or 2 percent of the cation loss in throughfall and stemflow (table 1). The net cation loss from the canopy for this same period was 16.28 × 10^{-5} meq/ha. It was therefore concluded that as much as 27 percent of the leaching which occurred from the forest canopy can be accounted for by hydrogen exchange from the rain (Eaton et al. 1973).

The removal of hydrogen ions by exchange in the canopy lessens the potential impact of acidic precipitation on forest soils at Hubbard Brook. Also, exchange in the canopy increases the nutrient content of rainfall reaching the forest floor, and most of the added nutrients are probably in a form directly available for plant use. These advantageous effects of the forest canopy coincide with the season of maximum acidity. However, these effects should not at this point be construed as lessening the potential problems of precipitation acidity. The sources and biologic significance of the leached ions and the ultimate fate of hydrogen ions remaining in the canopy must be determined, as well as the impact of the large quantities of sulfur that are associated with the higher summer acidities.

The important chemical changes that occur as precipitation passes through the summer canopy raise the question of what may happen when the forest canopy is removed. In an earlier study at Hubbard Brook, in which a previously forested watershed was devegetated for a 3-year period, the stream water pH decreased from 5.1 to 4.3 (Likens et al. 1970). This change represents about a fivefold increase in hydrogen ion content of stream water. There were many complex changes in the chemical composition of the stream as a result of devegetation. However, the absence of hydrogen ion exchange in the canopy may have contributed to the increased acidity of stream water after vegetation was eliminated.

During the dormant season the leafless hardwood canopy has less impact on precipitation passing through it. However, in places where a snowpack develops, there are opportunities for further changes in the acidity of precipitation before it infiltrates the soil. We have been studying the chemistry of the snowpack for the past three winters at the Hubbard Brook Experimental Forest (Hornbeck and Likens 1974a and b). The annual snowpack reaches a maximum accumulation of 1 to 2 meters and has a water equivalent of 20 to 40 cm, about 30 percent of annual precipitation.

Our findings show that the snowpack is generally less acid than the incident precipitation (fig. 3). Hydrogen ion concentrations in the snowpack seldom exceed 25 μeq/l, whereas in incoming precipitation they average more than 50 μeq/l and their maximum values exceed 100 μeq/l. These findings are similar to those of an earlier study in Wyoming (Clement 1966), which showed that as snow ages it becomes less acid.

Most of our chemical data for the snowpack were determined from all the meltwater from weekly snowpack samples. However, for seven

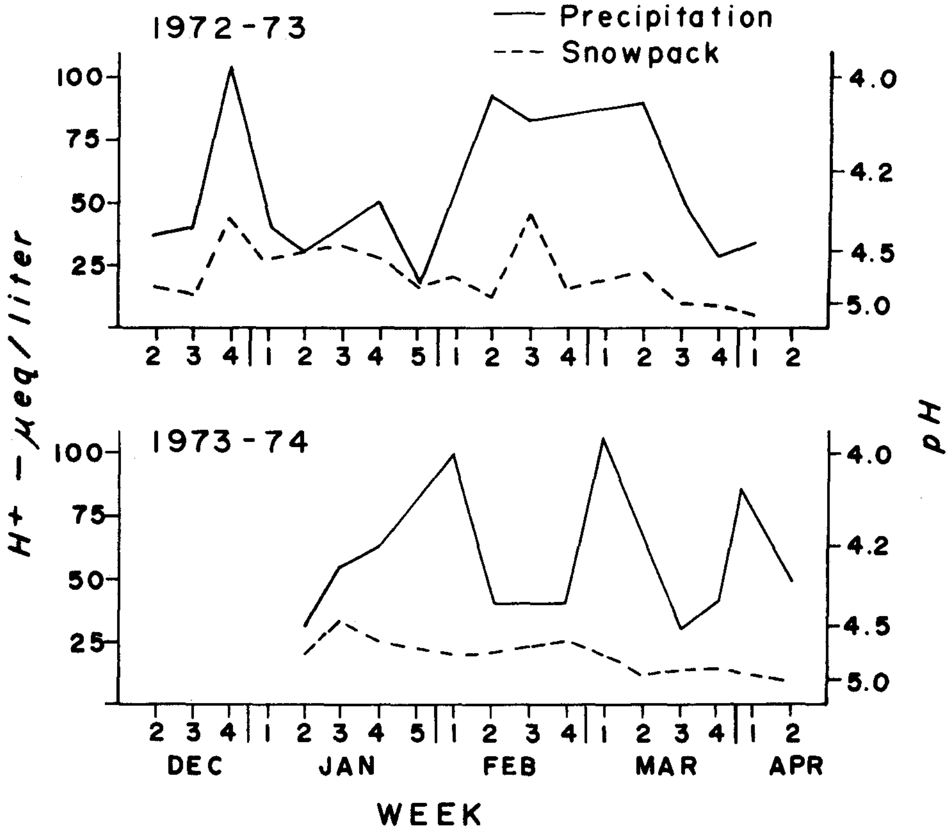

Figure 3. Hydrogen ion concentration and pH for incident precipitation and snowpack at Hubbard Brook.

dates during the first 2 years of our study, we also compared the first 20 percent of the meltwater from a sample with the final 80 percent of the meltwater. The average hydrogen ion concentration in the first 20 percent of the meltwater was 33 μeq/l, compared to 21 μeq/l in the final 80 percent. Most other ions showed a similar pattern; greater concentration in the first 20 percent of the meltwater. Thus part of the decline in acidity while precipitation is stored as snow can be explained by a differential contribution of ions from the snowpack.

The decline in acidity may also be partly the result of hydrogen ion exchange with cations from organic material. Organic material, in the form of birch cone scales and seeds, leaves, twigs, and bark fragments, is transported to the snowpack by wind or precipitation in surprisingly large quantities. Hydrogen may exchange with several different cations in the organic materials, but potassium seems to be one of the most important. Our data showed that potassium content was about four times as great in the snowpack as in the incident precipitation.

EFFECTS OF PRECIPITATION ACIDITY ON STREAMFLOW

We have discussed seasonal patterns in acidity that would seemingly affect stream water. However, there are other variables that must be considered in discussing the acidity of streams. For example, as precipitation infiltrates the soil at Hubbard Brook and moves toward stream channels, it encounters a variety of conditions of soil acidity and chemistry. The organic and A_2 horizons are extremely acid, having pH values of 3 to 4. The upper B horizons have pH's between 4 and 5, and the lower B and the C horizons usually have pH's greater than 5. The cation exchange capacity and degree of base saturation also vary greatly between horizons.

In addition to the variety of acidities encountered, soil water may also be subject to varying residence times, depending on season. For example, in summer when evapotranspiration is maximal, soil water deficits occur and movement of water is slowed.

Despite the seasonal patterns in acidity of precipitation, the varying conditions of acidity encountered in the soil, and variations in residence time, the streamflow acidity at Hubbard Brook is remarkably uniform (fig. 4). For 9 years of record, the mean hydrogen ion concentration for the 12 individual months ranged between 10 and 17 μeq/l. In contrast, precipitation for the same period had a range from 46 to 102 μeq/l. The variation in streamflow acidity is usually low, as attested to by small standard deviations (fig. 4) and coefficients of variation that never exceeded 40 percent.

The stability of stream water acidity at Hubbard Brook indicates a uniform buffering action by forest vegetation and soils that reduces the hydrogen ion content of precipitation by a factor of between 5 and 10. The fact that streamflow retains some acidity (hydrogen ion concentrations of 10 to 17 μeq/l) suggests that the weathering reaction in soils is incomplete. The reasons for this are unclear, but Johnson et al. (1972) have suggested that it may be the result of microscopic coatings of alumina and clay on rock surfaces and mineral grains. Incomplete weathering means a slower rate of cationic denudation with one tradeoff being more acidic streamflow.

CONCLUSION

To sum up our conclusions we have prepared an illustration of the acidity conditions at Hubbard Brook in summer and in winter (fig. 5). Precipitation is decidedly more acid in the summer, entering the canopy

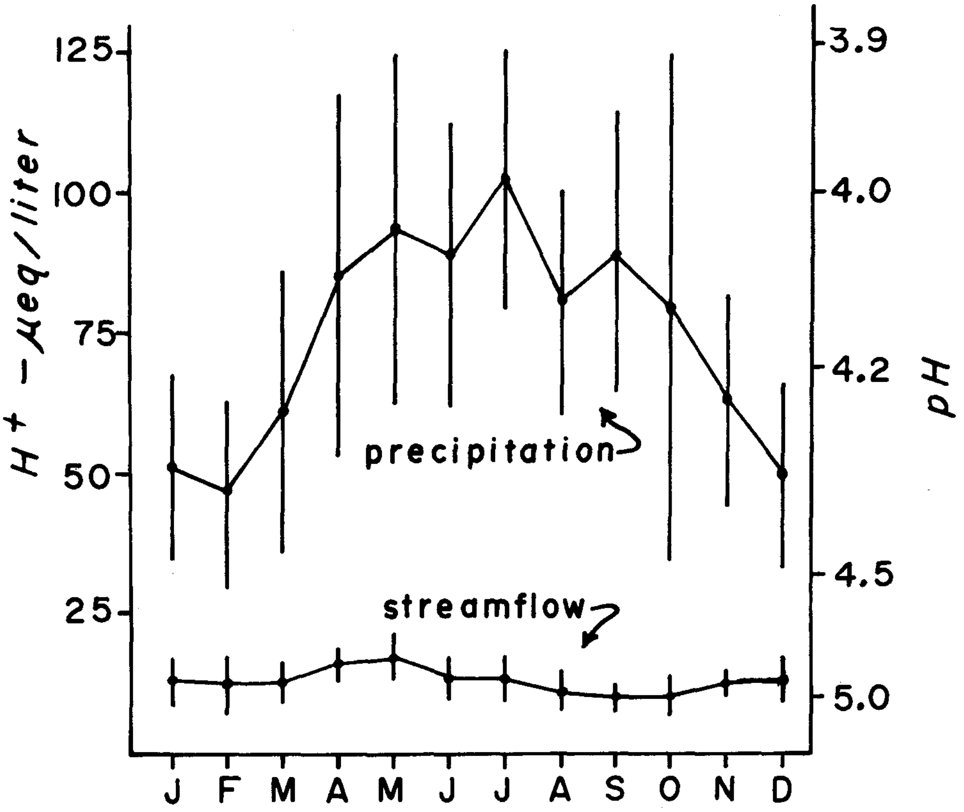

Figure 4. Weighted monthly hydrogen ion concentration and pH of precipitation and streamflow at Hubbard Brook from 1965 to 1974. The vertical lines for each month represent one standard deviation.

with a hydrogen ion concentration of 85 to 100 μeq/l. As precipitation passes through the canopy, the hydrogen ion concentration is lowered to 10 to 20 μeq/l. The precipitation that infiltrates and becomes soil water passes through soil horizons with widely different acidities, before emerging as streamflow with a hydrogen ion concentration of 10 to 15 μeq/l.

The less acid winter precipitation has hydrogen ion concentrations in the range of 50 to 60 μeq/l. While it is stored in the snowpack, its acidity declines to around 25 μeq/l. Meltwater leaves the snowpack at varying acidities to pass through the soil and becomes streamflow with hydrogen ion concentrations of 10 to 15 μeq/l (fig. 5).

The acidity of precipitation in spring and autumn is intermediate between summer and winter values. In the absence of a leaf canopy or snowpack, the acidity of precipitation entering the soil during spring and autumn may be higher. However, the streamflow acidity shows little effect, remaining fairly constant year-round at 10 to 15 μeq/l.

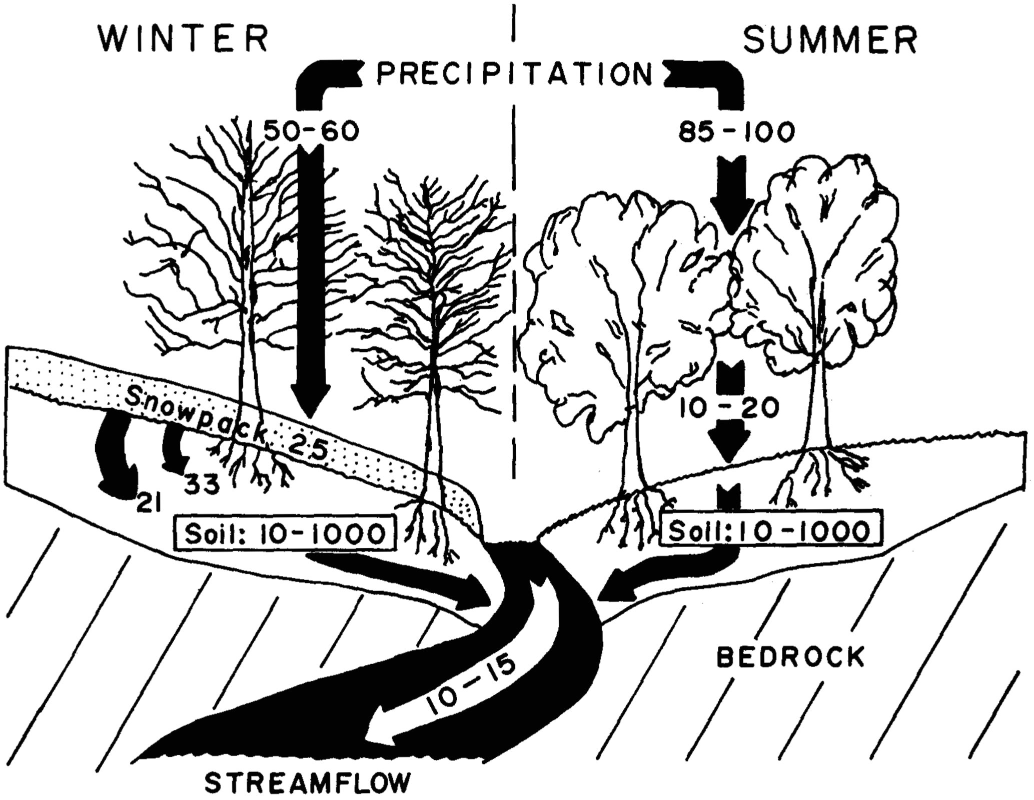

Figure 5. Acidity of water at two seasons at Hubbard Brook. The values are hydrogen ion concentrations in μeq/l.

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