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Hydrogen ion budget of an aggrading forested ecosystem

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ABSTRACT

A detailed hydrogen ion budget was developed for the Hubbard Brook Experimental Forest, in W. Thornton, New Hampshire, U.S.A. Hydrogen ion sources (2541 eq H^+ ha^{-1} yr^{-1}) were found to approximately balance hydrogen ion sinks (2428 eq H^+ ha^{-1} yr^{-1}). Atmospheric hydrogen ion inputs contributed 52% of the total hydrogen ion sources for the ecosystem. Based on this budget, projections of changes in precipitation hydrogen ion loading on water quality were made. Changes in H_2SO_4 precipitation inputs would have more influence on water quality than HNO_3 inputs.

1. Introduction

The hydrogen ion cycle is one of the most complex of the elemental cycles. Virtually every biogeochemical reaction affects the hydrogen ion cycle (Garrels et al., 1975; Reuss, 1976; Driscoll, 1980). With the increased concern over elevated atmospheric fluxes of hydrogen ion and surface water acidification (Dochinger and Seliga, 1976; Drablos and Tollan, 1980) a qualitative assessment of the overall hydrogen ion budget for an ecosystem is of great interest.

Input–output budgets of hydrogen ion for Norwegian watersheds have previously been compiled (Gjessing et al., 1976; Wright and Henriksen, 1977). About 30–70% of hydrogen ion deposited in the form of precipitation was neutralized within these watersheds. A hydrogen ion budget for an acid (pH 4.7) lake in Norway, revealed that 30% of the incoming hydrogen ion was neutralized within the lake (Wright and Johannessen, 1980). This neutralization was attributed to sulfate reduction or net primary production.

The development of a detailed hydrogen ion budget for an ecosystem is a major undertaking. However, this task was facilitated by the years of research conducted at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire. There is an extensive base of information on precipitation, stream and soil chemistry for this ecosystem, as well as estimates of forest biomass and forest nutrient reservoirs and turnover values (Gosz et al., 1973; Whittaker et al., 1974; Likens et al., 1977; Whittaker et al., 1979). It was with this information that a hydrogen ion budget for the Hubbard Brook Experimental Forest was developed.

The hydrogen ion cycle of an ecosystem can be viewed as having four principal components (Fig. 1). The first would be allochthonous sources. For the Hubbard Brook Experimental Forest, these inputs of hydrogen ion principally come from atmospheric sources and enter as "free" hydrogen ion or bound to ammonia and carbonate (Likens et al., 1977). The second component of the cycle is the production of hydrogen ion within the ecosystem. Reactions such as oxidation of reduced compounds (e.g. FeS_2, NH_4^+) in the soil, the partial oxidation of natural organic matter generating organic acids and an accumulation of cations in the forest floor and forest biomass, all could generate hydrogen ion. This accumulation of cations may take many forms. It may result from the uptake of cationic nutrients by soil organisms and forest vegetation,

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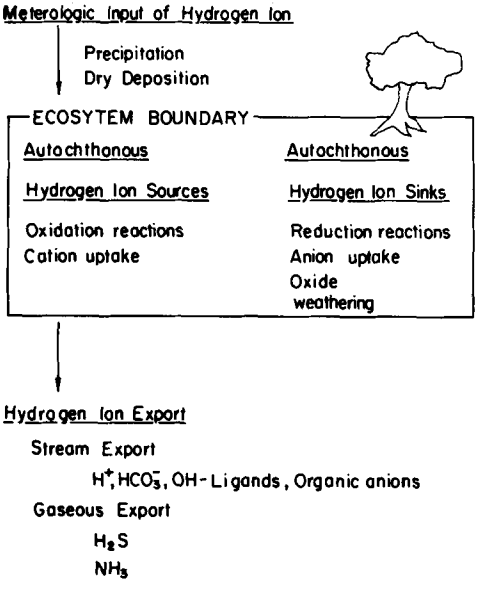

Fig. 1. A conceptual model of the hydrogen ion budget for a forested ecosystem at Hubbard Brook. The model is based on the small watershed technique (Bormann and Likens, 1967; Likens et al., 1977) where a small monitored watershed is considered to be an ecosystem. The model is based on four principal components: meterological inputs of hydrogen ion in wet and dry deposition (gases and/or aerosols), internal hydrogen ion sources, internal hydrogen ion sinks and hydrogen ion export. The latter consists of exports in stream water draining the watershed and gaseous exports. At this time gaseous exports of hydrogen ion are considered to be insignificant.

the exchange of cations on soil exchange sites or the accumulation of cations associated with the accumulation litter and dead biomass within the forest floor. It is noteworthy, that the concept of hydrogen ion generation by cation uptake is somewhat controversial. Many researchers have suggested that, when plants take up an excess of cations over anions, protons will be released in order to maintain electroneutrality (Epstein, 1972; Reuss, 1976; Rosenqvist, 1977). However, Gorham, Vitousek and Reiners (1979) maintain that biological uptake of cations in the soil environment will not contribute to the export of hydrogen ion from an ecosystem (or acidification of downstream aquatic systems).

Coincidentally, the third component of the hydrogen ion cycle, the neutralization of hydrogen ion, occurs within the ecosystem. Examples of hydrogen ion sinks within the Hubbard Brook Experimental Forest include: the weathering of oxide minerals, the reduction of materials (e.g. denitrification, sulfate reduction) and the accumulation (or uptake) of anions by the forest floor and forest biomass. Like cation accumulation, anion accumulation can be thought of as the composite of several processes. The hydrogen ion cycle is completed by the export of "free" or bound hydrogen ion from the ecosystem. In the Hubbard Brook Experimental Forest, this fourth component of the cycle principally occurs through stream flow out of the ecosystem.

Qualitative discussions of the relative contribution of atmospheric hydrogen ion inputs to the overall hydrogen ion budget have been presented by Norwegian investigators. Rosenqvist (1977) maintains that atmospheric hydrogen ion inputs represent a minor contribution to the overall hydrogen ion budget of an ecosystem. Other researchers (Tollan, 1977; Likens et al., 1977) suggest that acid precipitation is important in the hydrogen ion budget of many small watershed ecosystems and is the principal cause of surface water acidification. In view of these contentions a detailed evaluation of the hydrogen ion budget for an ecosystem subjected to acid precipitation is long overdue.

2. Budget assumptions and calculations

The following assumptions were made to compile this budget:

1. Cations (Ca^{++}, Mg^{++}, Na^+, K^+ and Al) that enter the ecosystem from weathering reactions are all in the form of oxide coordinated metals (e.g. feldspars, micas) and consume one equivalent of hydrogen ion for each equivalent of metal dissolved (Garrels and Christ, 1965).

2. Cations (Ca^{++}, Mg^{++}, Na^+, K^+, Fe and NH_4^+) that are accumulated within the forest biomass and forest floor are assimilated in the "free" (uncomplexed) form and are exchanged for an equivalent amount of hydrogen ion.

3. Aluminum accumulation into the forest floor and forest biomass is insignificant in the overall hydrogen ion budget. Annual aluminum uptake on soil exchange sites, contributes little to the overall hydrogen ion budget (Eaton, 1980). No infor-

mation is available on aluminum assimilation by forest biomass at the Hubbard Brook Experimental Forest.

4. Anions ($SO_4^=$, NO_3^- and $PO_4^{\equiv}$) that are accumulated within the forest floor and forest biomass are assimilated in the "free" (uncomplexed) form and are exchanged for an equivalent amount of hydroxide ion (Brewer and Goldman, 1976).

5. Sulfur that enters the ecosystem by weathering reactions originates from pyrite (FeS_2) dissolution (Johnson, 1978).

6. Phosphorus enters and leaves the ecosystem as $H_2PO_4^-$. This assumption is reasonable because most (>70%) aqueous phosphorus is molybdate reactive phosphorus. The aqueous pH of precipitation and stream water generally falls between the first ($pK_{a1} = 2.1$) and second ($pK_{a2} = 7.2$) proton dissociation constants of orthophosphate (Stumm and Morgan, 1970). As a result the proton association/dissociation reactions of orthophosphate are an insignificant contribution to the overall hydrogen ion budget.

7. The discrepancy in charge balance of cations and anions leaving the ecosystem through stream water is due to organic anions or hydroxide ligands coordinated to metal cations (e.g. $Al(OH)^{+2}$). The production of organic acids and organic acid weathering are potentially important aspects of the hydrogen ion budget for the HBEF. It is extremely difficult to estimate organic anion export and therefore organic acid contribution to the budget. While the discrepancy in charge balance approach is not particularly satisfactory, it is one of the few methods available and it has been used by other investigators (Cronin et al., 1978).

The data required to calculate this budget were mainly summarized by Likens et al. (1977). Information on nutrient assimilation by the forest floor and forest biomass was taken from Gosz et al. (1973), Whittaker et al. (1974, 1979). Calculations for the nitrogen component of the hydrogen ion budget were obtained from Bormann et al. (1977). Dry deposition information for sulfur was obtained from Eaton et al. (1980). Dry deposition of nitrogen compounds was not included in this analysis.

It is important to note that this budget is a compilation of the *net* transformations that occur within the Hubbard Brook Experimental Forest throughout a year. It in no way attempts to quantify the gross hydrogen ion transformations within the ecosystem. To illustrate this concept, consider an equivalence of aqueous potassium, that is available for metabolism within the forest floor or forest biomass. If after an annual cycle this equivalence of potassium were assimilated into the forest floor or forest biomass, it would contribute one equivalence of protons toward a net hydrogen ion budget. In actuality, this potassium may have been assimilated and released by the vegetation or organisms in the forest floor several times over an annual cycle. Each of these transformations would represent hydrogen ion sink and hydrogen ion source contributions to a gross hydrogen ion budget. It is virtually impossible to quantify all of the individual, internal cycling of elements that occur within an ecosystem. However, we can quantify the net transformations that take place. In this respect this budget represents an annual net hydrogen ion budget.

In the Hubbard Brook Experimental Forest there is a substantial flux of hydrogen associated with the cycling of water through the watershed ecosystem (hydrologic cycle). Water enters the ecosystem through precipitation and is exported by stream runoff or evapotranspiration. In an aggrading ecosystem there is also a net accumulation of hydrogen within the forest vegetation and forest floor. It is noteworthy that this tabulation is not a *hydrogen* budget, but merely an electroneutrality balance, of which *hydrogen ion* serves as measure.

The Hubbard Brook hydrogen ion budget is fundamentally different from the input–output budgets of other investigators (Gjessing et al., 1976; Wright and Henriksen, 1977). These budgets generally assume steady-state with respect to forest biomass and forest floor accumulation (i.e. the forest is neither aggrading nor degrading). Weathering rates are never directly measured but are obtained by difference from input–output data. In our analysis, changes in nutrient storage and weathering are measured directly and included in the overall hydrogen ion budget.

The forest ecosystem at Hubbard Brook is aggrading, undergoing a net accumulation of living and dead biomass (Bormann and Likens, 1979). This has a strong effect on the hydrogen ion budget. The Hubbard Brook Biomass Accumulation Model (Bormann and Likens, 1979a, b) indicates that biomass accumulation will ultimately level off and decline. Hydrogen ion budgets for

these phases of development will be quite different from the one presented here.

3. Discussion of the hydrogen ion budget

It is apparent that the estimated hydrogen ion budget does not exactly balance (Fig. 2). Hydrogen ion sources (2541 eq H^+ ha^{-1} yr^{-1}) exceed hydrogen ion sinks (2428 eq H^+ ha^{-1} yr^{-1}) by 113 eq H^+ ha^{-1} yr^{-1}. This discrepancy may be due to analytical error, an inaccuracy of assumptions made in formulating the budget or a comparison of component averages determined for different time periods. However, considering the magnitude of the hydrogen ion cycle a 5% difference is considered acceptable.

There are some aspects of the hydrogen ion budget that should be closely considered. Inputs of atmospheric free hydrogen ion represent 52% of the annual total hydrogen ion sources to the Hubbard Brook ecosystem. Of these inputs, 38% are in the form of precipitation (average pH 4.14) while 14% are in the form of dry deposition.

The oxidation of reduced sulfur is an insignificant portion (<1%) of the hydrogen ion sources at Hubbard Brook. In fact, sulfate assimilation by vegetation appears to have a much more sub-

HUBBARD BROOK HYDROGEN ION BUDGET

Meterologic Inputs
Precipitation +960
Dry Deposition +362

Weathering Reactions		Net Forest Accumulation		
		Forest Biomass	Forest Floor	Total
Ca - 1055	Ca	+ 405	+ 70	+ 475
Mg - 288	Mg	+ 57	+ 17	+ 74
Na - 252	Na	+ 7	< 1	+ 7
K - 182	K	+ 147	+ 9	+ 156
S + 25	S	- 75	- 50	- 125
Al - 211	Fe	+ 40	+ 63	+ 103
Fe - 78	NO_3^-	—	—	- 47
P + 83	NH_4^+	—	—	+ 144
	P	- 74	- 16	- 90
TOTAL - 1957		TOTAL		+ 697

Stream Exports

Stream pH (H^+)	- 100
Stream alkalinity (HCO_3^-)	+ 126
Discrepancy in charge balance (organic anions, hydroxide ligands)	+ 26

SUMMARY

Hydrogen Ion Sources	+	2541
Hydrogen Ion Sinks	−	2428
Budget Discrepancy	+	113

Fig. 2. A hydrogen ion budget for the Hubbard Brook Experimental Forest. Units of hydrogen ion flux are eq H^+ ha^{-1} yr^{-1}. A positive quantity indicates hydrogen ion generation (source), a negative quantity indicates hydrogen ion consumption (sink). The budget is subdivided to illustrate the contribution of individual element transformations to the overall hydrogen ion cycle. It is not possible to distinguish between NO_3^- and NH_4^+ accumulation in the forest floor and forest biomass. Therefore only total NO_3^- and NH_4^+ values are presented.

stantial impact on the overall hydrogen ion budget. The hydroxyl ion supplied to the ecosystem by sulfate assimilation more than offsets the hydrogen ion generated by reduced sulfur oxidation.

Ammonia which neutralized hydrogen ion in precipitation, will ultimately release this hydrogen ion back into the ecosystem, as ammonia is assimilated into the biomass of the ecosystem. The mean annual input of ammonium is 2.3 kg N ha^{-1} yr^{-1} (Likens et al., 1977); if this quantity were entirely assimilated by forest biomass, 161 eq H^+ ha^{-1} yr^{-1} would be generated within the ecosystem. It is noteworthy that ammonium uptake by forest biomass may occur via two mechanisms: direct ammonium uptake (eq. 1)

$$NH_4^+ + R = R{-}NH_3 \text{ (organic nitrogen)} + H^+ \quad (1)$$

or ammonium oxidation (nitrification, eq. 2) and nitrate uptake (eq. 3).

$$NH_4 + 2O_2 = NO_3^- + 2H^+ + H_2O \quad (2)$$

$$NO_3^- + H^+ + H_2O + R = R{-}NH_3 \text{ (organic nitrogen)} + 2O_2 \quad (3)$$

$$NH_4^+ + R = R{-}NH_3 \text{ (organic nitrogen)} + H^+ \quad (4)$$

overall reaction

The net reaction is identical for either pathway (eqs. 1 and 4); so the specific pathway of ammonium assimilation is not important when accounting for the contribution to the overall hydrogen ion budget.

When computing the nitrogen cycle components of the hydrogen ion budget, it was assumed, as suggested by Bormann et al. (1977), that 14.7 kg N ha^{-1} yr^{-1} entered the ecosystem through nitrogen fixation. This flux was not directly measured, but was calculated by the difference needed to complete a mass balance for the nitrogen cycle of the Hubbard Brook Experimental Forest. If this nitrogen input was due to $(NH_4)_2SO_4$ aerosols rather than nitrogen fixation, there would be a profound effect on the hydrogen ion budget computations. The reason for this is that atmospheric inputs via nitrogen fixation reactions do not directly generate or consume hydrogen ion (Garrels et al., 1975) while ammonium inputs ultimately become a proton source upon biological uptake of ammonia nitrogen (eq. 1). If the 14.7 kg N ha^{-1} yr^{-1} were attributed to $(NH_4)_2SO_4$ aerosol inputs, an additional 1050 eq H^+ ha^{-1} yr^{-1} of hydrogen ion would be generated within the ecosystem, thus placing the budget considerably out of balance. By similar reasoning, if this input were attributed to dry deposition of $(NH_4)NO_3$, there would be no change in the hydrogen ion budget (eqs. 1 and 3). However, this assumes that the biota of the ecosystem does not preferentially assimilate either ammonium or nitrate, nitrogen sources.

It is evident that calcium cycling is a very important component of the ecosystem hydrogen ion cycle. Calcium weathering reactions represent 44% of the total reactions consuming hydrogen ion within the ecosystem. Net calcium accumulation in the forest floor and forest biomass represents 19% of the supply of hydrogen ion for the ecosystem.

4. Perturbations affecting the hydrogen ion budget

With a hydrogen ion budget for the ecosystem, a logical extension is to project how changes in atmospheric loadings of hydrogen ion would alter the export of hydrogen ion from the ecosystem (stream pH). To make such predictions, it is necessary to make some assumptions concerning the response of a forested ecosystem to increases and decreases in atmospheric hydrogen ion inputs. These assumptions are:

1. The organic mass of the vegetation and forest floor will accumulate the loadings of nitrate and sulfate associated with changes in atmospheric hydrogen ion inputs to the same degree as at present. Nitrogen and sulfur budgets for HBEF indicate that 80% of the nitrogen and 10% of the sulfur annually entering the ecosystem are stored in forest vegetation or in the forest floor.

The fact that 80% of the input nitrogen is assimilated implies that nitrogen is a limiting nutrient. Therefore, it is reasonable to assume that changes in nitrogen loading will be assimilated to the degree that they currently are. Sulfur inputs are assimilated to a lesser extent. It is difficult to state with confidence the degree to which changes in sulfur loading will be assimilated. In addition to being a nutrient, sulfate–sulfur has a high affinity for hydrous aluminum and iron oxides, abundant in the forest soils of HBEF. Therefore several mechanisms may control sulfur export from the watershed ecosystem. Little is known about the specifics

of sulfur transformations during perturbations to a forest ecosystem. So while the ambient level accumulation assumption is not entirely satisfactory it is the best we currently have available.

2. Changes in the input of atmospheric sources of hydrogen ion will not alter the degree to which the forest floor and vegetation accumulate other nutrients (e.g. Ca^{++}, NH_4^+, Fe).

3. Projected changes in hydrogen ion loading will not alter the extent of mineral weathering, with the exception of aluminum dissolution. Evidence that weathering rates have not increased due to increased atmospheric hydrogen ion inputs has been suggested for Hubbard Brook (Johnson et al., 1981), as well as for Norway (Henriksen, 1979) and through long-term water quality data for Hinkley Reservoir, a water body in the Adirondack region of New York State (Schofield, 1977). However, in the Canadian Shield area of Ontario, it appears that weathering rates have increased due to increased atmospheric inputs of acid (Dillon et al., 1980).

4. Aluminum dissolution is controlled by an aluminum trihydroxide ($Al(OH)_3$) mineral phase. Aquo aluminum levels in the Falls Brook drainage of the Hubbard Brook Experiment Forest, appear to be controlled by an aluminum trihydroxide phase (Johnson et al., 1981). A mean ion activity quotient of

$$\frac{\{Al^{+3}\}}{\{H^+\}^3} = 10^{8.66}$$

was observed for this system. This model is considered to be the most appropriate for the Hubbard Brook system (Johnson et al., 1981).

5. Thermodynamic equilibrium relationships for aluminum–fluoride and sulfate complexation suggested by Burrows (1977) and for soluble aluminum hydroxide complexation suggested by May et al. (1979) are valid for the aqueous system.

6. Aqueous fluoride levels observed for Falls Brook (0.05 mg F/l; Johnson et al., 1981) are realistic for streams throughout the Hubbard Brook Experimental Forest.

7. The stream water is in equilibrium with 400 p.p.m. atmospheric CO_2. This value is slightly in excess of the 316 p.p.m. of atmospheric CO_2 usually utilized in equilibrium models (Stumm and Morgan, 1970). However, this value appears to be a reasonable average value for a temperate forest ecosystem (Woodwell and Botkin, 1970).

8. The aqueous aluminum levels (0.24 mg Al/l) for the HBEF (Likens et al., 1977) were supersaturated with respect to the aluminum trihydroxide model. To account for this supersaturation, 0.13 mg Al/l was assumed to be complexed with organic ligands that might not readily participate in hydrolysis reactions (Driscoll, 1980). Comparable estimates for organically complexed aluminum have been observed in Falls Brook (Johnson et al., 1981).

9. The weighted annual mean temperature of the stream system is 7°C.

10. Of the 132.2 cm of precipitation that falls on each unit area of watershed annually 62% (83.3 cm) is exported from the ecosystem through streamflow, the balance (48.9 cm) is lost from the system through evapotranspiration (Likens et al., 1977).

To estimate changes in water quality due to changes in hydrogen ion loading, a modified chemical equilibrium model (Westall et al., 1976) was utilized. The model was incrementally titrated with strong acid or strong base corresponding to the incremental change in hydrogen ion loading. Inputs were concentrated due to evapotranspiration. pH and total aluminum values for stream water were determined for various loadings from these calculations.

Ambient precipitation inputs of atmospheric hydrogen ion are 960 eq H^+ ha^{-1} yr^{-1}. These loadings correspond to an annual mean hydrogen ion concentration in precipitation of 72.4 μeq/l (pH 4.14) for an annual precipitation of 132.2 cm (Likens et al., 1977).

Three changes in precipitation loading of hydrogen ion to the ecosystem were examined. These changes were made as nitric acid, as sulfuric acid and as a combination of nitric and sulfuric acids corresponding to the ambient stoichiometry in precipitation. The magnitude of these hydrogen ion loading changes ranged from a 50% increase, to the lowest possible decrease based on the concentration of nitrate and sulfate in ambient precipitation (Fig. 3). Similar calculations can be made for changes in total acidic (wet and dry) deposition to HBEF.

It is apparent from these scenarios that the form of the acid input is important in the response of stream water quality to changes in hydrogen ion

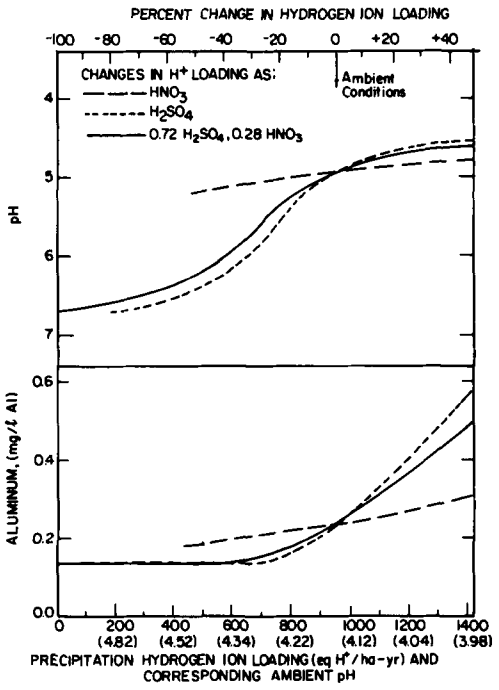

Fig. 3. Projected changes in annual weighted mean streamwater pH and aluminum concentration for changes in hydrogen ion loading through precipitation (132.3 cm, annual average). These changes were calculated as if the change in loading occurred as only nitric acid, only sulfuric acid and a combination of nitric and sulfuric acid corresponding to the ambient stoichiometry of Hubbard Brook precipitation. The lower limits of decreases in HNO_3 and H_2SO_4 loading are governed by average concentrations of nitrate and sulfate in ambient precipitation. The abscissa is expressed as hydrogen ion loading in precipitation (eq H^+ ha^{-1} yr^{-1}), ambient precipitation pH and percent change in precipitation hydrogen ion loading.

inputs. This forest ecosystem has a relatively high affinity for nitrogen and a relatively low affinity for sulfur (Likens et al., 1977). Increased inputs of nitrate nitrogen will be readily assimilated into the forest system releasing hydroxyl ion that will partially neutralize the associated hydrogen ion. Conversely, sulfate is relatively conservative and will be more readily exported from this forest ecosystem. Therefore sulfate assimilation will only slightly diminish the associated levels of hydrogen ion in inputs of sulfuric acid.

Another important consideration of these calculations is the role of aluminum in the buffering of hydrogen ion in this ecosystem. Because of the low pH of the aqueous environment, the carbonate buffering system is not as significant as it is in higher ionic strength waters. Aluminum trihydroxide is a very strong buffer and limits the export of hydrogen ion from these watershed ecosystems. However, the increased loading of hydrogen ion results in a potential problem: the mobilization of aluminum from the edaphic to the aquatic environment. Elevated levels of aqueous aluminum have been shown to have deleterious effects on fish populations (Schofield and Trojnar, 1980; Driscoll et al., 1980).

While it is virtually impossible to verify this model, it is useful to compare it against an individual year of elevated hydrogen ion loading. For the Hubbard Brook Experimental Forest, 1970–71 was such a year; there was a 30% increase in hydrogen ion loading (1180 eq H^+ ha^{-1} yr^{-1} for a 126 cm precipitation year, 94 μeq/l, pH 4.03) as compared to average conditions (960 eq H^+ ha^{-1} yr^{-1} for the average 132.2 cm precipitation year, 72.4 μeq/l, pH 4.14). The problem with such a comparison lies with determining the anion(s) associated with this increase in hydrogen ion loading. When comparing the weighted mean anion concentration in precipitation for the average year with the 1970–71 year there was less in sulfate (60.4 μeq/l to 57.3 μeq/l) and more in nitrate (23.7 μeq/l to 27.7 μeq/l) and chloride (13.2 μeq/l to 24.7 μeq/l). Based on these differences in anion composition it might be reasonable to first assume that the increased loading would be due to HNO_3 rather than H_2SO_4 inputs. With this assumption the predicted annual weighted mean stream pH for 1970–71 would be 4.82; in actuality it was 4.75. If the increase in hydrogen ion loading was attributed to more conservative anions like sulfate or perhaps more likely chloride, the model would predict corresponding lower stream pH values. If this 30% increase (1970–71) in hydrogen ion loading was due to H_2SO_4 inputs the predicted pH would be 4.63. Unfortunately aluminum determinations for stream water were not made for 1970–71 and therefore no comparisons could be made.

Little is known about ecosystem response to changes in hydrogen ion loading. Therefore the results presented from these perturbations are speculative. However, we believe this analysis provides a conceptual framework through which

changes in hydrogen ion loading to an ecosystem may be qualitatively evaluated.

5. Limitations of the budget

While such calculations are interesting and provide some insight into mechanisms within the ecosystem, it is important to realize the limitations of this budget. Johnson et al. (1981), in a recent study of water chemistry of a 1st through 3rd order stream, at Hubbard Brook observed profound spatial variations in the water chemistry through stream order. Solution chemistry of headwater sites was dominated by acid cations (H^+, Al); basic cations (Ca^{++}, Mg^{++}, Na^+, K^+) increased in concentration in progressively higher stream orders with a corresponding decrease in acid cation levels. This study suggests that the relative magnitude of the individual components that comprise a hydrogen ion budget would be significantly influenced by the spatial position of the ecosystem boundary.

To illustrate, consider a small watershed, typical of the Hubbard Brook Experimental Forest that borders on a divide and has a stream draining it (Fig. 4). To compile an input–output budget for the ecosystem it is necessary to monitor the ecosystem inputs, which are predominantly atmospheric in origin, as well as the exports, which occur predominantly via streamflow. The chemical inputs are evenly distributed over the watershed. Thus spatial variations of inputs are minimal, but such is not the case for outputs. Consider two stream export monitoring sites (and therefore two ecosystem boundaries) as suggested in Fig. 4. The first (1) is a headwater site, and would be characterized by a short hydrologic retention time, due to elevation as well as the thin, porous, poorly developed soils, characteristic of high elevation systems. Because of the short retention time, the stream chemistry and ecosystem export would be characterized by high levels of acidic cations and low levels of basic cations. Conversely if the watershed boundaries were increased by moving the stream monitoring site to a lower elevation, site 2 (Fig. 4), the stream chemistry might be different (Johnson et al., 1981). Deeper soils and lower slopes increase in importance as watershed area increases.

If a hydrogen ion budget were compiled for each of these ecosystems, the results might be different.

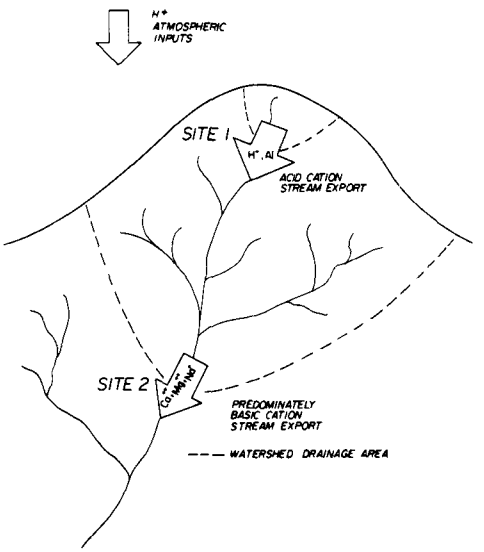

Fig. 4. The influence of watershed drainage area on the hydrogen ion budget. In a headwater watershed (site 1) there is significant export of acid cations (H^+ and Al). The hydrogen ion budget for such an ecosystem would be significantly influenced by atmospheric inputs of hydrogen ion. Over a larger watershed drainage area (site 2) atmospheric inputs of hydrogen ion are insignificant when compared with the internal cycling of hydrogen ion within the ecosystem.

The headwater system (1) would be strongly influenced by atmospheric hydrogen ion inputs, and this would be realized by the export of acid cations. As the drainage area and therefore hydrologic retention time of the watershed increases, the magnitude of hydrogen ion consuming and generating reactions with the ecosystem also increases, thus effectively ameliorating the inputs of atmospheric hydrogen ion to the overall hydrogen ion budget.

While the budget present in Fig. 2 is valid, it should be noted that the relative contribution of the individual components in the budget for a watershed ecosystem may shift, with a shift in watershed boundary. Thus watershed ecosystems that are most strongly influenced by the atmospheric contribution of hydrogen ion are headwater systems with small drainage areas. Larger watershed ecosystems that include more area with deeper soils and lower slopes will be less affected.

Seasonal variations in the hydrogen ion cycle are not considered in this analysis. However, it is well

established that there are large temporal variations in the export of chemical solutes from the Hubbard Brook Experimental Forest (Likens et al., 1977). The largest export of most major chemical constituents occurs during the months of March, April, and May because this is a period of substantial hydrological export (snowmelt) as well as a period of relative biological inactivity. While the present budget is computed for a year, seasonal variations in ecosystem activity should not be disregarded.

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