

## Heterogeneous geochemistry of catchment acidification

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**Abstract**—Many ions in catchment runoff are primarily controlled by heterogeneous reactions. The mass law governing heterogeneous equilibria leads directly to a simple, general expression for catchment acid buffering, which can be estimated from bulk catchment runoff composition. This analysis requires no particular assumptions or data regarding catchment minerals, water flowpaths, reaction pathways, or equilibrium constants. Thus, a catchment's vulnerability to acidification can be assessed directly from its runoff chemistry.

Critical tests using data from four intensively studied catchments (Hubbard Brook, USA, and Sogndal, Risdalsheia, and Birkenes, Norway) reveal catchment-scale buffering behavior that is quantitatively comparable to that predicted from bulk runoff composition. Theoretical predictions and field data both indicate that reversing acidification at the acidified Norwegian catchments would require large decreases in sulfate concentrations.

Long-term acidification will occur where leaching of base cations, accelerated by acid anion loading, exceeds resupply from mineral weathering. Where the rate of depletion of adsorbed base cations can be estimated, the resulting acidification of runoff can be predicted analytically. Base cation leaching, partly offset by mineral weathering and acting in conjunction with declining acid anion loading, appears responsible for the long-term decline in base cation concentrations at Hubbard Brook.

A general method is proposed for evaluating the effects of spatial variability in catchment buffering mechanisms. Spatially averaged catchment runoff will generally yield whole-catchment buffering predictions that closely approximate the spatially averaged buffering properties of a collection of geochemically diverse source regions. Mechanistic prediction of catchment buffering does not require identifying discrete source regions, characterizing their individual geochemical properties, or tracing the hydrologic flowpaths that connect them. This considerably simplifies the problem of predicting whole-catchment buffering behavior.

### INTRODUCTION

ANTHROPOGENIC ACID DEPOSITION has been implicated in the acidification of lakes and streams in large regions of North America and northern Europe; the resulting chemical changes in surface waters have damaged some aquatic ecosystems (HAINES, 1986; SCHINDLER, 1988). Since the 1970s, when surface water acidification became widely recognized, considerable research effort has been directed toward understanding how anthropogenic acids affect lakes and streams, and toward predicting how surface waters would respond to future changes in acid loading.

Over the past decade, a substantial scientific consensus has emerged concerning major mechanisms by which acid deposition is thought to affect surface water chemistry. Sulfate and nitrate ions in deposition are evapoconcentrated in runoff, unless adsorbed or reduced in soils and sediments, or taken up by biomass (BAKER et al., 1985; SCHINDLER et al., 1986). As these "mobile anions" (JOHNSON and COLE, 1977; SEIP, 1980) move through catchment soils and tills, some of their accompanying hydrogen ions will be neutralized by bicarbonate, or removed from solution (and replaced by base cations or aluminum ions) via ion exchange or mineral weathering reactions (REUSS et al., 1987). Thus, increases in acid anion loading will be accompanied, to varying degrees, by reductions in bicarbonate and increases in runoff concentrations of hydrogen ions, aluminum ions, and base cations (HENRIKSEN, 1984). If base cation production by mineral

weathering cannot keep pace with leaching by acid anions (or uptake by aggrading biomass), base cations will be gradually depleted from catchment ion-exchange media and replaced by aluminum or hydrogen ions. As base cations become depleted from soils and thus less available to runoff, both soils and runoff will acidify (GALLOWAY et al., 1983; REUSS and JOHNSON, 1986). This consensus view has been embodied, to various degrees, in a wide variety of computer simulation models used to analyze the effects of changing acid deposition on surface water quality (e.g., CHRISTOPHERSEN et al., 1982; GHERINI et al., 1985; COSBY et al., 1985a; SCHNOOR et al., 1984).

However, despite the scientific consensus outlined above, and despite the environmental, economic, and political importance of surface water acidification and of proposed control measures, the goal of developing a testable, physically based, widely applicable a priori method for predicting catchment sensitivity to acidification has remained elusive (REUSS and JOHNSON, 1986; COSBY et al., 1986; LEE et al., 1990; HOOPER et al., 1990). The relative importance of various buffering mechanisms differs from one catchment to another, making development of general models difficult. Typical catchment simulation models (e.g., CHRISTOPHERSEN et al., 1982; GHERINI et al., 1985; COSBY et al., 1985a; NIKOLAIDIS et al., 1988) are complex and are calibrated to reproduce observed trends in chemical data by adjusting free coefficients, such as unmeasured reaction constants or hydrologic parameters. Because the flexibility introduced by

these free coefficients exceeds the power of typical data sets to constrain them (COSBY et al., 1985a; BECK et al., 1990; HOOPER et al., 1988), the resulting model predictions generally have large uncertainties (COSBY et al., 1986; EARY et al., 1989; LEE et al., 1990), and model validity is difficult to test (HOOPER et al., 1990; DE GROSBOIS et al., 1988). The complexity of typical catchment models also hinders their use outside the few catchments where large calibration data sets exist.

Here, I propose that much of the buffering behavior observed in acid-sensitive catchments (and embodied, to greater or lesser degree, in various simulation models) can be predicted a priori from a very general theoretical analysis. Because catchment buffering reactions are, to first approximation, heterogeneous equilibria (i.e., equilibria between the aqueous phase and solid, gas, or adsorbed phases), there are simple functional relationships between a catchment's average runoff chemistry and its response to changes in acid anion concentrations. Here, I derive these functional relationships and illustrate how they can be applied. My intent is not to challenge the general consensus outlined above. Rather, I intend to show that this consensus view is consistent with a more general analysis and to demonstrate how that analysis yields explicit quantitative measures of catchment acidification sensitivity that are simple, general, widely applicable, easily interpreted, amenable to critical falsification tests, and predictively useful.

The charge balance for typical acid-sensitive waters can be written as:

$$2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{OA}^-] = 2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] + 3[\text{Al}^{+3}] + 2[\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] + 2[\text{AlF}^{+2}] + [\text{AlF}_2^+] - [\text{HCO}_3^-] - [\text{OH}^-] - [\text{F}^-] + \dots \quad (1)$$

by gathering together, on the left-hand side, the strong acid anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ ) and organic anions ( $\text{OA}^-$ ). These mobile anions are considered the driving agents of runoff acidification in the analysis that follows. One objective of this analysis is to predict how the species on the right-hand side of Eqn. (1) will respond when atmospheric deposition, or internal catchment biogeochemical processes, alter the acid anion concentrations on the left-hand side. Another objective is to predict how the right-hand side of Eqn. (1) will be affected if mineral weathering cannot keep pace with base cation losses from the catchment, and adsorbed base cations become depleted. Equation (1) can be condensed as

$$\Sigma \text{acids} = \text{SBC} + [\text{H}^+] + \Sigma \text{Al}_i - [\text{HCO}_3^-] - [\text{OH}^-] - [\text{F}^-] + \dots, \quad (2)$$

where

$$\begin{aligned} \Sigma \text{acids} &= 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{OA}^-], \\ \text{SBC} &= 2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+], \\ \Sigma \text{Al}_i &= 3[\text{Al}^{+3}] + 2[\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] + 2[\text{AlF}^{+2}] + [\text{AlF}_2^+], \quad (3) \end{aligned}$$

and where the ellipsis indicates that additional weak acids and bases may be present. To the extent that increases in acid anions ( $\Sigma \text{acids}$ ) are not offset by shifts in the sum of base cations (SBC), they will decrease the bicarbonate alkalinity of runoff and increase its concentrations of inorganic aluminum ( $\Sigma \text{Al}_i$ ) and hydrogen ions, the principal agents of biological damage in aquatic ecosystems (DRISCOLL et al., 1980; SCHINDLER et al., 1985; SCHINDLER, 1988). Thus, runoff sensitivity to this "direct acidification" will depend on how catchment response to increases in  $\Sigma \text{acids}$  is distributed among the ions on the right-hand side of Eqn. (2) (HENRIKSEN, 1984).

Here, I derive a simple, general function expressing catchment sensitivity to direct acidification, based on the heterogeneous (i.e., mixed-phase) character of the reactions controlling runoff chemistry. This function can be estimated directly from the bulk composition of runoff (and, in alkaline catchments, the partial pressure of  $\text{CO}_2$  in the soil porewaters). I use data from four intensively studied catchments to show that this analysis accurately predicts how runoff base cation, hydrogen ion, and inorganic aluminum concentrations will shift as acid anion concentrations change. These results are demonstrably insensitive to spatial heterogeneity in catchment geochemical properties and to errors in measurement or speciation of minor components of the charge balance. These predictions do not require that hydrologic flowpaths be known or predicted, that catchment buffering reactions be specified, or that reaction constants be chosen. Thus, a catchment's runoff chemistry can be used to directly infer its sensitivity to acidification.

Long-term acidification will also occur where leaching of base cations, accelerated by high acid loading, exceeds re-supply from mineral weathering (GALLOWAY et al., 1983; KIRCHNER, 1990). Under such "progressive acidification," the catchment's stock of adsorbed bases accessible to runoff can become depleted, leading to chronic acidification, even when acid loading is constant or declining (KIRCHNER, 1990). Where the net leaching of adsorbed bases can be estimated, this analysis can be extended to predict the resulting progressive acidification of runoff. Using the long-term stream chemistry record at Hubbard Brook, I show that these predictions are quantitatively reasonable.

A table of symbols is provided in Appendix 3.

### BUFFERING BY HETEROGENEOUS EQUILIBRIA

I begin with the premise that to first approximation and in the short term, the main chemical constituents in runoff from acid-sensitive catchments are controlled in one of two ways. First, the acid anions on the left-hand side of Eqn. (1) are largely controlled by atmospheric deposition, biomass nitrate uptake, decomposition of organic matter, and, in some catchments, sulfate adsorption by soils. The processes controlling these "external species" are outside the domain of my analysis, which will take the concentrations of these mobile anions as given. Second, I hypothesize that the major components on the right-hand side are primarily controlled, directly or indirectly, by equilibria with solid, adsorbed, and gas phases (i.e., heterogeneous equilibria). The cations, for example, may participate in ion exchange reactions with ad-

sorbed phases or may be controlled by the solubility of various minerals. Bicarbonate is controlled by equilibrium with CO<sub>2</sub> gas. All of these ions are linked, via hydrolysis or ion exchange, with pH. Thus, to first approximation, the ions on the right-hand side of Eqn. (1) can be considered as a set of mutually interacting species controlled by heterogeneous reactions (here termed a "heterogeneous system").

I denote this heterogeneous system by  $n$  species with molar concentrations  $C_i$  and valences  $z_i$ ,  $i = 1 \dots n$  and rewrite Eqn. (1) as

$$\Sigma acids = \sum_{i=1}^n z_i C_i. \quad (4)$$

If the concentrations  $C_i$  are controlled by heterogeneous, mass-law equilibria, then the activities of any two ions  $j$  and  $k$  are related by the expression:

$$\gamma_j C_j = K_{j,k} (\gamma_k C_k)^{z_j/z_k}, \quad (5)$$

where the  $\gamma$ s are single-ion activity coefficients, and the reaction constant  $K_{j,k}$  subsumes the thermodynamic equilibrium constant, the activity of the nonaqueous phase, and any intermediate reactions. (Note that in a heterogeneous system, Eqn. (5) applies, not only to ion pairs that react directly with a nonaqueous phase, but, by subsuming intermediate reactions, to every pair of ions in the interacting set.) In the short term, the activities of nonaqueous phases can be considered approximately constant. If the solution composition shifts incrementally, changes in the activity coefficients will be negligible. The relative shift in the two concentrations is thus, from Eqn. (5),

$$\frac{\partial C_j}{\partial C_k} = \frac{z_j}{z_k} \frac{C_j}{C_k}. \quad (6)$$

Equation (6) says that when equilibria shift in a heterogeneous system, the percentage change in the concentration of each ion will be proportional to its valence. Thus, under heterogeneous equilibrium, ion ratios do not remain constant; instead, the ratio between two ions' concentrations will shift in proportion to the ratio of their valences. A homogeneous, aqueous phase reaction will also obey Eqns. (5) and (6) if the concentrations of any reactants other than ions  $j$  and  $k$  are either fixed, or so large compared to  $C_j$  and  $C_k$  that the reaction's effect on them is trivial. Thus, for example, H<sup>+</sup> and OH<sup>-</sup> will satisfy Eqn. (6) because the concentration of their (homogeneous) reaction product, H<sub>2</sub>O, will not be materially affected by reactions between them.

This is an equilibrium analysis, but equilibrium need not prevail in all possible reactions. For example, on the time scale of interest (the residence time of water in typical catchments), many silicate mineral weathering reactions will not approach equilibrium. My analysis assumes only that on appropriate time scales, all heterogeneous reactions either are close enough to equilibrium that Eqn. (6) applies, or are far from equilibrium and do not directly affect the equilibrium relationships. (Kinetically limited, disequilibrium weathering reactions may affect the mass balances of base cations and, thus, indirectly influence the activity of adsorbed bases over time; I develop methods for treating the effects of base cation depletion below).

Now, how will changes in  $\Sigma acids$  be partitioned within the heterogeneous system? How much would such changes affect the concentration of, say, the  $j^{\text{th}}$  ion? Under heterogeneous equilibrium, percentage shifts in concentration must be proportional to valence (Eqn. 6), but the sum of all shifts in concentration must preserve electroneutrality (Eqn. 4). Differentiating Eqn. (4), and applying Eqn. (6) throughout, one can express the relative shifts in  $C_j$  and  $\Sigma acids$  ( $dC_j/d\Sigma acids$ , here also called  $f_j$  for brevity) as:

$$d\Sigma acids = \sum_{i=1}^n z_i \frac{\partial C_i}{\partial C_j} dC_j = \frac{\sum_{i=1}^n z_i^2 C_i}{z_j C_j} dC_j, \quad (7)$$

or

$$f_j = \frac{dC_j}{d\Sigma acids} = \frac{z_j C_j}{\sum_{i=1}^n z_i^2 C_i} = \frac{z_j C_j}{h}, \quad (8)$$

where the buffer term  $h$ ,

$$h = \sum_{i=1}^n z_i^2 C_i, \quad (9)$$

encompasses the  $n$  members of the heterogeneous system, that is, the members of the right-hand side of Eqn. (2). Equation (8) says that each ion in the heterogeneous system responds to shifts in  $\Sigma acids$  in proportion to its concentration and valence, with all ions' shifts normalized by the buffer term  $h$ . Here, valence is a signed quantity; for an increase in  $\Sigma acids$ , concentrations of cations in the heterogeneous system will increase and anion concentrations will decrease. Equation (8) directly implies that shifts in  $\Sigma acids$  will primarily be accommodated within the heterogeneous system by ions with high concentrations and large valences, rather than by large shifts in minor ions.

The interaction ratios  $f_j$  (Eqn. 8) can be summed to express the effect of changes in  $\Sigma acids$  on various combinations of ion concentrations, such as the sum of base cations (SBC),

$$F_{\text{SBC}} = \frac{d\text{SBC}}{d\Sigma acids} = \frac{4[\text{Ca}^{+2}] + 4[\text{Mg}^{+2}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+]}{h}. \quad (10)$$

Here, because SBC is an equivalent sum rather than a molar sum, the coefficients in the numerator are  $z_j^2$  (when measured in equivalents, each ion in a heterogeneous system shifts in proportion to its contribution to the heterogeneous buffer term  $h$ ). Because its derivation is general, Eqn. (8) applies to all ions in the heterogeneous system, including hydrogen ions, trivalent aluminum ions, or the sum of inorganic aluminum species ( $\Sigma \text{Al}_i$ , here given in equivalents),

$$F_{\Sigma \text{Al}_i} = \frac{d\Sigma \text{Al}_i}{d\Sigma acids} = \frac{9[\text{Al}^{3+}] + 4[\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] + 4[\text{AlF}^{+2}] + [\text{AlF}_2^+]}{h}. \quad (11)$$

In typical natural waters, the titratable acid neutralizing capacity (ANC) can be expressed as (GALLOWAY et al., 1984):

$$\text{ANC} \approx \text{SBC} + 3([\text{Al}^{+3}] + [\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] - \Sigma \text{acids}), \quad (12)$$

unless organic anion concentrations are large (HEMOND, 1990). (Here, ANC is operationally defined as the result of the standard acidimetric titration procedure; ANC differs from the alkalinity, Alk, because weak acids may be protonated before the titration endpoint is reached.) If organic anion concentrations are small or are relatively constant, from Eqn. (12) one can solve directly for the effect of acid anion shifts on runoff ANC,

$$F_{\text{ANC}} = \frac{d\text{ANC}}{d\Sigma \text{acids}} \approx \frac{4[\text{Ca}^{+2}] + 4[\text{Mg}^{+2}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + 9[\text{Al}^{+3}] + 6[\text{Al}(\text{OH})^{+2}] + 3[\text{Al}(\text{OH})_2^+]}{h} - 1. \quad (13)$$

Finally, Eqn. (8) can be extended straightforwardly to derive the familiar buffer intensity (MOREL et al., 1976) of the heterogeneous system, illustrating the effect of  $\Sigma \text{acids}$  on the solution pH:

$$F_{\text{pH}} = \frac{d\text{pH}}{d\Sigma \text{acids}} = \frac{-\log_{10} e}{[\text{H}^+]} \frac{d[\text{H}^+]}{d\Sigma \text{acids}} = \frac{-0.434}{h} = \frac{-1}{\beta_{\text{H}}}. \quad (14)$$

Because the predicted interaction ratios  $f_j$  are explicit functions, I can directly assess the effects of possible errors in measuring or speciating the concentrations  $C_i$ . Differentiating Eqn. (8), I observe that,

$$\frac{df_j}{f_j} = \left( 1 - \frac{z_j^2 C_j}{\sum_{i=1}^n z_i^2 C_i} \right) \frac{dC_j}{C_j}. \quad (15)$$

Thus, a given percentage error in the concentration  $C_j$  will result in an equal or smaller percentage error in the associated interaction ratio  $f_j$ ; the error is smaller for species that make up a large fraction of the heterogeneous buffer factor  $h$ . Percentage errors in the concentrations  $C_k$  of other ions  $k$ ,  $k \neq j$ , will result in smaller percentage errors in the  $f_j$ . Again differentiating Eqn. (8),

$$\frac{df_j}{f_j} = - \frac{z_k^2 C_k}{\sum_{i=1}^n z_i^2 C_i} \frac{dC_k}{C_k}, \quad k \neq j. \quad (16)$$

Note that for species  $k$  that account for a small fraction of the heterogeneous system, even large percentage errors in the  $C_k$  will give rise to small percentage errors in the interaction ratios  $f_j$  estimated for other ions  $j$ . The percentage error in  $f_j$  will be smaller than the percentage error in  $C_k$  by the factor  $z_k^2 C_k / h$ . Thus, even large percentage errors in measuring or speciating a minor ion (for example, a particular aluminum hydroxide complex) will have very little effect on the inter-

action ratio  $f_j$  for a major ion (for example, calcium or magnesium). Acidification responses can therefore be predicted for major ions even if precise measurement of minor ions is impossible.

This analysis is based on the general proposition that an aqueous geochemical solution can be divided into two types of ions: those that are controlled by heterogeneous equilibrium (the heterogeneous system), and those that are controlled by other processes (the external species). If the sum of the external species is altered, charge balance (Eqn. 4) requires that the sum of the heterogeneous system will shift to compensate, and the constraints of heterogeneous equilibrium (Eqn. 6) jointly specify how this shift will be distributed within the heterogeneous system. The mobile acid anions,  $\Sigma \text{acids}$ , are grouped on the left-hand side of Eqn. (4), not because of their chemical properties as acid anions, but because they are external species, hypothesized to be controlled by mechanisms other than heterogeneous equilibrium. Another way of stating the hypothesis underlying this analysis is that the formal distinction between the heterogeneous system and the external species (which could be used to partition any aqueous system) corresponds, in acid-sensitive catchments, to a distinction between mobile acid anions and all other major species in runoff. The analysis above outlines how this hypothesis, if valid, would be useful in predicting catchment response to acid loading. Below, I use these predictions to test the validity of the hypothesis.

### Critical Test

Unlike typical catchment acidification models (CHRISTOPHERSEN et al., 1982; GOLDSTEIN et al., 1984; SCHNOOR et al., 1984), this analysis is not calibrated to match the observed buffering behavior of the catchment, as revealed by chemical time series. Such data can, therefore, be used in a critical test: Can one predict a priori, from the bulk composition of runoff and Eqns. (8)–(11), how runoff chemistry will change in response to variations in acid anion loading (as reflected in  $\Sigma \text{acids}$ )? Here, using data from four intensively studied catchments, I present such a test (Figs. 1–2).

In applying this analysis to real catchment data, two complications must be addressed. First, the heterogeneous system (and thus  $h$ ) includes a number of species that are usually not measured directly, such as aluminum complexes, organic anions, and bicarbonate. Concentrations of these species can be estimated from the typical suite of measurements, using various models of aqueous speciation and organic complexation (JOHNSON et al., 1981; SCHECHER and DRISCOLL, 1987; TIPPING et al., 1988; OLIVER et al., 1983).

Second, because the heterogeneous reactions primarily occur underground, the concentrations in Eqns. (4)–(14) should ideally be those of the catchment porewaters before they emerge as runoff. In porewaters, the partial pressure of carbon dioxide is often significantly greater than that in surface waters. When alkalinity is greater than roughly  $-10 \mu\text{equiv. l}^{-1}$  (and particularly when  $\text{Alk} > 10 \mu\text{equiv. l}^{-1}$ ), the pH of runoff increases markedly when it emerges to become surface water and releases dissolved carbon dioxide (NORTON and HENRIKSEN, 1983; REUSS and JOHNSON, 1986). Concentrations of “conservative” species, such as base

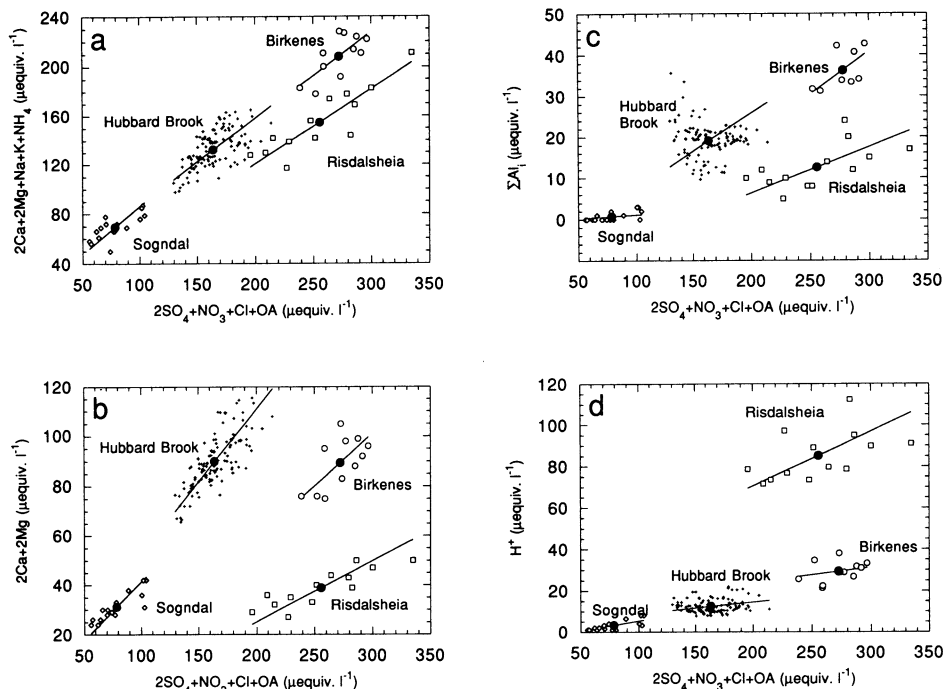


FIG. 1. Effect of sum of strong acid anions on cation concentrations (open symbols) in catchment runoff, compared to relationships predicted by Eqns. (8)–(11) from mean runoff composition (solid symbols) at each site (Tables 1 and 2). Hubbard Brook data are monthly means of weekly streamwater samples, 1971–1980 (Hubbard Brook Ecosystem Study, unpubl. data); one outlier deleted. Birkenes data are annual volume-weighted means, 1975–1988 (data missing in 1979, 1980, and 1984) (SFT, 1989). Sogndal and Risdalsheia data are volume-weighted means averaged over periods from three months to one year and include all periods and catchments reported by WRIGHT et al. (1988); 1984 Sogndal data excluded due to anomalously high sea salt inputs.

Lines show predicted slopes, not fitted trends. Slopes of fitted regression lines and reduced major axes given in Table 2 for comparison. Equation (8), if applied to all components of the heterogeneous system and integrated over a range of  $\Sigma acids$ , predicts slightly nonlinear relationship between  $C_j$  and  $\Sigma acids$ . For all ions shown, however, linear approximation (derived by extrapolating  $dC_j/d\Sigma acids$  from mean concentrations) deviates from nonlinear relationship by less than  $\pm 2 \mu\text{equiv. l}^{-1}$ .

cations, strong acid anions, and alkalinity, are usually preserved under this shift in pH, but bicarbonate,  $[\text{H}^+]$ , aluminum speciation, and organic complexation may change substantially. Thus, to apply this analysis to nonacidic runoff waters, speciation calculations should be corrected for the higher  $\text{CO}_2$  partial pressure prevailing in the porewater environment. Such a correction has been applied to all of the catchments considered here (see notes accompanying Table 1), but its effect is only significant at Sogndal, where runoff alkalinity is  $\approx 5 \mu\text{equiv. l}^{-1}$ .

Loss of dissolved  $\text{CO}_2$  may mean that concentration shifts for nonconservative ions in nonacidic runoff will differ from their interaction ratios  $f_j$  in the  $\text{CO}_2$ -rich porewaters. However, predicted responses of conservative quantities, such as base cations and alkalinity, will be similar in runoff and porewater, even at nonacidic sites such as Sogndal. And at sites with runoff pH below roughly 5,  $\text{CO}_2$  degassing will have little effect on pH (because only a small fraction of dissolved  $\text{CO}_2$  will be present as  $\text{HCO}_3^-$ ), so runoff and porewater responses of all species should be comparable.

Responses of SBC,  $[\text{Ca}] + [\text{Mg}]$ ,  $\Sigma\text{Al}_i$ , and  $[\text{H}^+]$  to variation in  $\Sigma acids$  at the study sites (Fig. 1; Table 2) are quantitatively comparable to those predicted by Eqn. (8). Note that the lines in Fig. 1 indicate the predicted relationship, not the slope of the data. Because the analysis tested here has

no adjustable parameters, this critical test is qualitatively different from the typical tests of calibrated catchment simulation models, which are epistemologically weak (DE GROSBOSIS et al., 1988; HOOPER et al., 1990).

At Birkenes, Norway (CHRISTOPHERSEN et al., 1982, 1990a; MULDER et al., 1990; FROGNER, 1990), and Hubbard Brook, USA (LIKENS et al., 1977; BORMANN and LIKENS, 1979; JOHNSON et al., 1981), variation in  $\Sigma acids$  reflects fluctuations in acid anion loading, including long-term declining trends in sulfate (CHRISTOPHERSEN et al., 1990b; DRISCOLL et al., 1989a). At Sogndal and Risdalsheia, Norway, ambient variation in acid and sea salt deposition was supplemented by experimental additions and exclusions of sulfate and nitrate by WRIGHT et al. (1988). At Sogndal, ambient deposition was augmented with dilute  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  at experimental catchments; controls received ambient deposition. At Risdalsheia, ambient acid deposition was excluded by a roof, with neutral precipitation added beneath; controls were an unroofed catchment, and a roofed catchment with ambient deposition recycled beneath.

That these changes in  $\Sigma acids$  will be accommodated by changes in cation concentrations (or organic anions and, in nonacid waters, bicarbonate) is obviously guaranteed by electroneutrality (Eqn. 2). What is not obvious, and what the heterogeneous equilibrium theory predicts a priori, is how

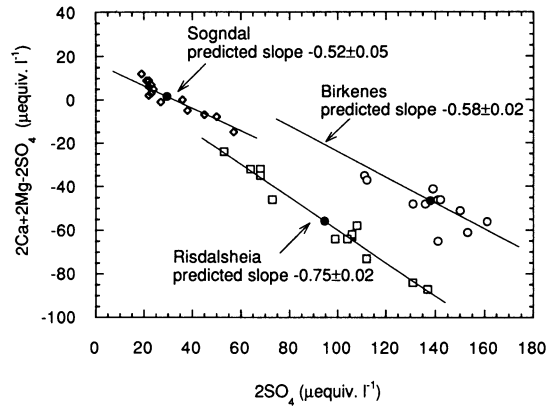


FIG. 2. Sum of calcium and magnesium minus sulfate, an approximate measure of runoff alkalinity (assuming sodium and chloride are roughly equal), as a function of runoff sulfate at Norwegian sites. Lines show relationship predicted by Eqn. (8) from mean runoff concentrations (solid symbols). Use of Eqn. (8) here assumes that changes in  $\text{SO}_4$  are uncorrelated with  $\text{Cl}$  or  $\text{NO}_3$ , and thus interpretable as comparable changes in  $\Sigma\text{acids}$ . Lines shown are predicted relationships, not fitted trends. Artificial correlation introduced by plotting  $\text{SO}_4$  on both axes (KENNEY, 1982) is small because  $\text{Ca} + \text{Mg}$  and  $\text{SO}_4$  are themselves highly correlated ( $0.87 \leq r \leq 0.92$  in all three data sets). A similar plot is not shown for Hubbard Brook data because in those data artificial correlation would be large.

these shifts will be partitioned among base cations, hydrogen ions, aluminum, and the other species making up the right-hand side of Eqn. (2). This partitioning is crucial; if increases in  $\Sigma\text{acids}$  are offset by increases in  $[\text{H}^+]$  or  $\Sigma\text{Al}$ , rather than SBC, they will acidify runoff. For example, although Risdalsheia receives deposition comparable to that at nearby Birkenes, it is both predicted and observed to have lower ability to offset increases in  $\Sigma\text{acids}$  with SBC (Fig. 1, Table 2); it consequently has substantially more acidic runoff (Table 1).

Because sea salt inputs are a major component of both base cations and acid anions at the three Norwegian sites, SBC and  $\Sigma\text{acids}$  could be correlated in Fig. 1 simply through variations in sea salt loading. However, only at Sogndal are SBC and chloride in runoff highly correlated ( $r = 0.76$ ); at Risdalsheia and Birkenes, the correlation is weaker ( $r = 0.38$  and  $0.34$ , respectively). Furthermore, when  $[\text{Ca}] + [\text{Mg}]$  alone is plotted as a function of  $\Sigma\text{acids}$ , both the collinearity of the data themselves, and their agreement with the theoretical predictions, are generally as close as when SBC is plotted against  $\Sigma\text{acids}$  (Fig. 1). Finally, the influence of sea salts can be excluded almost entirely by considering  $[\text{Ca}] + [\text{Mg}]$  as a function of sulfate alone (Fig. 2);  $[\text{Ca}] + [\text{Mg}]$  is much more tightly correlated with sulfate ( $r > 0.87$  at all three Norwegian sites) and nitrate ( $0.43 < r < 0.77$ ) than chloride ( $r < 0.17$ ).

This theoretical analysis presumes that the major constituents of catchment runoff (except for the mobile acid anions  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{OA}^-$ ) are controlled by heterogeneous reactions and that approximate equilibrium prevails in these reactions. I have adopted the premise of heterogeneous equilibrium as a working hypothesis rather than an established fact; it is conceivable that other processes, such as kinetically limited (disequilibrium) mineral dissolution, could control

runoff concentrations of some ions. The critical test performed here, however, shows that the heterogeneous equilibrium hypothesis yields a priori predictions of relationships between ion concentrations that are borne out by catchment runoff data (except where the data show very large scatter). Thus, the tentative hypothesis of heterogeneous equilibrium is strongly supported by the results of this critical test.

Table 1. Bulk runoff composition and calculated porewater speciation<sup>(a)</sup>

	Sogndal	Risdalsheia	Birkenes	Hubbard Brook
Measured runoff concentrations ( $\mu\text{mol l}^{-1}$ ) <sup>(b)</sup>				
pH	5.50±0.33	4.08±0.06	4.54±0.08	4.91±0.1
$\text{Ca}^{+2}$	10.6±2.1	7.7±1.5	27.8±3.1	31.6±3.8
$\text{Mg}^{+2}$	5.0±0.9	11.7±2.6	16.9±2.3	13.4±2.2
$\text{Na}^+$	35.9±7.9	93.6±14.4	112.7±9.4	36.5±8.5
$\text{K}^+$	1.9±1.4	7.2±2.8	6.1±2.3	5.0±2.5
$\text{NH}_4^+$	0.4±1.3	15.2±8.9	-	0.9±0.5
$\text{SO}_4^{2-}$	14.8±5.9	47.3±13.3	69.0±7.7	63.3±5.7
$\text{NO}_3^-$	1.4±1.6	29.2±20.5	8.6±3.9	22.3±19.1
$\text{Cl}^-$	33.6±9.3	108.6±15.0	117.6±17.2	13.7±3.4
$\text{F}_T$ <sup>(c)</sup>	1.0	2.0	4.0	3.7
$\text{Al}_T$ <sup>(f)</sup>	0.5±0.7	5.0±1.9	19.8±3.5	11.7±2.3
TOC ( $\text{mg l}^{-1}$ ) <sup>(d)</sup>	1.6±0.7	12.1±4.1	8.0	1.0
Derived porewater speciation ( $\mu\text{mol l}^{-1}$ ) <sup>(e)</sup>				
$\text{H}^+$	12.3±2.4	83.1±11.1	30.9±4.3	17.7±2.3
$\text{F}^-$ <sup>(f)</sup>	0.5±0.3	0.1±0.1	0.1±0.0	0.1±0.3
$\text{Al}^{+3}$ <sup>(f)</sup>	0.1±0.1	3.1±1.8	8.1±2.3	4.5±1.3
$\text{Al}(\text{OH})^{+2}$ <sup>(f)</sup>	<	0.1±0.1	0.8±0.2	0.8±0.2
$\text{Al}(\text{OH})_2^{+}$ <sup>(f)</sup>	<	<	0.1±0.0	0.2±0.1
$\text{AlF}_2^{+}$ <sup>(f)</sup>	0.3±0.2	1.8±0.1	3.7±0.1	3.3±0.3
$\text{AlF}_2^{+}$ <sup>(f)</sup>	0.1±0.0	0.1±0.0	0.1±0.0	0.1±0.0
$\text{AlO}_g$ <sup>(g)</sup>	-	-	7.2±1.3	2.9±0.6
$\text{HCO}_3^-$	15.5±3.9	2.4±0.3	6.4±0.9	11.1±1.3
$\text{OA}^-$ <sup>(h)</sup>	12.2±6.2	23.5±8.2	6.4±3.7	0.4±1.3

<sup>a</sup> Quantities given as mean±standard deviations; standard deviations omitted where only a single average estimate is available. Dashes indicate missing data; < indicates value less than 0.05.

<sup>b</sup> Measurements for Risdalsheia include all catchments and periods reported by Wright et al. (1988) and Frogner (1990); Sogndal data from 1984 excluded due to anomalously high seasalt inputs. Birkenes data are average of annual mean runoff concentrations, 1975-1988 (SFT, 1989). Hubbard Brook watershed 6 (geochemical reference catchment) measurements are average of monthly means, 1971-1980 (unpublished data, Hubbard Brook Ecosystem Study); one month with anomalous data excluded.

<sup>c</sup> Total fluorine ( $\text{F}_T$ ) values for Sogndal and Risdalsheia from R.F. Wright (pers. comm.), for Birkenes from Christophersen et al. (1990a), and for Hubbard Brook from Johnson et al. (1981).

<sup>d</sup> Total organic carbon (TOC) for Birkenes from Christophersen et al. (1990a); TOC value for Hubbard Brook (Likens et al., 1977) is dissolved organic carbon.

<sup>e</sup> Porewater composition estimated by varying pH until charge balance, given speciation described in (f)-(h) and assumed porewater conditions (temperature 10 °C, porewater  $p(\text{CO}_2)$  0.007 atm), equals charge balance achieved under assumed laboratory conditions (temperature 25 °C, effective  $p(\text{CO}_2)$  0.0007 atm). Except at Sogndal, predictions derived without correcting for porewater  $p(\text{CO}_2)$  agree with predictions from corrected speciation, within stated error bounds.

<sup>f</sup> Aluminum speciation calculated using equilibrium constants given by Schecher and Driscoll (1987) corrected to ambient temperature, with total aluminum ( $\text{Al}_T$ ) assumed conservative (Nordstrom and Ball, 1986). Complexation of Al by sulfate ignored; full speciation including  $\text{Al}(\text{SO}_4)$  complexes showed these never exceeded 4 percent of total Al.

<sup>g</sup> Organic complexes of Al ( $\text{AlO}_g$ ) calculated by the Backes and Tipping (1987) formula, using Tipping et al.'s (1988) Lake Hovvatn and Falls Brook coefficients for Birkenes and Hubbard Brook, respectively.  $\text{AlO}_g$  ignored for Risdalsheia and Sogndal, because total aluminum values for those catchments (Wright et al., 1988) exclude organic aluminum.

<sup>h</sup> Organic anions ( $\text{OA}^-$ ) calculated via Oliver et al. (1983) method, with carboxyl contents ( $\mu\text{equiv. per mg TOC}$  or  $\text{DOC}$ ) of 10.0, 3.5, 5.3, and 12.7 for Sogndal, Risdalsheia, Birkenes, and Hubbard Brook, respectively. These values chosen to yield approximate charge balance, on average, for speciations under laboratory conditions.

Table 2. Predicted and observed response to acid anion variation

	predicted <sup>(a)</sup>	observed		r <sup>2</sup>
		OLS <sup>(b)</sup>	RMA <sup>(c)</sup>	
<i>F<sub>SBC</sub> = dSBC/dΣacids</i>				
Sogndal	0.77±0.02	0.46±0.11	0.61±0.11	0.56
Risdalsheia	0.62±0.04	0.58±0.09	0.66±0.09	0.78
Birkenes	0.70±0.03	0.70±0.23	0.98±0.23	0.52
Hubbard Brook	0.72±0.05	0.56±0.06	0.88±0.06	0.41
<i>F<sub>Ca+Mg</sub> = d(2Ca+2Mg)/dΣacids</i>				
Sogndal	0.48±0.05	0.30±0.05	0.34±0.05	0.74
Risdalsheia	0.25±0.02	0.16±0.03	0.19±0.03	0.75
Birkenes	0.42±0.02	0.37±0.15	0.58±0.15	0.41
Hubbard Brook	0.58±0.04	0.46±0.04	0.60±0.04	0.59
<i>F<sub>ΣAl</sub> = dΣAl/dΣacids</i>				
Sogndal	0.02±0.02	0.04±0.01	0.07±0.01	0.44
Risdalsheia	0.11±0.04	0.08±0.03	0.13±0.03	0.38
Birkenes	0.21±0.03	0.27±0.11	0.41±0.11	0.42
Hubbard Brook	0.19±0.05	*	*	0.02
<i>F<sub>H</sub> = dH/dΣacids</i>				
Sogndal	0.09±0.02	0.11±0.03	0.15±0.03	0.58
Risdalsheia	0.26±0.04	0.15±0.08	0.30±0.08	0.26
Birkenes	0.07±0.01	0.11±0.09	0.28±0.09	0.14
Hubbard Brook	0.06±0.01	*	*	0.03

<sup>a</sup> Predictions calculated via Eqns. (8)-(11) from mean concentrations in Table 1. Error estimates shown are standard deviations of predictions calculated for individual data.

<sup>b</sup> Slope (mean±standard error) of Ordinary Least Squares regression of data points shown in Fig. 1. OLS regression estimates linear functional relationship in data. Regression slopes omitted for data with r<sup>2</sup> less than 0.1.

<sup>c</sup> Slope (mean±standard error) of Reduced Major Axis (Kermack and Haldane, 1950; Davis, 1986) of data points shown in Fig. 1. RMA method estimates linear structural relationship in data, and may be preferable to OLS where neither variable is controlled and both are subject to error (Mark and Church, 1977; Troutman and Williams, 1987).

### BASE CATION DEPLETION

Direct acidification by the mobile anion effect, as outlined and analyzed above, is not the only mechanism by which acid deposition may acidify runoff. In particular, long-term acidification will occur where leaching of base cations, accelerated by acid anion loading (BERGKVIST, 1986) or forest aggradation, exceeds resupply from mineral weathering. Generally, weathering of silicate minerals will not keep pace with cation leaching in acidified catchments (KIRCHNER, 1990, because silicate weathering rates are roughly proportional to [H<sup>+</sup>]<sup>0.5</sup> or [H<sup>+</sup>]<sup>1.0</sup> (WOLLAST and CHOU, 1988) whereas equilibrium porewater concentrations (and thus loss rates) of calcium and magnesium can be expected to scale as [H<sup>+</sup>]<sup>2</sup> (Eqn. 5). Thus, increases in acid loading can be expected to accelerate base cation leaching more than they accelerate silicate mineral weathering. As adsorbed bases become depleted from the catchment's cation-exchange media (FALKENGREN-GRERUP et al., 1986), long-term acidification of soils (TAMM and HALLBÄCKEN, 1986) and runoff (GALLOWAY et al., 1983) may result, even under acid loading that is constant or declining (KIRCHNER, 1990). The rate of this "progressive acidification" can be predicted by extending the methods outlined above.

Where the concentration  $C_i$  of an ion is affected both by direct acidification (from changes in acid anion loading) and by progressive acidification (from depletion of an adsorbed

base cation  $XC_j$ , where  $X$  denotes the adsorbed phase, and  $j$  may, but need not, be equal to  $i$ ), the combined effect of these mechanisms can be expressed generally as:

$$\frac{dC_i}{dt} = \frac{\partial C_i}{\partial \Sigma acids} \frac{d\Sigma acids}{dt} + \frac{\partial C_i}{\partial XC_j} \frac{dXC_j}{dt} \quad (17)$$

The first partial derivative is simply  $f_i$  (Eqn. 8); here I show how the latter partial derivative can be derived and applied.

In the theory developed above, I assumed that the activities of all nonaqueous phases remain constant. Because depletion of adsorbed bases changes the activities of the adsorbed phase, I relax that assumption here. In ion-exchange reactions, the reaction coefficient  $K_{j,k}$  in Eqn. (5) depends on the composition of the ion-exchange medium:

$$K_{j,k} = \kappa_{j,k} \frac{\{XC_j\}}{\{XC_k\}^{z_j/z_k}}, \quad (18)$$

where  $\kappa_{j,k}$  is the thermodynamic constant for the particular ion-exchange reaction, and  $\{XC_j\}$  is the activity of the adsorbed phase of the  $j^{\text{th}}$  ion, which can be related to its concentration  $XC_j$  by a number of different conventions (VANSELOW, 1932; GAINES and THOMAS, 1953). The complications introduced by these conventions can be subsumed in a coefficient, here called  $\alpha_{j,k}$ , and the effect of displacing the adsorbed phase of the  $j^{\text{th}}$  ion with the  $k^{\text{th}}$  ion can be expressed in nondimensional form as:

$$\frac{dK_{j,k}}{K_{j,k}} = \alpha_{j,k} \frac{dXC_j}{XC_j}, \quad (19)$$

where  $\alpha_{j,k}$  is a function of the ratio  $z_j/z_k$  and the composition of the adsorbed phase (Appendix 1). In the limit of  $XC_j \ll XC_k$ ,  $\alpha_{j,k}$  approaches unity; for replacement of a base cation  $j$  by an acid cation  $k$ ,  $0.9 < \alpha_{j,k} < 1.5$  for the low base saturation fractions (BSF < 0.2) typical of acid-sensitive catchments (Fig. 3). When the composition of the ion-exchange medium changes, the concentrations of the various aqueous ions can be expected to shift as well. The relationship between the shifts in the  $i^{\text{th}}$  and  $k^{\text{th}}$  ions is, from Eqns. (5) and (19),

$$\frac{dC_i}{C_i} = \delta_{ij} \alpha_{j,k} \frac{dXC_j}{XC_j} + \frac{z_i}{z_k} \frac{dC_k}{C_k}, \quad (20)$$

where  $\delta_{ij}$  is the Kronecker delta. The sum of these shifts over all  $i$ ,  $i = 1 \dots n$ , is constrained by charge balance (Eqn. 4), such that:

$$z_j C_j \alpha_{j,k} \frac{dXC_j}{XC_j} + \frac{\sum_{i=1}^n z_i^2 C_i}{z_k C_k} dC_k = d\Sigma acids. \quad (21)$$

Combining Eqns. (20) and (21) and rearranging terms yields the change in the  $i^{\text{th}}$  ion due to the combination of mobile anion effects and changes in the adsorbed phase of the  $j^{\text{th}}$  ion,

$$\frac{dC_i}{dt} = f_i \frac{d\Sigma acids}{dt} + (\delta_{ij} - z_j f_i) \alpha_{j,k} C_j \frac{dXC_j/dt}{XC_j}, \quad (22)$$

where  $f_i$  is defined as in Eqn. (8), which can now be viewed as a special case of Eqn. (22) for constant ion exchange medium composition,  $dXC_j = 0$ . Like Eqn. (8), Eqn. (22) can

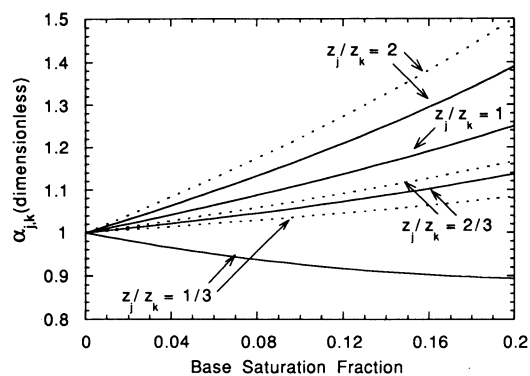


FIG. 3. Values of  $\alpha_{j,k}$  coefficient under Vanselow (solid lines) and Gaines-Thomas (dashed lines) conventions (see Appendix 1), for displacement of base cation of valence  $z_j$  by acid cation of valence  $z_k$ . Note that for displacement of divalent base cations (e.g., calcium and magnesium) by a trivalent cation (e.g.,  $Al^{+3}$ ),  $1 \leq \alpha_{j,k} \leq 1.16$  for base saturation fractions of less than 0.2, under either the Vanselow or Gaines-Thomas conventions.

be summed over the base cations, yielding the net change in the sum of bases resulting from changes in both acid anion loading and any adsorbed base cation  $XC_j$ ,

$$\frac{dSBC}{dt} = F_{SBC} \frac{d\Sigma acids}{dt} + (1 - F_{SBC}) \alpha_{j,k} z_j C_j \frac{dXC_j/dt}{XC_j}, \quad (23)$$

where  $F_{SBC}$  is defined as in Eqn. (10) and, for depletion of  $XC_j$ ,  $dXC_j < 0$ . Note that Eqns. (22) and (23) indicate that the rate of progressive acidification is proportional to the percentage rate of depletion of adsorbed bases. Catchments with thin soils, low cation exchange capacity, and low base saturation (and thus low  $XC_j$ ) are therefore more vulnerable to progressive acidification from a given base cation depletion rate  $dXC_j/dt$ .

It should be obvious that Eqn. (8), Eqn. (22), and their by-products both depend on runoff chemistry and predict changes in it. Thus, integration of these differential equations will reveal that solution chemistry varies nonlinearly with respect to both  $\Sigma acids$  and time. In particular, because Eqn. (22) depends on solution chemistry in multiple ways (both explicitly and implicitly in the interaction ratios  $f_j$  and the mass balance that determines  $dXC_j$ ), its behavior over time could be particularly complex. Nonetheless, in all the examples discussed here, deviations from linearity are small and, for simplicity, will be ignored.

## Test

Testing Eqn. (23) as a predictor of progressive acidification requires a site where high-quality long-term records of runoff chemistry are available, where the stock of exchangeable adsorbed ions can be estimated, and where a catchment mass balance for base cations can be constructed. The geochemical reference catchment at Hubbard Brook Experimental Forest (LIKENS et al., 1977; BORMANN and LIKENS, 1979) is one such site. There, sulfate concentrations in runoff have declined ( $-1.8 \pm 0.15 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ) since 1971, mirroring declines

in sulfate deposition (DRISCOLL et al., 1989a,b). Runoff base cation concentrations, however, have fallen still faster ( $-2.6 \pm 0.33 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ), leading to long-term alkalinity decline, despite decreases in acid loading (Fig. 4).

Here I quantitatively test the hypothesis that this trend could result from depletion of exchangeable bases, superimposed on declining acid loading. Adsorbed base depletion can be estimated from a catchment base cation balance (Table 3):

$$\frac{dXC_j}{dt} = D_j + W_j - B_j - rC_j, \quad (24)$$

where  $D_j$ ,  $W_j$ , and  $B_j$  are atmospheric deposition, production by mineral dissolution, and net biomass uptake, respectively, of the  $j^{\text{th}}$  ion, and  $r$  is the volume flux of runoff.

A lower bound for the rate of runoff base cation decline can be estimated by assuming that the composition of the catchment's ion-exchange media has not changed over the study period ( $dXC_j/dt = 0$ ), that is, that mineral weathering balances other cation fluxes. Under this assumption, Eqn. (23) predicts a decline in base cation concentrations ( $-1.29 \pm 0.13 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ) roughly half as large as observed (Fig. 4). An upper bound can be estimated by assuming that the base cation contribution from mineral weathering is negligible (Table 3); this yields a predicted rate of base cation decrease ( $-3.45 \pm 0.35 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ) somewhat larger

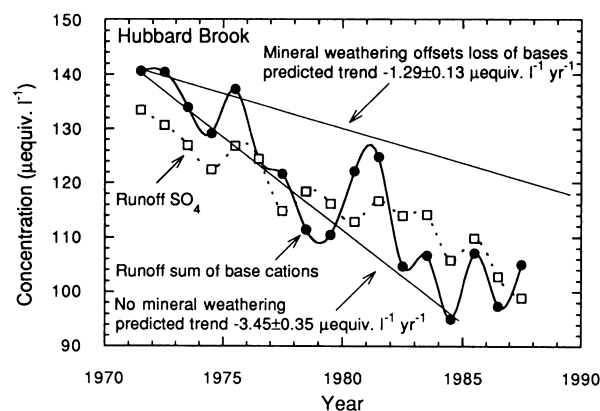


FIG. 4. Annual volume-weighted mean concentrations of sum of base cations (solid circles) and sulfate (open squares) at watershed 6, Hubbard Brook Experimental Forest (DRISCOLL et al., 1989a), compared to SBC trends predicted from Eqn. (23) for two extreme assumptions of mineral weathering rates. Trend labeled "mineral weathering offsets loss of bases" assumes  $dXC_j/dt = 0$  (i.e., base cation production by mineral dissolution balances other fluxes). Trend labeled "no mineral weathering" is based on  $dXC_j/dt$  estimated from balance of precipitation inputs, losses to runoff, and biomass accumulation, excluding cation supply from mineral dissolution (Table 3).

Sum of base cation trends predicted from Eqn. (23), using  $F_{SBC}$  (Eqn. 10) estimated from bulk runoff chemistry (Table 1).  $d\Sigma acids/dt$  assumed equal to  $dSO_4/dt$  ( $-1.8 \pm 0.2 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ); no significant trends in nitrate have been observed (DRISCOLL et al., 1989a), and chloride is a minor ion (Table 1). Exchangeable aluminum dominates exchangeable acidity in Hubbard Brook soils, and base saturation is  $0.10 \pm 0.01$  (JOHNSON et al., 1991); the coefficient  $\alpha_{j,k}$  for these conditions is  $1.06 \pm 0.01$  under either the Vanselow or Gaines-Thomas conventions (Fig. 3). All other input data from Tables 1–3.



Table 3. Base cation fluxes (means±standard errors) at watershed 6, Hubbard Brook Experimental Forest, New Hampshire

	Calcium	Magnesium
Fluxes (mmol m <sup>-2</sup> yr <sup>-1</sup> ):		
Bulk deposition (a)	3.1±0.3	1.6±0.2
Runoff (a)	-29.4±2.6	-11.7±1.0
Biomass accumulation (b)	-23.7±4.7	-3.7±0.7
Net (excluding weathering)	-50.0±5.4	-13.8±1.2
Stocks (mmol m <sup>-2</sup> ):		
Exchangeable cation pool (c)	676±55	146±8

<sup>a</sup> Deposition and runoff fluxes calculated from average of annual volume-weighted mean dissolved concentrations in deposition and runoff, 1971-1980 (Hubbard Brook Ecosystem Study, unpublished data).

<sup>b</sup> Biomass accumulation (Bormann and Likens, 1979) assumed to have relative standard error of 20 percent.

<sup>c</sup> Exchangeable cation pools are means for 59 pits sampled in adjacent catchment (watershed 5) in 1983 (Johnson et al., 1991).

than observed. Thus, the observed trend is bracketed by these estimates, suggesting that base cation leaching, partially (but not completely) offset by mineral weathering, and acting simultaneously with declines in acid loading, is responsible for the long-term trends in runoff at Hubbard Brook.

Alternatively, one can use the analysis outlined above to calculate the rate of loss of adsorbed base cations that is consistent with the observed time series describing solution concentrations of acid anions and base cations. Rearranging Eqn. (22) yields the percentage rate of loss of an adsorbed base cation  $XC_j$ ,

$$\frac{dXC_j/dt}{XC_j} = \frac{\frac{dC_j}{dt} - f_j \frac{d\Sigma acids}{dt}}{(1 - z_j f_j) \alpha_{j,k} C_j}, \quad (25)$$

given only the solution chemistry, trends in  $\Sigma acids$  and  $C_j$ , and an estimate of  $\alpha_{j,k}$  (which will be near unity if base saturation is low, as is common in acid-sensitive soils). Or, inverting Eqn. (23), one can use the trend in the sum of base cations to estimate the percentage loss of  $XC_j$ ,

$$\frac{dXC_j/dt}{XC_j} = \frac{\frac{dSBC}{dt} - F_{SBC} \frac{d\Sigma acids}{dt}}{(1 - F_{SBC}) \alpha_{j,k} z_j C_j}, \quad (26)$$

if one assumes that a single ion, or a group of ions that can be pooled (such as Ca and Mg), are being depleted. Using Eqn. (26) and the data presented above, one can directly calculate the inferred loss rate of adsorbed (Ca + Mg) at Hubbard Brook as  $5 \pm 1.5\%$  per year, or  $40 \pm 12$  mmol m<sup>-2</sup> yr<sup>-1</sup>. This rate of adsorbed base cation depletion, in conjunction with the data in Table 3, implies catchment-averaged mineral weathering rate of  $24 \pm 14$  mmol (Ca + Mg) m<sup>-2</sup> yr<sup>-1</sup>. This result is consistent, within roughly a factor of two, with other field estimates of silicate mineral dissolution rates (e.g., APRIL et al., 1986; FROGNER, 1990).

I caution the reader that uncritical application of Eqns. (25) and (26), particularly to short time series where trends are ill-defined, may lead to thoroughly unreliable results. Because time trends such as  $dC_j/dt$ ,  $dSBC/dt$ , and  $d\Sigma acids/dt$

are determined by the differences between somewhat stochastic measurements, the standard errors of the trends can be as large as (or even larger than) the trends themselves. The numerators of Eqns. (25) and (26) are, in turn, calculated from the differences between these trends, further compounding the effects of measurement or sampling variation and leading to potentially large standard errors. If base cation depletion rates are estimated from catchment runoff chemistry time series, error propagation analysis should be conscientiously applied.

### SPATIAL HETEROGENEITY AND SAMPLING VARIABILITY

The heterogeneous (multiphase) reactions controlling catchment runoff are spatially heterogeneous as well. Runoff combines the solution compositions, and the acidification responses, of the individual points that contribute to it. These discrete locations (e.g., distinct subdrainages, soil horizons, etc.) may have different geochemical properties, and thus different runoff compositions and acidification responses. In practice, however, the sensitivity to acidification at each point cannot be known, and the acidification response of the whole catchment must be assessed from its spatially averaged runoff.

In typical catchment geochemical models, spatially lumped parameters, estimated by model calibration, are assumed to represent spatially heterogeneous geochemical properties of the catchment. Underlying such models is the untested (and often unstated) premise that the calibrated parameters average the catchment's underlying geochemical variability in a way that will generate accurate predictions of the catchment's spatially averaged response to changes in acid loading. Procedures for systematically exploring the consequences of such spatial "lumping" have not been developed.

Under the assumption of heterogeneous equilibrium, however, one can show that a catchment's spatially averaged runoff will generally yield a predicted acidification response  $f_j$  that closely approximates the average of the acidification responses of each contributing point. To see why, consider waters draining a number of geochemically distinct locations, each with different runoff chemistry and different  $f_j$ . Assume, for simplicity, that runoff from each source is equal in volume and is acidic (so CO<sub>2</sub> degassing effects can be ignored, and most species will be, to first approximation, conservative). Assume, further, that the change in acid anion loading ( $d\Sigma acids$ ) is equal for each source (these assumptions are not crucial, but they simplify the analysis). The response,  $f_j$ , of the combined runoff can then be approximated (APPENDIX 2) by the mean of the second-order Taylor series expansions for the  $f_j$  of each source,

$$\bar{f}_j \approx \frac{z_j \bar{C}_j}{\bar{h}} \left( 1 + \frac{\text{Var}(h)}{\bar{h}^2} - \frac{\text{Cov}(C_j, h)}{\bar{C}_j \cdot \bar{h}} \right) \approx \frac{z_j \bar{C}_j}{\bar{h}}, \quad (27)$$

where the variances and covariances are evaluated across the different sources, and the means  $\bar{C}_j$  and  $\bar{h}$  are those of the averaged runoff. (Variance and covariance functions are used here simply for notational convenience and do not imply that  $C_j$  or  $h$  have any particular probability distribution).

Because the variance and covariance terms in Eqn. (27) are generally small (Appendix 2) and generally of opposite

sign (since  $C_j$  is itself a component of  $h$ ), the approximation to strict equality will usually be quite close. Thus, the acidification response  $f_j$  calculated from the spatially averaged runoff will be a good approximation of the spatially averaged response of the geochemically diverse points contributing to it. As an extreme hypothetical example, imagine mixing equal flows of runoff from circumneutral Sogndal and highly acidic Risdalsheia (Table 1). The value of  $F_{\text{SBC}}$  (Eqn. 10) derived from the bulk chemistry of the combined runoff (0.67) approximates the  $F_{\text{SBC}}$  expected to occur (0.69, the average of the  $F_{\text{SBC}}$  for the two sites), despite the fact that the runoff solutions being averaged differ by more than twofold in SBC, more than threefold in  $\Sigma\text{acids}$ , and 1.4 units in pH.

Runoff chemistry is both spatially and temporally variable. Averaging a series of samples taken at a given point over a period of time (as in Fig. 1) presents the same problem as averaging runoff from multiple sources in a spatially heterogeneous catchment. Whether individual samples are averaged over space or over time, the derivation of Eqn. (27) is the same; Eqn. (27) can thus be used to assess whether the average concentrations in temporally variable runoff will provide a reasonable estimate of the average of the interaction ratios  $f_j$  over the period. As Eqn. (27) predicts, and Fig. 5a illustrates, temporally averaged runoff concentrations yield predicted acidification responses that closely approximate the average of the acidification responses predicted for the sep-

arate data points in Fig. 1. Thus, sample variability produces no significant bias in predicted acidification responses.

Because runoff chemistry in individual stream samples will vary, it would be useful to have a measure of how much the acidification responses calculated from these samples will themselves vary. Approximating Eqn. (8) by a first-order Taylor series, one can show that the standard deviation of  $f_j$  values calculated from individual data points is (see Appendix 2),

$$\sigma(f_j) \approx \frac{z_j \bar{C}_j}{\bar{h}} \left( \frac{\text{Var}(C_j)}{\bar{C}_j^2} - 2 \frac{\text{Cov}(C_j, h)}{\bar{C}_j \bar{h}} + \frac{\text{Var}(h)}{\bar{h}^2} \right)^{1/2}. \quad (28)$$

As Fig. 5b illustrates, Eqn. (28) accurately predicts how variability in individual stream chemistry measurements will affect the predicted interaction ratios  $f_j$ . As Eqns. (15) and (16) indicate, variations in concentration measurements will generally have a less-than-proportional effect on the calculated  $f_j$ . Furthermore, because the middle term in Eqn. (28) will tend to offset the other two (since the covariance between species is usually positive), the expected variability in the  $f_j$  is relatively small. Indeed, if acidification responses are predicted for each of the individual data points in Fig. 1, their standard deviations (i.e., the prediction error bounds given in Table 2) are usually about 10–15% of the mean value. Thus, acidification response predictions derived from individual data points could be expected to have an error of roughly 10–15% due to sampling variability. Because predicted acidification response is relatively insensitive to sampling variability, even small numbers of samples should yield reliable estimates of catchment acidification behavior.

Equation (27) demonstrates that the acidification response of heterogeneous systems can be predicted, even when the sampled runoff combines flow from geochemically diverse sources. It does not, however, imply that the characteristics of the individual sources, or the relative amounts of discharge from each, are irrelevant. Indeed, changes in the relative contributions from different sources, particularly different soil horizons, are widely thought to be responsible for the observed correlation between discharge and chemical composition in streamflow (e.g., HOOPER et al., 1990). Because this analysis contains no hydrologic information, it cannot predict how streamflow chemistry will change with discharge. It can, however, predict how the runoff chemistry representing a particular discharge level (and thus mix of sources) will change as acid anion loading changes, even if the individual contributing sources, and their geochemical characteristics, are not known.

This analysis does not assume that the individual "sources" can be identified as discrete locations within the catchment, each chemically isolated from its neighbors. Clearly, waters flowing from one soil horizon through another, or from tills of one lithology to another, may be altered by (and may also alter) the geochemical environments through which they subsequently flow, before emerging as bulk runoff somewhere downstream. This analysis shows that whatever the various geochemical media contributing their chemical signatures to the flows forming runoff, the buffering behavior of the bulk runoff can be predicted from that bulk runoff chemistry itself.

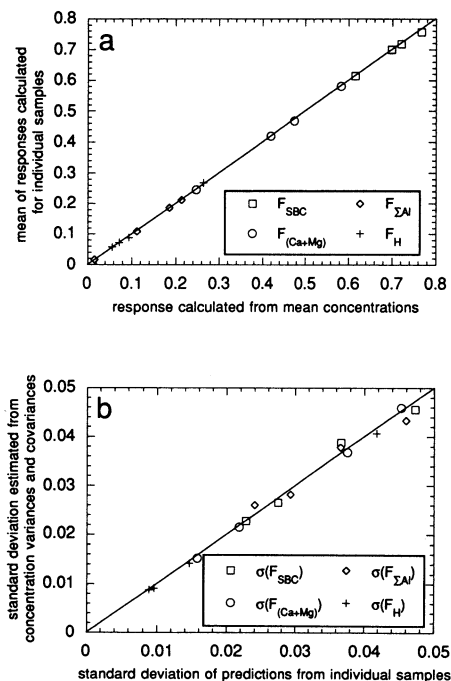


FIG. 5. Slopes of predicted acidification responses (a) calculated from mean concentrations (Tables 1 and 2), compared to means of predictions calculated from individual data. Close agreement verifies that approximate equality in Eqn. (27) holds for data showing scatter comparable to that in Fig. 1. Standard deviations of predictions (b) calculated from individual data, compared to standard deviations estimated from covariance matrix of concentrations in individual data, via Eqn. (28). Close agreement verifies that Eqn. (28) accurately estimates expected error in calculated acidification responses due to sample variability.

The point of this analysis is that mechanistically predicting certain aspects of runoff acidification does not require identifying individual geochemical source regions, characterizing their geochemical properties, or tracing the myriad hydrologic flowpaths that connect them. Thus, the problem of predicting whole-catchment geochemical behavior is simplified considerably.

## DISCUSSION

This analysis proposes a parsimonious method for assessing catchment vulnerability to acidification. The formal advantages of this approach are that its assumptions can be clearly and concisely stated, it requires no parameter calibration or ad hoc empiricisms, and it consists of direct algebraic calculations, so that results are generalizable and simulation algorithms do not obscure the underlying relationships. The practical advantages of this method are that it is widely applicable, insensitive to sample variability, efficient in its use of data, and demonstrably successful in predicting acidification trends observed at a number of intensively monitored catchments.

These methods provide a mechanistic basis for using the average chemistry of catchment runoff to draw quantitatively accurate a priori inferences regarding catchment acid buffering behavior (Fig. 1). Where these methods accurately predict catchment response to changes in acid anion loading, their extrapolation provides a rough estimate of how much runoff acid anion concentrations must decrease in order to reverse direct acidification. At the acidified Norwegian sites (Risdalsheia and Birkenes), for example, achieving positive runoff alkalinity will apparently require decreasing sulfate concentrations to a small fraction of their current levels (Fig. 2).

Inspection of Fig. 2 suggests that the three Norwegian sites share a common geochemical heritage. The roughly parallel acidification trajectories predicted and observed at all three sites suggest that under low sulfate loading, Birkenes and Risdalsheia would have circumneutral runoff alkalinities, similar to those at Sogndal. It will be interesting to see whether other geochemically comparable catchments fall within the acidification "envelope" defined by the three sites in Fig. 2. It is also possible that base cation depletion has played a role in the historical acidification of Birkenes and Risdalsheia. Progressive acidification would, over time, shift the buffering curves in Fig. 2 downward, and also steepen them by diminishing base cation concentrations and, thus, the  $f_j$  for bases (Fig. 6).

Runoff acidification is often measured by changes in the difference between runoff base cations and strong acid anions, or alkalinity:

$$\text{Alk} = \text{SBC} - ([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-]). \quad (29)$$

(Note that Alk differs somewhat from ANC, the acid neutralizing capacity as measured by acidimetric titration.) If changes in organic acid anions are small or are uncorrelated with changes in sulfate, nitrate, and chloride, then:

$$\frac{d\text{Alk}}{dt} = \frac{d\text{SBC}}{dt} - \frac{d\Sigma\text{acids}}{dt}. \quad (30)$$

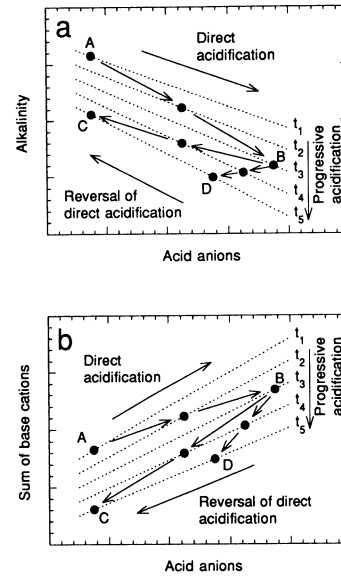


FIG. 6. Conceptual diagram illustrating combined effects of direct and progressive acidification on runoff alkalinity and sum of base cations under increasing and decreasing acid loading. Catchment moves reversibly along equilibrium buffer curves (dotted lines) due to mobile anion effects. Under progressive acidification, buffer curves shift downward as time progresses from  $t_1$  to  $t_5$ . Path taken by catchment system (solid dots) will not follow buffer curves if significant progressive acidification takes place. Assuming this path results solely from buffering behavior may result in misleading estimates of catchment recovery. In particular, note that runoff alkalinity may either recover or decline under decreasing acid loading. The rate of reversal of direct acidification, relative to the rate of progressive acidification, determines whether runoff alkalinity rises (as along the path from A to B to C) or continues to fall (as along the path from A to B to D) in response to acid loading reductions.

Combining Eqns. (23) and (30), one can express the joint effect of acid anion loading and base cation depletion on runoff alkalinity as:

$$\frac{d\text{Alk}}{dt} = (1 - F_{\text{SBC}}) \left( \alpha_{j,k} z_j C_j \frac{dXC_j/dt}{XC_j} - \frac{d\Sigma\text{acids}}{dt} \right). \quad (31)$$

Thus, the quantity  $F_{\text{SBC}}$ , defined in Eqn. (10), emerges as a common factor in catchment sensitivity to both direct and progressive acidification.  $F_{\text{SBC}}$  bears some resemblance to Henriksen's empirical parameter  $F = \Delta(\text{Ca} + \text{Mg})/\Delta\text{SO}_4$ , widely used to describe catchment resistance to acidification (WRIGHT and HENRIKSEN, 1983; HENRIKSEN, 1984; HENRIKSEN and BRAKKE, 1988; HENRIKSEN et al., 1988). Henriksen's  $F$  is generally estimated phenomenologically, after the fact, by comparing current, acidified runoff with an assumed preacidification runoff chemistry. Henriksen's analysis is intended for use where progressive acidification is not occurring. However, it is difficult to know whether the changes in runoff chemistry observed (or inferred) at a particular catchment are the result of mobile anion effects (direct acidification), base cation depletion (progressive acidification), or both. Henriksen's  $F$ , as evaluated from a catchment's chemical evolution over time (e.g., from the slope between points in Fig. 6), may therefore be substantially greater or smaller than  $F_{\text{SBC}}$ , the slope of the catchment buffering curves (e.g., the dotted lines in Fig. 6). Because estimates of Hen-

riksen's  $F$  conflate mobile anion effects and progressive acidification processes, they may yield misleading projections of catchment response to changes in acid loading (Fig. 6).

Equations (23) and (31), by contrast, recognize that over the long run, changes in runoff chemistry are not controlled by acid loading alone. At Hubbard Brook, for example, declining acid anion concentrations coincide with an even steeper base cation decline, but my analysis suggests they are only responsible for roughly half of it (see above); the remainder is attributable to depletion of adsorbed bases by biomass uptake and accelerated cation leaching. Equation (31) predicts that if progressive acidification were not occurring, the recent reductions in acid loading would have raised alkalinity by roughly  $0.5 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ . Instead, alkalinity has decreased ( $-0.8 \pm 0.4 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$ ).

Progressive acidification may, likewise, complicate the interpretation of the critical test shown in Figs. 1 and 2. If, as at Hubbard Brook, progressive acidification is superimposed on declining acid anion loading, base cation concentrations will plot as a steeper function of acid anions than is expected from mobile anion effects alone. However, as indicated above, progressive acidification is probably responsible for roughly  $1.3 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$  of the observed decline in base cations at Hubbard Brook. Over the ten years of data shown in Fig. 1, then, progressive acidification would account for roughly 15–20% of the range spanned by the sum of base cations; note that the monthly data plotted in Fig. 1 include seasonal variations that are averaged out in the annual data shown in Fig. 4. Progressive acidification may also be occurring at Birkenes, as CHRISTOPHERSEN et al. (1990b) have suggested; it is currently difficult to estimate how much this would affect the Birkenes data in Figs. 1 and 2. It is unlikely that progressive acidification has significantly affected the data shown for Sogndal or Risdalsheia because those data span a short period of time, during which acid anion loading was substantially altered by experimental manipulations. These circumstances should maximize mobile anion effects while minimizing the effects of base cation depletion.

Direct acidification is "direct" in the following sense: increases in acid anion loading produce proportional decreases in runoff alkalinity, net of partially offsetting proportional increases in base cation concentrations. Progressive acidification, by contrast, arises not from changes in external conditions but instead from an imbalance in the base cation fluxes under those conditions (whether or not they are changing).

For example, my analysis suggests that the progressive acidification observed at Hubbard Brook is not the result of a recent change in base cation fluxes, as proposed by DRISCOLL et al. (1989a). Whereas DRISCOLL et al. argue that the observed runoff base cation decline results from a similar decrease in base cations in bulk precipitation, DILLON (1989) points out that although base cation deposition declined at Hubbard Brook in the 1960s and early 1970s, it has remained essentially constant since the mid-1970s, during precisely the period that runoff base cation concentrations have declined. My analysis shows that it is mechanistically and quantitatively plausible that the observed acidification at Hubbard Brook is caused by substantial, persistent losses of exchangeable bases resulting from base cation leaching accelerated by high acid

anion loading (Fig. 4). Where depletion of adsorbed bases is rapid ( $dXC_j/dt \ll 0$  in Eqn. 31), alkalinity may decline even though acid loading is decreasing ( $d\Sigma\text{acids}/dt < 0$ ). I propose that this process, illustrated by the path connecting points B and D in Fig. 6, is the primary cause of the trends observed at Hubbard Brook.

Progressive acidification results from depletion of adsorbed bases, and thus from high levels of acid anion leaching (BERGKVIST, 1986), rather than from shifts in acid loading per se. Analyses at some North American sites subject to acid deposition suggest that large reductions in acid loading may restore approximate equilibrium between base cation fluxes (KIRCHNER, 1990). But as acid loading declines, progressive acidification will persist until the base cation balance becomes positive, and it will not be completely reversed until a positive balance is maintained long enough for the depleted bases to be restored. Where rates of mineral weathering are small in comparison to current rates of base cation leaching, recovery from progressive acidification will take much longer than the acidification that preceded it (KIRCHNER, 1990).

Even if progressive acidification is not reversed, it may be offset, in the short run, by sufficiently rapid reductions in acid loading (Fig. 6). From Eqn. (31), the rate of change in acid anions required to balance the effects of depleting adsorbed bases  $XC_j$  may be expressed as:

$$\frac{d\Sigma\text{acids}}{dt} = \alpha_{j,k} z_j C_j \frac{dXC_j/dt}{XC_j} \quad (32)$$

If base saturation is low (and thus  $\alpha_{j,k} \approx 1$ ), a given percentage loss of adsorbed bases can be offset by decreases in acid anions comprising the same percentage of the solution concentration of  $C_j$  (in equivalents). At Hubbard Brook, offsetting progressive acidification (assuming mineral weathering of  $24 \pm 14 \text{ mmol Ca} + \text{Mg m}^{-2} \text{yr}^{-1}$ , as inferred above) would require decreases of  $4.6 \pm 1.5 \mu\text{equiv. l}^{-1} \text{yr}^{-1}$  in acid anions, over twice the observed rate (Fig. 4).

Many catchment simulation models (e.g., GHERINI et al., 1985; COSBY et al., 1985a; REUSS and JOHNSON, 1985; CHRISTOPHERSEN et al., 1982) are based on principles such as anion mobility and charge balance, as is the approach developed here. To the extent that simulation models are based on similar considerations and address similar questions, their results should be comparable to those presented here. This analysis can be considered to subsume some of these models' properties in more explicit and general form. However, even if the major difference between this approach and a particular simulation model is one of form, the significance of that distinction should not be underestimated.

My analysis yields analytic expressions for catchment sensitivity to acidification, e.g., Eqns. (8) and (22), rather than a series of model simulation results for particular scenarios. This confers several advantages. First, results are generalizable, rather than specific to the individual catchment for which a typical model might be calibrated. Second, the role of each factor controlling catchment acidification is explicit; by contrast, interpreting a collection of scenario simulations is more difficult. Third, parameter calibration is not required; thus, critical tests are feasible, and uncertainties are more constrained. Fourth, such extensions as error propagation analyses or assessments of spatial heterogeneity effects (Ap-

pendix 2) are straightforward; conducting similar analyses using simulation models typically requires procedures that are difficult to document, generalize, and interpret. Finally, these analytic methods can be applied to large numbers of catchments; detailed calibration data sets are not required. While I have used high-quality data sets from intensively studied catchments to critically test the theory presented here, I have also shown that its acidification predictions are relatively stable under sampling variability. Thus, large data sets are not needed to obtain reliable acidification predictions.

The validity of the predictions derived here obviously depends on whether approximate heterogeneous equilibrium prevails between the dominant ions in catchment runoff. This may not always be the case. For example, there is considerable disagreement over whether aluminum concentrations in streamwater reflect control by a single solid phase (NORDSTROM and BALL, 1986; SULLIVAN et al., 1986; SEIP et al., 1989). Data appearing to show that no single phase controls aluminum concentrations, however, typically combine samples from a wide range of discharges. Because pH and discharge are usually highly correlated, the aluminum-pH relationship used to evaluate solubility controls is confounded in such data by discharge variation (SULLIVAN et al., 1986; SEIP et al., 1989). Thus, the existing literature is compatible with the hypothesis that aluminum participates in multiple heterogeneous equilibria, as represented here, with discharge variations altering the relative mix of different sources.

As with any analytical exercise, errors resulting from misspecification (i.e., imputing heterogeneous equilibria where other mechanisms actually control runoff chemistry) are difficult to quantify. The sign of any such error is known, however. The buffer intensity of a heterogeneous system is greater than that of any other equilibrium system with equivalent aqueous composition (MOREL et al., 1976; MOREL, 1983). Thus, to the extent that a catchment's runoff contains ions (other than acid anions) that deviate from heterogeneous equilibrium, it will be more sensitive to direct acidification than this method predicts.

This approach provides a general method for characterizing the effects of acid anion mobility, charge balance constraints, and the manifold equilibria between the aqueous phase and the geochemically complex, spatially variable soils and rocks in catchments. To the extent that its treatment of these processes is valid and useful, it should serve to focus attention on three central problems that still remain in predicting acid deposition effects on surface waters.

First, although this analysis describes how porewaters will respond to changes in acid anion concentrations, it does not predict how acid anion concentrations will themselves respond to acid deposition. Empirical relationships between sulfate concentrations in rainfall and lakewaters in Norway and North America (WRIGHT and HENRIKSEN, 1983) suggest that a simple proportionality constant may link changes in runoff concentrations with those in precipitation. If one can define the mechanistic relationship between precipitation and runoff acid anion concentrations, the slope of that relationship could be multiplied by the  $f_j$  derived here, to yield the direct effect of precipitation acid anions on the full suite of ions in runoff. Defining this relationship in a way that can be readily applied at a wide variety of catchments, however, remains

difficult. In many catchments, nitrate deposition is largely taken up by the biota, keeping porewater and runoff nitrate concentrations low (REUSS and JOHNSON, 1986). Unless nitrate deposition rates exceed the uptake capacity of the biota, they will likely have little direct effect on runoff nitrate levels. Soils in some catchments, however, can adsorb or mineralize significant quantities of sulfate. Such processes will not affect the relationships among aqueous ions predicted here, but they may moderate the response of acid anion concentrations to changes in deposition rates.

Second, this analysis shows how progressive acidification can be predicted, if the rate of loss of adsorbed base cations is known, but it does not provide a direct method for estimating cation resupply from mineral weathering, and thus cannot independently determine rates of depletion of adsorbed bases. This is a general problem confronting any efforts to predict long-term catchment acidification. Calibrating a weathering parameter in a simulation model is unlikely to shed much light here because weathering rates will generally have only a small and indirect effect on the catchment's short-term behavior, to which such models must be calibrated. Over long time scales (long, that is, compared to the time required to alter catchment pools of adsorbed bases), base cation supply to runoff is fixed by the rate of base cation supply from mineral dissolution. Thus, it remains an urgent priority in catchment acidification research to devise and test methods for directly measuring (or predicting) rates of mineral weathering under field conditions.

Third, this analysis does not attempt to predict catchment hydrology; thus it cannot predict how changes in hydrologic regime will affect runoff chemistry. Changes in discharge alter hydrologic pathways, vary the relative contributions of different geochemical source regions (e.g., soil horizons), and thus change the chemistry of catchment runoff. This analysis estimates how the mobile anion effect, and progressive acidification, will affect runoff that combines flows from diverse geochemical sources, but it does not represent those sources explicitly. The advantage of this approach is that the individual sources need not be identified or characterized; the drawback is that the effects of changing their relative contributions cannot be explicitly predicted. If a particular discharge level is characterized by a distinctive runoff chemistry (and thus a specific, though perhaps unknown, mix of sources), this method should be useful in predicting how runoff chemistry, at that discharge, will respond to acidification.

In my analysis, catchment vulnerability to acidification is expressed in terms of interaction ratios  $f_j$ , described by a single general expression (Eqn. 8) that can be evaluated from mean concentrations in bulk runoff, and, where runoff is alkaline, estimated porewater  $p(\text{CO}_2)$ . Catchment-specific process studies or chemical time series data are not required. Thus, this analysis may be useful for estimating vulnerability to acidification in the many catchments where current runoff chemistry is the only available information. The validity of such estimates obviously depends on whether the sampled runoff is representative of the catchment and the hydrologic conditions for which predictions are desired. For example, buffering behavior inferred from the chemistry of autumn low flows may not accurately predict buffering observed during spring runoff.

Beyond the general premise of heterogeneous equilibrium, this analysis has made no assumptions whatever concerning the reaction pathways controlling runoff chemistry, or the reaction constants involved. For example, base cation concentrations may be controlled by an ion exchange equilibrium, or the solubility of a mineral; in either case, Eqn. (8) has precisely the same form (Eqns. (17)–(23) and (31)–(32); however, obviously assume that base cations are controlled by cation exchange). Reaction pathways and equilibrium constants will affect the equilibrium concentrations  $C_i$  and thus the calculated values of  $f_j$ , but they need not be determined directly because all the information required to specify  $f_j$  is contained in the solution composition itself. This is useful because the equilibrium reactions controlling runoff chemistry are probably numerous, varied, and complex. This analysis demonstrates that the behavior of these complicated geochemical systems can be predicted even when relatively little is known about the detailed mechanisms controlling them.

Finally, it is worth noting that little in this analysis restricts its application to catchment acidification alone. The adsorption, leaching, and transport of various natural and anthropogenic contaminants, and their effects on groundwater or runoff chemistry, are central to many environmental problems (such as toxic mine drainage, waste disposal, and site reclamation). Many important contaminants (including, for example, toxic metals) are likely to be regulated, in part, by heterogeneous equilibria with catchment geochemical materials. Extensions of the methods developed here may shed light on this broader class of problems as well.

### CONCLUSIONS

- 1) The hypothesis of heterogeneous equilibrium implies that short-term catchment response to changes in acid anion concentrations can be predicted analytically from the current bulk chemistry of catchment runoff. Critical tests using data from four intensively studied watersheds (Hubbard Brook, USA, and Sogndal, Risdalsheia, and Birkenes, Norway) confirm the quantitative accuracy of these predictions (Fig. 1; Table 2).
- 2) This theoretical analysis predicts, and the field data confirm, that the three Norwegian sites share parallel acidification paths. Acidified Birkenes and Risdalsheia would, under low sulfate loading, have circumneutral runoff alkalinities comparable to those at the pristine site, Sogndal. Reversing acidification at Birkenes and Risdalsheia would require decreasing sulfate concentrations to a small fraction of current levels (Fig. 2).
- 3) From first principles, closed-form analytic expressions are derived that predict the rate of progressive acidification resulting from depletion of exchangeable bases. Applying these expressions requires that a catchment's cation exchange pools can be estimated, and a mass balance for base cations can be constructed.
- 4) Comparison of predicted rates of acidification with the observed long-term trends at Hubbard Brook suggests that those trends result from declining acid loading and from base cation leaching, partially offset by mineral weathering (Fig. 4). Depletion of exchangeable bases is responsible for roughly half of the observed decline in runoff base cations.
- 5) A simple method is proposed for evaluating the effects of spatial heterogeneity in catchment geochemical properties. Catchment buffering behavior inferred from spatially averaged runoff closely approximates the average of the buffering properties of the geochemically diverse points contributing to it. Runoff response to changes in acid anion loading can thus be predicted, even when the individual contributing sources, and their geochemical characteristics, are unknown.
- 6) Methods are also proposed for evaluating the effects of stream chemistry sampling variability on predicted response to acid anion loading. Sampling variability does not bias derived acidification predictions (Fig. 5a). Acidification predictions are also relatively stable under sampling variability (Fig. 5b); thus, reliable predictions can be derived from relatively small numbers of samples.

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## APPENDIX 1

The Vanselow convention (VANSELOW, 1932), in keeping with ideal solid solution theory, holds that the activity of an adsorbed ion is its molar fraction of the total adsorbed phase. The Gaines-Thomas convention (GAINES and THOMAS, 1953), which does not have the same rigorous thermodynamic basis, considers an adsorbed ion's activity to be its fraction of the total equivalents of adsorbed phase. For ion exchange in which the  $j^{\text{th}}$  ion is leached out into the solution and replaced with an equal number of equivalents of the  $k^{\text{th}}$  ion (so that the total number of adsorbed equivalents does not change), the Gaines-Thomas convention leads to the expression

$$\alpha_{j,k} = 1 + \frac{z_j^2 X C_j}{z_k^2 X C_k}, \quad (33)$$

where  $\alpha_{j,k}$  is the coefficient found in Eqn. (19), and  $z_j$  and  $z_k$  are the valences of two adsorbed ions with concentrations  $X C_j$  and  $X C_k$  in the adsorbed phase. If  $X C_j$  represents an adsorbed base cation and  $X C_k$  represents an adsorbed acid (and no other adsorbed ions are present), then

$$\alpha_{j,k} = 1 + \frac{z_j}{z_k} \frac{\text{BSF}}{1 - \text{BSF}}, \quad (34)$$

where BSF is the familiar base saturation fraction. The Vanselow convention leads to a somewhat more complex expression, which coincides with the Gaines-Thomas result in the special case of  $z_j = z_k$ :

$$\alpha_{j,k} = 1 + \frac{z_j}{z_k} \frac{\text{BSF}}{1 - \text{BSF}} + \left( \frac{z_j}{z_k} - 1 \right) \frac{\text{BSF}}{\text{BSF} + \frac{1}{\frac{z_k}{z_j} - 1}}. \quad (35)$$

As Fig. 3 shows, when the base saturation fraction is small, the choice between the two conventions has little effect on  $\alpha_{j,k}$ , and thus has little effect on predicted catchment response to base cation depletion.

## APPENDIX 2

The implications of spatial and temporal heterogeneity can be explored through techniques of measurement theory (e.g., ANG and TANG, 1975). Consider a catchment that mixes runoff from  $m$  separate regions, each having solution concentrations  $C_i$  and heterogeneous buffer factors  $h$  (Eqn. 9); in other words, consider  $C_i$  and  $h$  as variables that may take on different values in each source region. If the runoff solutions are acidic (so that each of the  $C_i$  will be approximately conservative), the means observed in the catchment's averaged outflow will be, simply,

$$\bar{C}_i = \sum \frac{1}{m} C_i, \quad (36)$$

and

$$\bar{h} = \sum \frac{1}{m} h = \sum \frac{z_i^2 \bar{C}_i}{i=1} \quad (37)$$

The problem at hand, then, is finding the average interaction ratio  $\bar{f}_j$ :

$$\bar{f}_j = \sum \frac{1}{m} f_j, \quad (38)$$

and determining how much it deviates from the estimated interaction ratio  $\hat{f}_j$ :

$$\hat{f}_j = \frac{z_j \bar{C}_j}{\bar{h}}, \quad (39)$$

which is necessarily evaluated in terms of the spatially averaged  $\bar{C}_j$  and  $\bar{h}$ . Because  $f_j$  is a nonlinear function, the mean of this function,  $\bar{f}_j$ , will not generally equal the function of the means,  $\hat{f}_j$ . The objective is to estimate how well the function of the means approximates the mean of the function.

If heterogeneous equilibrium holds in each region, Eqn. (8) can be applied to each:

$$f_j = \frac{z_j C_j}{\sum_{i=1}^n z_i^2 C_i} = \frac{z_j C_j}{h}. \quad (40)$$

The  $f_j$  for each region can be approximated by the second-order Taylor expansion about the averaged  $\bar{C}_j$  and  $\bar{h}$ :

$$f_j \approx \frac{z_j \bar{C}_j}{\bar{h}} + \frac{z_j}{\bar{h}} (C_j - \bar{C}_j) - \frac{z_j \bar{C}_j}{\bar{h}^2} (h - \bar{h}) + \frac{z_j \bar{C}_j}{\bar{h}^3} (h - \bar{h})^2 - \frac{z_j}{\bar{h}^2} (C_j - \bar{C}_j)(h - \bar{h}). \quad (41)$$

When the Taylor expansions for the  $f_j$  are averaged, by substituting Eqn. (41) into Eqn. (38), the second and third terms vanish, and the fourth and fifth terms become a variance and covariance, respectively, yielding

$$\bar{f}_j \approx \frac{z_j \bar{C}_j}{\bar{h}} + \frac{z_j \bar{C}_j}{\bar{h}^3} \text{Var}(h) - \frac{z_j}{\bar{h}^2} \text{Cov}(C_j, h), \quad (42)$$

which can be rearranged to yield

$$\bar{f}_j \approx \hat{f}_j \left( 1 + \frac{\text{Var}(h)}{\bar{h}^2} - \frac{\text{Cov}(C_j, h)}{\bar{C}_j \bar{h}} \right), \quad (43)$$

which appears above as Eqn. (27). In terms of the individual concentrations  $C_i$ , Eqn. (43) is

$$\bar{f}_j \approx \hat{f}_j \left( 1 + \sum_{i=1}^n \frac{z_i^2 z_k^2 \text{Cov}(C_i, C_k)}{\bar{h}^2} - \sum_{i=1}^n \frac{z_i^2 \text{Cov}(C_i, C_j)}{\bar{C}_j \bar{h}} \right). \quad (44)$$

Note that the only mathematical approximation that is made here is that higher-order terms are omitted from Eqns. (41) and (47), the Taylor expansions of the  $f_j$ . Apart from that approximation, the calculations in Eqns. (42)–(50) are exact. Note further that variance



and covariance functions are used here simply as a compact formalism for their equivalent formulas, e.g.,

$$\text{Cov}(C_j, h) = \sum \frac{1}{m} (C_j - \bar{C}_j)(h - \bar{h}), \quad (45)$$

so the calculations are exact regardless of how the values of  $C_j$ ,  $h$ , etc., are distributed (e.g., they need not obey a normal distribution).

It was assumed above that each region contributes an equal volume to runoff and that each region experiences an equal change in acid anion concentrations. What are the implications of relaxing this assumption? If each region contributes a flux of  $q$  to runoff and experiences a shift in acid anion concentrations of  $d\Sigma\text{acids}$  (where  $q$  and  $d\Sigma\text{acids}$  vary across sources), the scheme of analysis outlined above yields the result:

$$\bar{f}_j \approx \hat{f}_j \left( 1 + \frac{\text{Var}(qh)}{(\bar{q}\bar{h})^2} - \frac{\text{Cov}(qC_j, qh)}{(\bar{q}\bar{C}_j)(\bar{q}\bar{h})} + \frac{\text{Cov}(qC_j, qd\Sigma\text{acids})}{(\bar{q}\bar{C}_j)(\bar{q}d\Sigma\text{acids})} - \frac{\text{Cov}(qd\Sigma\text{acids}, qh)}{(\bar{q}d\Sigma\text{acids})(\bar{q}\bar{h})} \right), \quad (46)$$

where  $\bar{C}_j$ ,  $\bar{h}$ , and  $\bar{d\Sigma\text{acids}}$  are the flux-weighted averages observed in the catchment outflow. In Eqn. (46), as in Eqns. (42)–(44), the variance and covariance terms can be expected to be small because variances and covariances in the solution concentrations can be expected to be considerably smaller than the products of means by which they are divided. Thus, Eqns. (43) and (46) both imply that within relatively small deviations,  $f_j$  values estimated from the mean concentrations (Eqn. 39) will be a good approximation to the mean interaction ratio of the combined sources (Eqn. 38). This result is expected because  $f_j$  is not a strongly nonlinear function of the linearly averaged solution concentrations.

The problem of averaging temporally variable runoff chemistry is directly analogous to that of averaging over spatial variation. This analysis thus shows that  $f_j$  values computed from simple means (Eqns. (42)–(44)) or volume-weighted means (Eqn. 46) of sample concentrations in a runoff time series will approximate the average of the acidification responses expected from each sample over the period (Fig. 5a).

Similar methods can be used to estimate the average variation in calculated  $f_j$  values that would be expected from sample variability. For example, one might want to estimate  $f_j$  from runoff chemistry samples that vary from one sampling date to the next. If only a few samples were available, what is the likely error in the derived  $f_j$ ? Given an estimate of how variable runoff chemistry is (i.e., given an estimate of the covariance matrix for the ion concentrations measured in the samples), one can calculate how variable the corresponding estimates of  $f_j$  are. That is, one can calculate how much  $f_j$  values inferred from an individual sample would be expected to differ from the average for a large group of samples.

Approximating Eqn. (8) by its first-order Taylor series:

$$f_j \approx \frac{z_j \bar{C}_j}{\bar{h}} \left( 1 + \frac{(C_j - \bar{C}_j)}{\bar{C}_j} - \sum_{i=1}^n \frac{z_i^2 (C_i - \bar{C}_i)}{\bar{h}} \right), \quad (47)$$

(which is simply the first three terms of Eqn. 41, in slightly different form) and computing its standard deviation over the  $m$  individual samples:

$$\sigma(f_j) = (\text{Var}(f_j))^{1/2} = \left( \sum \frac{1}{m} \left( f_j - \sum \frac{1}{m} f_j \right)^2 \right)^{1/2}, \quad (48)$$

one obtains directly:

$$\sigma(f_j) \approx \hat{f}_j \left( \frac{\text{Var}(C_j)}{\bar{C}_j^2} - 2 \sum_{i=1}^n \frac{z_i^2 \text{Cov}(C_i, C_j)}{\bar{C}_j \bar{h}} + \sum_{i=1}^n \sum_{k=1}^n \frac{z_i^2 z_k^2 \text{Cov}(C_i, C_k)}{\bar{h}^2} \right)^{1/2}, \quad (49)$$

or, equivalently,

$$\sigma(f_j) \approx \hat{f}_j \left( \frac{\text{Var}(C_j)}{\bar{C}_j^2} - 2 \frac{\text{Cov}(C_j, h)}{\bar{C}_j \bar{h}} + \frac{\text{Var}(h)}{\bar{h}^2} \right)^{1/2}. \quad (50)$$

Standard deviations calculated by Eqn. (50) are close to the standard deviations of acidification responses calculated for the individual data at the study sites (Fig. 5b); this analysis accurately predicts the expected variability of the  $f_j$ . Note that, in general, the variance and covariance terms of Eqns. (49)–(50) are small, and are of opposite sign (because  $C_j$  is generally positively correlated with the other  $C_i$  and thus with  $h$ ). Thus, even when runoff chemistry is as variable as the data in Fig. 1 suggest, predicted acidification response will be relatively insensitive to sample variability (see, for example, the standard deviations of predictions in Table 2). Therefore, catchment response to mobile anion effects can probably be estimated reliably from small numbers of samples.

### APPENDIX 3

Table of symbols

Equation (a)	Definition	units (b)
$\Sigma\text{acids}$	3 sum of strong acid anions and organic acid anions	$\mu\text{N}$
$\Sigma\text{Al}_i$	3 equivalent sum of inorganic aluminum species	$\mu\text{N}$
$\text{Alk}$	29 alkalinity	$\mu\text{N}$
$\text{ANC}$	12 Gran titration acid neutralizing capacity	$\mu\text{N}$
$B_j$	24 biomass uptake of $j^{\text{th}}$ ion	$\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$
$B\text{SF}$	34 base saturation fraction	dimensionless
$C_j$	4 aqueous concentration of $j^{\text{th}}$ ion	$\mu\text{M}$
$\bar{C}_j$	36 $C_j$ for spatially or temporally averaged runoff	$\mu\text{M}$
$D_j$	24 atmospheric deposition of $j^{\text{th}}$ ion	$\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$
$f_j$	8 interaction ratio of $j^{\text{th}}$ ion, $dC_j/d\Sigma\text{acids}$	$\mu\text{M} \mu\text{N}^{-1}$
$\hat{f}_j$	38 true $f_j$ for spatially or temporally averaged runoff	$\mu\text{M} \mu\text{N}^{-1}$
$\hat{f}_j$	40 $f_j$ estimated from spatially or temporally averaged runoff	$\mu\text{M} \mu\text{N}^{-1}$
$F_{\Sigma\text{Al}}$	11 interaction ratio of inorganic aluminum, $d\Sigma\text{Al}_i/d\Sigma\text{acids}$	dimensionless
$F_{\text{ANC}}$	13 interaction ratio of acid neutralizing capacity, $d\text{ANC}/d\Sigma\text{acids}$	dimensionless
$F_{\text{pH}}$	14 interaction ratio of pH, $d\text{pH}/d\Sigma\text{acids}$	$\mu\text{N}^{-1}$
$F_{\text{SBC}}$	10 interaction ratio of sum of base cations, $d\text{SBC}/d\Sigma\text{acids}$	dimensionless
$h$	9 heterogeneous buffering term	$\mu\text{N}^2 \mu\text{M}^{-1}$
$\bar{h}$	37 $h$ for spatially or temporally averaged runoff	$\mu\text{N}^2 \mu\text{M}^{-1}$
$K_{j,k}$	5 constant for reaction between $j^{\text{th}}$ and $k^{\text{th}}$ ions	$\text{l sec}^{-1}$
$q$	46 runoff from individual source regions in catchment	$\text{m yr}^{-1}$
$r$	24 catchment runoff (in units of depth)	$\mu\text{N}$
$\text{SBC}$	3 sum of base cations	$\mu\text{N}$
$t$	17 time	$\text{yr}$
$W_j$	24 production of $j^{\text{th}}$ ion by mineral weathering	$\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$
$\text{XC}_j$	17 concentration of adsorbed phase of $j^{\text{th}}$ ion	$\text{mmol} \cdot \text{m}^{-2}$
$z_j$	4 valence of $j^{\text{th}}$ ion	$\mu\text{N} \mu\text{M}^{-1}$
$\alpha_{j,k}$	19 ion exchange coefficient for $j^{\text{th}}$ and $k^{\text{th}}$ ions	dimensionless
$\gamma$	5 single-ion activity coefficient	dimensionless
$\delta_{i,j}$	20 Kronecker delta ( $\delta_{i,j}=1$ if $i=j$ , $\delta_{i,j}=0$ otherwise)	dimensionless
$\sigma(f_j)$	28 standard deviation of $f_j$	$\mu\text{M} \mu\text{N}^{-1}$

a Equation where symbol is defined or first used. Some symbols used only once are omitted.

b Any consistent set of units may be used.  $\mu\text{M}$ : micromoles per liter.  $\mu\text{N}$ : microequivalents per liter. Units of  $K_{j,k}$  depend on values of  $z_j$  and  $z_k$ .