

# Separating Hydrological and Geochemical Influences on Runoff Acidification in Spatially Heterogeneous Catchments

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Geochemical reactions and hydrologic regime both affect runoff chemistry in many catchments. Each factor can obscure the effects of the other. This complicates efforts to interpret and predict catchments' geochemical and hydrological behavior. Here we present simple empirical techniques for separating effects of discharge fluctuations and effects of changes in acid anion concentrations in catchment monitoring data. We illustrate these techniques with data from central Ontario. Statistically subtracting acid anion effects reveals that important water quality variables (e.g., sum of base cations, acid neutralizing capacity,  $H^+$ , Al) are simple functions of the logarithm of catchment discharge. Likewise, correcting for discharge effects reveals that these water quality variables are roughly linear functions of runoff acid anion concentrations. The linear functions linking acid anion concentrations to water quality can be reliably predicted from bulk catchment runoff chemistry. Therefore acid anions' effects on water quality can be reliably predicted, even if they are obscured by discharge fluctuations in catchment monitoring data.

## INTRODUCTION

Runoff is often a mixture of flows coming from geochemically diverse sources within a catchment. It has not been clear whether the chemical behavior of such mixtures (for example, their response to changes in acid anion concentrations) could be predicted, unless the individual sources were identified and characterized. In a companion paper [Kirchner *et al.*, this issue] we showed that the acid buffering behavior of these mixtures can be predicted from the bulk chemistry of the combined runoff itself, without any information concerning the individual source regions. In other words, runoff integrates the chemical effects of geochemically diverse source regions, but does so in a way that still permits the whole catchment's acid buffering behavior to be inferred.

However, catchment runoff often does not simply reflect a fixed mixture of geochemically diverse source regions. Instead, the proportions being mixed are constantly changing, as changes in catchment hydrology alter the relative contributions from different sources [e.g., Genereux *et al.*, 1993]. Changes in the relative importance of different catchment flow paths are thought to be responsible for acid episodes in some catchments [e.g., Schofield *et al.*, 1985; Bishop *et al.*, 1990; Mulder *et al.*, 1990]. For example, during high flow a greater fraction of runoff may come from upper soil horizons, with lower base cation concentrations and alkalinity, and higher concentrations of hydrogen ions and inorganic aluminum. During drier conditions, flows from deeper soil horizons and groundwater may predominate, yielding catchment runoff with higher base cation concentrations and alkalinity, and lower concentrations of hydrogen ions and inorganic aluminum. Catchment chemical responses to other

environmental factors, such as acid loading, will be superimposed on the chemical signals produced by changes in hydrological regime.

Figure 1 shows time series data for one catchment where base cation concentrations and acid neutralizing capacity show the effects of both brief acid pulses and longer-term changes in discharge. Like the catchments analyzed in our two previous papers [Kirchner *et al.*, 1992; Kirchner *et al.*, this issue], this catchment was subject to repeated drought-induced acid pulses. Unlike the streams analyzed in our previous papers, however, this stream did not completely dry up during the droughts. Runoff alkalinity and base cation concentrations differed substantially during the drought and nondrought flow regimes. The effects of the drought-induced acid pulses (increases in base cation concentrations, and decreases in alkalinity) are overprinted on the seasonal pattern produced by the low flows themselves (increases in base cations, and increases in alkalinity).

The marked differences in stream chemistry between high and low flows in Figure 1 may result from relatively alkaline base flow mixing with varying amounts of more acidic water from shallower flow paths. In our companion paper [Kirchner *et al.*, this issue], we showed that the acid buffering behavior of a mixture of sources could be predicted from bulk runoff chemistry, if the mixing ratio were fixed. However, if mixing ratios change over time (as suggested by Figure 1), how can catchment acid buffering be predicted?

Dynamic simulation models [e.g., Christophersen *et al.*, 1982; Gherini *et al.*, 1985; Bergstrom *et al.*, 1985; Nikolaidis *et al.*, 1988] represent one approach to predicting catchment acid buffering under varying hydrologic conditions. However, even the largest and most detailed data sets are adequate to calibrate only the simplest flow path models [Hooper *et al.*, 1988; Beck *et al.*, 1990]. There is a need for techniques that predict or infer catchment geochemical behavior, without requiring detailed data concerning catchment flow paths.

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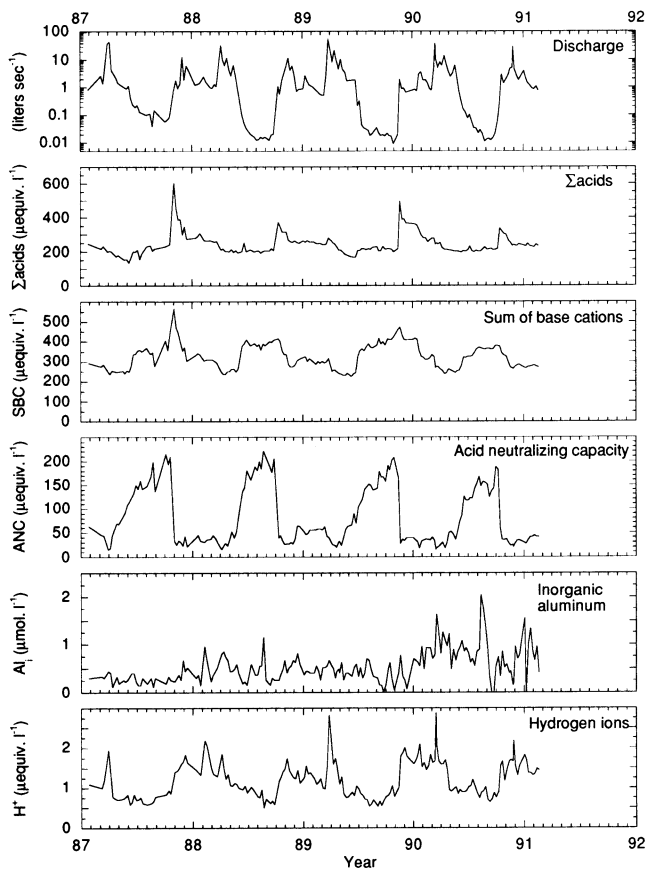


Fig. 1. Effects of summer droughts on stream discharge and runoff chemistry at catchment 3A, Harp Lake, Ontario. This catchment's drought response contrasts sharply with that of catchment 1, Plastic Lake, shown as Figure 1 in *Kirchner et al.* [1992]. At Harp 3A, discharge continued throughout each drought, although at very low flow rates. The drought periods were marked by sharply elevated base cation concentrations and acid neutralizing capacity (ANC). Acid anion pulses accompanied the end of each drought (and abruptly ended each of the high-ANC periods), although these pulses were briefer and smaller than those observed at Plastic Lake. Base cation concentrations and acid neutralizing capacity show the effects of these sharp acid pulses superimposed on a longer-term pattern reflecting changes in discharge. Variations in acid anion concentrations were almost entirely attributable to sulfate; for the period shown,  $\Sigma\text{acids} = 25 + 1.07 \text{SO}_4$  ( $r^2 = 0.93$ , with  $\Sigma\text{acids}$  and  $\text{SO}_4$  in  $\mu\text{equiv L}^{-1}$ ).

In this paper we propose that rather than combining hydrological and geochemical influences on runoff chemistry (as hydrogeochemical simulation models do), it may instead be productive to isolate them as separate factors, in order to analyze each without the confounding effects of the other. Here, we view direct acidification in a three-dimensional vector space, treating the chemical variable of interest (e.g., runoff concentrations of base cations, hydrogen ions, or inorganic aluminum) as a function of two variables: catchment discharge (as a proxy for catchment flow routing) and stream water acid anion concentrations (which reflect the combined effects of atmospheric acid deposition and catchment retention or release of acid anions):

$$y = f(\Sigma\text{acids}, q) \quad (1)$$

where  $y$  is some chemical variable of interest,  $q$  is catchment discharge, and  $\Sigma\text{acids}$  is the sum (in equivalents) of sulfate,

nitrate, chloride, and organic anions in runoff. Our working hypothesis is that while these two factors may affect  $y$  in various ways, to first approximation their joint effects are simply additive:

$$y = f_1(\Sigma\text{acids}) + f_2(q) \quad (2)$$

and thus they can be separated straightforwardly by multiple regression. If the two factors can be separated, then the problem of predicting catchment response to acid anion concentration changes can be made considerably simpler by removing the confounding effects of discharge variations.

Figure 2a illustrates how we view the joint effects of discharge and acid anion concentration changes on one chemical variable of interest, the sum of base cations (SBC). SBC depends directly on both causal factors (as indicated by the straight lines). However, when SBC is plotted as a function of one causal factor alone, but both factors vary, each can obscure the effect of the other (as indicated by the ellipses on the vertical facets of Figure 2a). This behavior is typical of catchments we have studied where base cation concentrations are strongly flow-dependent; Figures 2b and 2c illustrate this phenomenon with data from one such site.

Here we present numerical experiments and field data in which flow variations obscure the effects of acid anion concentrations on other chemical variables of interest. In each case, we show that simple statistical techniques can be used to isolate discharge fluctuations and acid anion variations as separate factors. The geochemical buffering behavior thus revealed is similar to predictions derived from the chemical composition of runoff using the heterogeneous equilibrium hypothesis [*Kirchner*, 1992]. Thus the average runoff chemistry from a catchment should reveal its chemical response to changes in stream water acid anion concentrations, even though that response may be obscured by discharge variations.

#### AN EXPERIMENT WITH FLOW-DEPENDENT RUNOFF MIXTURES

If fluctuations in flow regime alter the relative proportions of flow coming from different sources within the catchment, can we nonetheless separate flow effects from acid anion effects in catchment runoff data? Here we explore this question by creating a hypothetical catchment where the mixing ratio of flows from different sources is a function of catchment discharge. We then test whether flow and acid anion effects can be isolated in the synthetic runoff data from this hypothetical catchment. It is not obvious whether the chemical signals of discharge fluctuations and acid anion variations can be separated, once they are scrambled together. If this cannot be done using synthetic data, then it would be inappropriate to draw inferences from real catchment data with these techniques.

Our hypothetical catchment is formed by mathematically mixing runoff from two intensively monitored catchments in central Ontario, catchment 4 at Plastic Lake and catchment 6A at Harp Lake. These two source streams are also shown in Figures 3 and 6 of our companion paper [*Kirchner et al.*, this issue]. We chose these two particular streams because their runoff chemistries and responses to acidification are more clearly different than those of any other pair of streams at the Ontario study sites. These two streams also delimit a range of runoff chemistry that is similar to the hydrological-

ly-driven chemical variations seen in some catchments; Harp 6A could represent base flow runoff chemistry in a typical acid-sensitive catchment, whereas Plastic 4 could represent typical high-flow chemistry, with higher concentrations of hydrogen ions and inorganic aluminum, and lower titratable alkalinity.

For each shared sampling date (each time that both source streams were sampled on the same day or on consecutive days), we randomly selected a hypothetical catchment discharge from a lognormal distribution with mean of 1 and standard deviation of 0.65 log units (see Figure 3a). In many of our study catchments, discharge is roughly lognormal, with standard deviation between 0.6 and 0.7 log units. The size of the hypothetical merged catchment is arbitrary, so the mean discharge is of no particular significance; because the distribution is lognormal, the scale could be changed (by multiplying all discharges by a constant) without affecting the shape of the distribution.

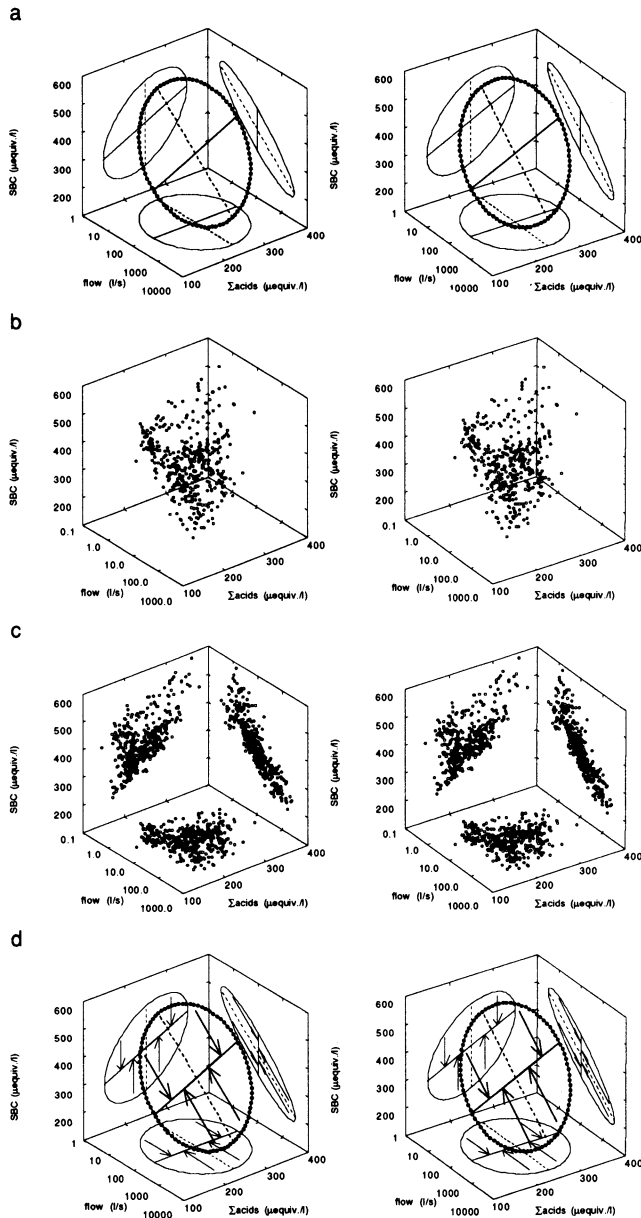


Fig. 2. (Opposite) Three-dimensional perspective plots illustrating possible relationships between the sum of base cations (SBC), the sum of acid anions ( $\Sigma\text{acids} = 2\text{SO}_4 + \text{NO}_3 + \text{Cl} + \text{organic anions}$ ), and catchment discharge, where base cation concentrations are flow-dependent. Each part can be viewed stereoscopically, by looking "through" the page (as though viewing a distant object) until the two images fuse into one. (a) Simplified relationships between SBC,  $\Sigma\text{acids}$ , and flow. The joint effect of flow and  $\Sigma\text{acids}$  on SBC is defined by a plane, indicated by the dark ellipse, that lies at an angle to all three coordinate axes. The two causal factors, flow and  $\Sigma\text{acids}$ , both vary but are uncorrelated, roughly filling a circle in the bottom plane of the coordinate cube. The straight lines indicate the effects of changes in  $\Sigma\text{acids}$  at constant flow (solid line) and changes in flow at constant  $\Sigma\text{acids}$  (dashed line). The relationship between flow and  $\Sigma\text{acids}$  on the floor of the coordinate cube can be projected vertically into the oblique plane defining their causal effect on SBC. If this relationship is then projected horizontally into either of the coordinate planes forming the back walls of the cube, one sees the apparent relationships that are observed when SBC is plotted as a function of either  $\Sigma\text{acids}$  or flow alone. The direct relationships (defined by the two straight lines) between SBC and either variable individually are clear in the back walls, but the ellipses describing the observed data show considerable scatter due to fluctuations in the other variable. For example, in the  $\Sigma\text{acids}$ -SBC plane the data form a broad ellipse, because the causal relationship between  $\Sigma\text{acids}$  and SBC (the solid line) is shifted up and down by variations in flow, along the vertical dashed line. The shape of the ellipses in these two back planes is a function of both the slope of the plane defining the causal relationship, and the shape of the relationship between flow and  $\Sigma\text{acids}$  in the bottom plane (see Figure 6). (b) Relationship between flow,  $\Sigma\text{acids}$ , and SBC observed at catchment 4, Harp Lake, Ontario. The data generally lie in a plane that slopes up, back, and left, similar to the dark ellipse shown above. (c) Observed relationships between each pair of variables (SBC as a function of  $\Sigma\text{acids}$ , SBC as a function of flow, and  $\Sigma\text{acids}$  as a function of flow) for the data shown in Figure 2b. Note that there is no clear correlation between  $\Sigma\text{acids}$  and flow, and that flow variations apparently obscure the relationship between  $\Sigma\text{acids}$  and SBC. Although the data points lie in a well-defined plane in the three-dimensional coordinate space, their projections into the two-dimensional coordinate planes are much less clear. (d) Illustration of procedure for correcting data for flow effects. Flow effects are removed from each data point (for example, an individual point in the dark ellipse) by moving it along the regression plane of the data, and parallel to the flow axis, until it intersects the mean log ( $q$ ). In the SBC- $\Sigma\text{acids}$  plane (the back left wall of the coordinate cube), this removes the scatter due to flow dependence in the data, compressing the data along the line that indicates the effect of acid anion variations under constant mean flow (the solid straight line).

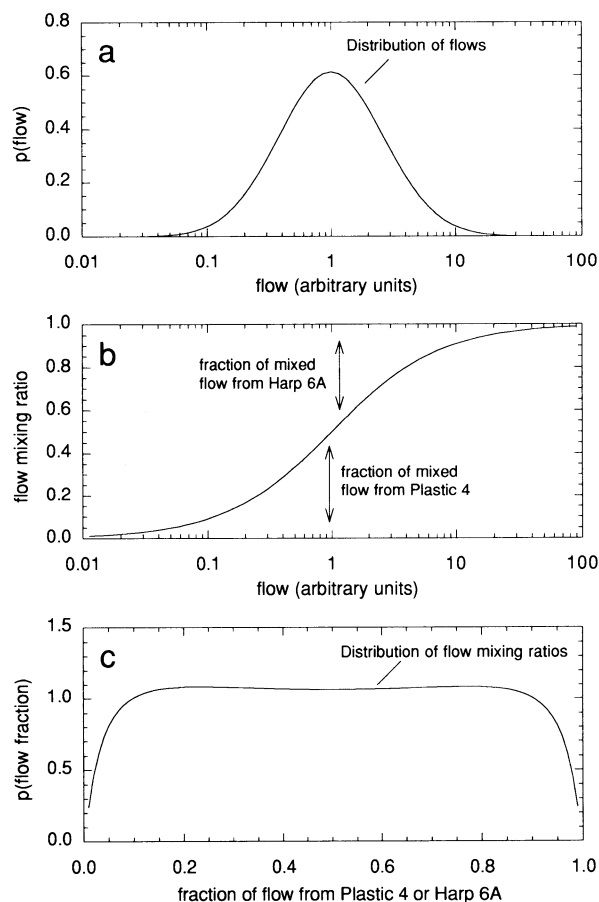


Fig. 3. Flow mixing distributions used in discharge-dependent mixing experiments (Figure 4). (a) The probability distribution of discharge is lognormal, with a standard deviation of 0.65 log units. (b) The fraction of flow mixed from each source is given by (3). (c) Weighting flow mixing ratios in Figure 3b with the probability distribution of flow in Figure 3a yields the probability distribution of the mixing ratio. The mixing ratio distribution is essentially flat, except that either source rarely makes up more than about 95% of the mixture.

From the assumed discharge, we calculated a mixing ratio for the two source streams. The fractions of flow coming from the high-flow source (Plastic 4) and the base flow source (Harp 6A) are calculated simply as

$$\frac{q_{\text{high}}}{q} = \frac{q}{q + q_{\text{ref}}}, \quad \frac{q_{\text{base}}}{q} = \frac{q_{\text{ref}}}{q + q_{\text{ref}}} \quad (3)$$

where  $q$  is the total catchment discharge,  $q_{\text{high}}$  and  $q_{\text{base}}$  are the discharge fluxes coming from the high-flow and base flow sources, and  $q_{\text{ref}}$  is the "reference" discharge at which the two sources are mixed in equal proportions. Here, we set  $q_{\text{ref}}$  equal to 1, the mean of the lognormal discharge distribution. As Figure 3b shows, the calculated mixing ratio shifts gradually and smoothly as discharge varies from low to high. The resulting probability distribution of mixing ratios is very flat (Figure 3c); all possible flow mixtures are almost equally likely (except for those in which one or the other flow source is completely absent).

We do not claim that the flow mixing relationship used here is mechanistically realistic, or that it is phenomenologically accurate for any particular catchment. Our primary

purpose is to illustrate how changes in discharge (and thus flow mixing) can obscure catchment response to changes in acid anion concentrations, not to demonstrate that a particular model of flow mixing actually describes catchment hydrology. There is no particular reason to assume that real catchment runoff is a mixture of only two sources (much less that those two sources are individually identifiable), and our objective is not to show that this is the case. Nor, indeed, would our hypothetical flow-mixing exercise be particularly effective in demonstrating this, because it begins by assuming that two such sources exist. Instead, our purpose is to illustrate how catchment runoff can be analyzed, when the individual contributing sources cannot be identified and the hydrological processes governing catchment flow mixing are unknown.

In the merged stream, the concentration of conservative solutes is the average of the measured concentrations in the two source streams, weighted by the flow fractions in (3),

$$C_{\text{merged}} = \frac{qC_{\text{high}} + q_{\text{ref}}C_{\text{base}}}{q + q_{\text{ref}}} \quad (4)$$

where  $C_{\text{merged}}$  is the solute concentration in the merged stream, and  $C_{\text{high}}$  and  $C_{\text{base}}$  are the concentrations measured in the high-flow and base flow sources, respectively (here,  $C_{\text{high}}$  and  $C_{\text{base}}$  are not averaged concentrations, but instead vary from one sampling date to another). From the concentrations of conservative solutes in the merged stream, we respiciated the concentrations of the weak acids and bases, including hydrogen ions, bicarbonate, aluminum species, and organic anions (see Kirchner *et al.* [this issue] for details). The calculated concentrations for the merged stream therefore approximate the chemical composition that would result if flows from the two source streams on the shared sampling dates were mixed in the proportions implied by the randomly chosen discharge.

Why did we opt to use randomly selected catchment discharges and the arbitrary flow mixing model described above, rather than actual measured discharges of the two streams on each sampling date? We did so because discharges in the two streams generally rise and fall in synchrony. Consequently, the measured flows yield mixing ratios that are nearly constant, whereas our purpose is to analyze chemical data that are substantially corrupted by large changes in mixing ratios.

Titrateable alkalinity, hydrogen ion concentrations, and total inorganic aluminum all vary with flow in the synthetic runoff data (Figure 4a). As a result, the effects of acid anion concentrations on these water quality indicators are much less clear in the hypothetical merged stream (Figure 4c) than in either of the source streams, or in the fixed-ratio mixtures shown in Figures 3 and 6 of Kirchner *et al.* [this issue]. Because Figure 4c includes a wide range of mixing ratios, it effectively overlays a series of mixing lines lying between the two source streams, obscuring the merged catchment's response to changing acid anion concentrations.

Can the confounding effects of flow variations be corrected for, in the runoff data from our hypothetical catchment? As Figure 4a shows, each of the chemical variables is roughly a linear function of the logarithm of discharge. The heterogeneous equilibrium hypothesis [Kirchner, 1992] also

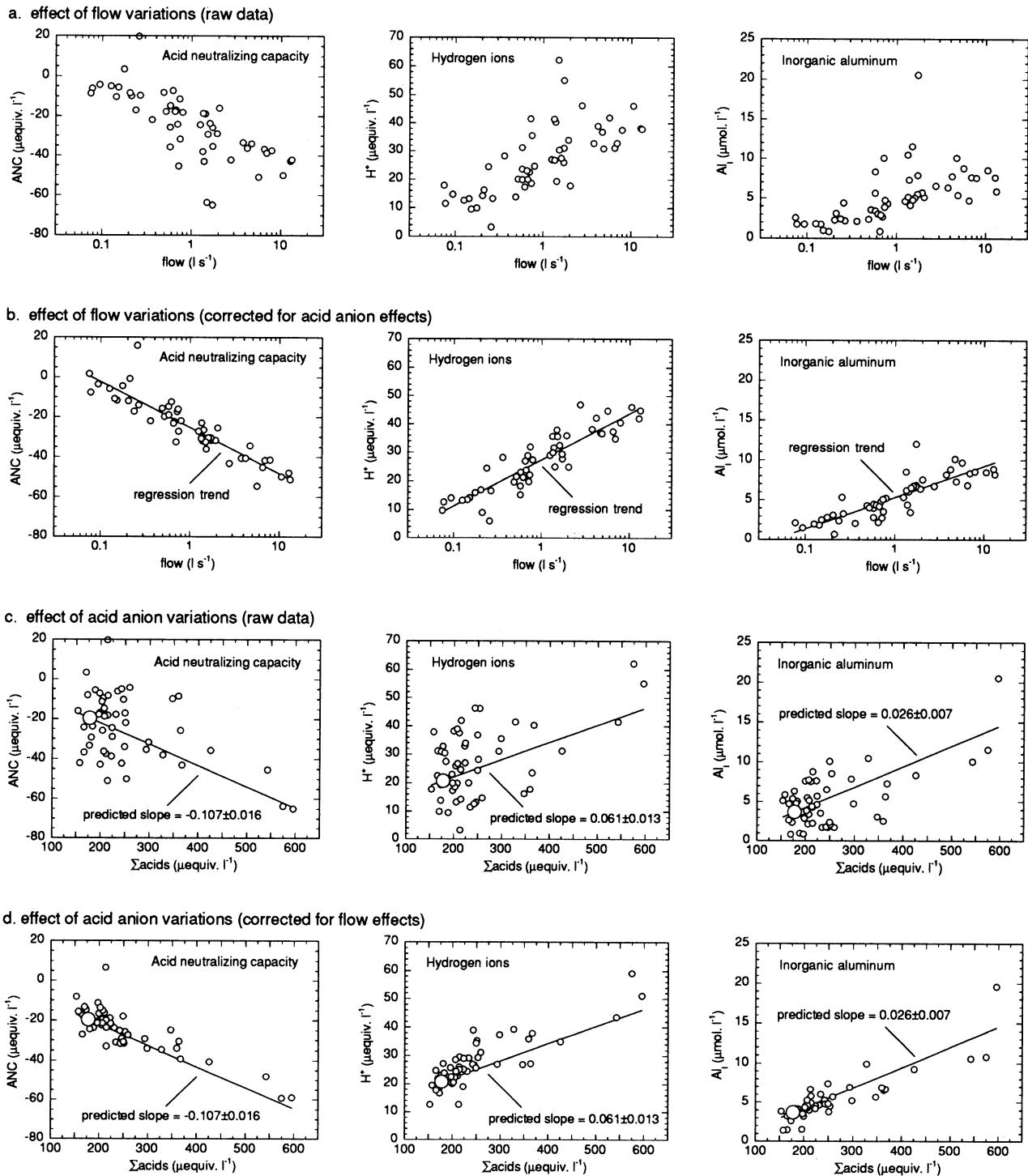


Fig. 4. Flow and acid anion effects on acid neutralizing capacity (ANC), hydrogen ion concentrations, and inorganic aluminum ( $Al_i$ ) in runoff from a hypothetical merged stream (see text). (a) Apparent relationship between water quality and flow, without correcting for acid anion effects. (b) Effect of flow on water quality, revealed by removing linear acid anion trend as described in (7). Line shown is log-linear trend fitted by multiple regression (see text). (c) Apparent relationship between water quality and acid anion concentrations, without correcting for flow effects. (d) Effect of acid anion concentrations on water quality, revealed by removing log-linear discharge trend as described in (6). Lines shown in Figures 4c and 4d are not fitted regression lines, but instead are relationships predicted by the heterogeneous equilibrium hypothesis from mean concentrations before the first acid pulse (uncorrected for flow effects) in merged stream runoff (large open circles).

leads us to expect that to first approximation, these chemical variables should be linearly dependent on  $\Sigma\text{acids}$ . These observations immediately suggest a multiple regression model for runoff chemistry in the hypothetical catchment:

$$y = m_1(\Sigma\text{acids}) + m_2 \log(q) + b \quad (5)$$

where  $m_1$ ,  $m_2$ , and  $b$  are fitted coefficients. Equation (5) is not based on the flow-mixing equations used to generate the

TABLE 1. Hypothetical Flow-Dependent Runoff Mixture: Predicted and Observed Response of Runoff Chemistry to Changes in Acid Anion Concentrations

	$\partial\text{SBC}/\partial\Sigma\text{acids}$ , $\mu\text{equiv SBC per}$ $\mu\text{equiv } \Sigma\text{acids}$	$\partial\text{ANC}/\partial\Sigma\text{acids}$ , $\mu\text{equiv ANC per}$ $\mu\text{equiv } \Sigma\text{acids}$	$\partial\text{Al}_i/\partial\Sigma\text{acids}$ , $\mu\text{mol Al}_i \text{ per}$ $\mu\text{equiv } \Sigma\text{acids}$	$\partial\text{H}^+/\partial\Sigma\text{acids}$ , $\mu\text{equiv H}^+ \text{ per}$ $\mu\text{equiv } \Sigma\text{acids}$
Observed catchment response				
corrected for discharge effects	$0.877 \pm 0.017$	$-0.097 \pm 0.009$	$0.025 \pm 0.002$	$0.074 \pm 0.007$
not corrected for discharge effects	$0.898 \pm 0.020$	$-0.082 \pm 0.021$	$0.022 \pm 0.004$	$0.063 \pm 0.015$
Catchment response predicted from				
average of mixed runoff	$0.857 \pm 0.029$	$-0.107 \pm 0.016$	$0.026 \pm 0.007$	$0.061 \pm 0.013$
flow-weighted average runoff	$0.769 \pm 0.022$	$-0.157 \pm 0.013$	$0.044 \pm 0.005$	$0.100 \pm 0.010$
high-flow source (Plastic 4)	$0.693 \pm 0.011$	$-0.201 \pm 0.008$	$0.059 \pm 0.004$	$0.133 \pm 0.007$
base flow source (Harp 6A)	$0.940 \pm 0.007$	$-0.059 \pm 0.007$	$0.003 \pm 0.000$	$0.015 \pm 0.002$

Observed response slopes (reported as means  $\pm$  standard errors) were estimated by multiple linear regression of runoff chemistry variables on  $\Sigma\text{acids}$  and  $\log(q)$  ("corrected for discharge effects") and simple linear regression on  $\Sigma\text{acids}$  alone ("not corrected for discharge effects"). Predicted response slopes were estimated by (5)–(8) of Kirchner *et al.* [1992] from average runoff concentrations in samples taken before the first drought (see text) from the merged stream (with and without flow weighting) and from each of the source streams. These predrought samples all have  $120 < \Sigma\text{acids} < 220 \mu\text{equiv L}^{-1}$ ; the predrought means therefore reflect a much smaller range of  $\Sigma\text{acids}$  than the range used to test the predictions.

data; instead, it represents simply an approximate empirical generalization. If (5) approximately accounts for flow effects on  $y$ , then we can correct for flow variations by converting each measured value of  $y$  to its equivalent value at the mean flow:

$$y_{\Sigma\text{acids}} \approx y - m_2(\log(q) - \overline{\log(q)}) \approx m_1(\Sigma\text{acids}) + b' \quad (6)$$

where  $y_{\Sigma\text{acids}}$  is the discharge-corrected counterpart to the observed  $y$ , overbars indicate averages, and the constant  $b'$  equals  $b + m_2 \log(\bar{q})$ . Equation (6) removes the linear component of the discharge dependence in the data. In terms of the three-dimensional graph shown in Figure 2d, (6) projects each point parallel to the multiple regression plane defined in (5), and parallel to the  $\log(q)$  axis, until it reaches the mean  $\log(q)$ . Similarly, we can correct for variations in acid anion concentrations by subtracting the linear component of the  $\Sigma\text{acids}$  dependence in the data:

$$y_q \approx y - m_1(\Sigma\text{acids} - \overline{\Sigma\text{acids}}) \approx m_2 \log(q) + b'' \quad (7)$$

where  $y_q$  is the acid anion-corrected counterpart to the observed  $y$ . If variation in either factor ( $q$  or  $\Sigma\text{acids}$ ) is obscuring the effects of the other, (6) and (7) should correct for the linear component of the confounding factor's effects.

Applying (7) to the data from our hypothetical flow-dependent catchment, we see that correcting for acid anion variations removes much of the scatter in the apparent relationship between catchment discharge and the water quality indicators (Figure 4b). Likewise, correcting for flow variations via (6) substantially sharpens the relationship between acid anion concentrations and the chemical quantities of interest (Figure 4d).

The way we mixed the two sources (equation (3)) makes this analysis simple because it makes runoff chemistry a roughly linear function of  $\log(q)$ ; if another mixing rule were used, runoff chemistry would be some other (potentially more complex) function of discharge. But although we created the hypothetical catchment from known source streams, our analysis of the data from it does not use any information about the individual sources, or about the way in which we mixed them. In any event, our aim is not to statistically "unmix" a runoff mixture, as in traditional hydrograph separations. Instead, our goal is to extract chemical information from runoff data that have been sub-

stantially corrupted by flow variations that obscure or distort the chemical signals.

The  $\Sigma\text{acids}$  dependence revealed in the data is close to the relationship predicted by the heterogeneous equilibrium hypothesis. We calculated the slopes of the lines in Figures 4c and 4d from the average runoff chemistry (without any flow correction) in the hypothetical merged stream before the first acid pulse (indicated by the large open symbols), assuming that heterogeneous equilibrium prevails [Kirchner *et al.*, 1992, equations (5)–(8)]. The discharge-corrected observations generally conform to the predicted relationships (as do the uncorrected data, though with more scatter). The regression slopes of the flow-corrected data are virtually identical to the slopes predicted by heterogeneous equilibrium (Table 1). In other words, the heterogeneous equilibrium hypothesis accurately describes the hypothetical catchment's response to acid anions, even though that response may be obscured by discharge fluctuations when chemical variables are plotted as functions of  $\Sigma\text{acids}$  without correcting for flow effects.

Although correcting for flow effects dramatically reduces the scatter in the data (Figures 4c and 4d), it does not substantially alter the regression slopes relating  $\Sigma\text{acids}$  to the various water quality indicators (Table 1). This results from the weak correlation ( $r = 0.10$ ) between  $\Sigma\text{acids}$  and  $\log(q)$ . As we explain in detail below, if these two factors were strongly correlated, flow effects could substantially distort the apparent slope of the relationship between  $\Sigma\text{acids}$  and the variable of interest (Figures 6c and 6d). This distortion can only be removed by determining, and then correcting for, the effects of discharge in the data.

As Table 1 shows, the merged stream's average runoff chemistry predicts the observed response to changes in  $\Sigma\text{acids}$  better than its flow-weighted runoff chemistry does. This happens because the simple average of the runoff chemistry better reflects the average mixing ratio of the two sources. Although the average mixing ratio is 50:50 (see Figure 3c), the "high-flow" source (Plastic 4) accounts for 78% of the total flow (because discharge is high when the mixing ratio favors the high-flow source). Flow-weighted average runoff concentrations are important for catchment mass balance purposes, but they are not representative of

the geochemical equilibria and flow mixing ratios that usually prevail in the catchment.

Finally, note that the runoff chemistries of the base flow and high-flow sources are not good predictors of the acid anion response observed in the merged stream (Table 1) even though they accurately predict the acid buffering behavior of their respective source streams (Figure 3 of *Kirchner et al.* [this issue]). This suggests that unless one knows how flows from different compartments within the catchment are mixed in runoff, whole-catchment geochemical behavior may not be predictable from the various pore water compositions and geochemical properties of those individual compartments, although it is predictable from the combined runoff. A salient advantage of the heterogeneous equilibrium approach is that it is based on catchment runoff chemistry itself, which reflects the catchment's individual sources of flow in proportion to their chemical influence on runoff. Although we created the hypothetical catchment data from known source streams, our analysis of those data does not use any information about the individual sources, or about the way in which we mixed them.

#### ILLUSTRATIONS WITH FLOW-DEPENDENT RUNOFF CHEMISTRY DATA

The experiment described above suggests that in catchment runoff data, the chemical effects of discharge variations can be statistically isolated and corrected for, thus clarifying catchment response to other factors (such as acid anion concentrations). We have shown above that this can be done in a simple hypothetical catchment with two geochemically distinct sources, combined by a simple discharge-dependent mixing relationship. Do these techniques also work in real catchment runoff data, where there may be many sources, and the mixing relationships may be complex?

Here we test these techniques using data from catchments 3A and 4 at Harp Lake, Ontario, where runoff chemistry is strongly dependent on flow. The chemical variable of interest will be the sum of base cations (SBC) because these streams are not acidic enough for  $H^+$  and  $Al_3$  to show clear chemical signals (among our monitored catchments, none of the acidic streams are as strongly flow dependent as those analyzed here).

At Harp 3A (shown in Figure 1) and Harp 4 (shown in Figures 2b and 2c) discharge variations have a pronounced effect on SBC. At Harp 4, low flows (discharges less than 3.5 L/s, comprising the lowest 25% of sampled flows) have SBC almost 200 microequivalents per liter higher, on average, than high flows (discharges greater than 18.3 L/s, comprising the highest 25% of sampled flows) at comparable acid anion concentrations (Figure 5a). Although runoff data from Harp 4 span almost a thousandfold range of discharge, runoff chemistry changes most markedly in the roughly fivefold range of discharge between these high and low flows (that is, the middle 50% of sampled flows). As a result, the relationship between SBC and  $\log(q)$  is distinctly nonlinear (Figures 5a and 5b). At Harp 3A the lowest one third of sampled flows have SBC roughly 100  $\mu\text{equiv L}^{-1}$  higher than the highest two-thirds of flows (Figures 5a and 5b).

Plotting each of the three discharge ranges at Harp 4 using different symbols, we see that SBC generally varies with  $\Sigma\text{acids}$  in each discharge range as predicted by heterogeneous equilibrium from mean runoff concentrations before

the first acid pulse (Figure 5c). This is similar to the behavior we observed in Figure 6 of *Kirchner et al.* [this issue] for a hypothetical merged stream. If the different discharge ranges were not identified by different plot symbols, however, the relationship between acid anion concentrations and SBC would be much less clear.

At Harp 3A, unlike Harp 4, the apparent relationship between  $\Sigma\text{acids}$  and SBC is surprisingly nonlinear (Figure 5c). For the lowest third of the sampled flows (solid symbols) SBC falls completely outside the trends defined by the data from the higher flows (open symbols). Under drought conditions, the catchment appears to switch to a different mode of geochemical behavior, with markedly higher base cation concentrations.

At Harp 3A, flow effects do not simply obscure the apparent relationship between SBC and  $\Sigma\text{acids}$ , they also distort it. Because high and low flows occur in all ranges of  $\Sigma\text{acids}$  at Harp 4, flow variations simply blur the underlying dependence of SBC on  $\Sigma\text{acids}$ . However, at Harp 3A, drought flows (and thus drought effects on SBC) occur only at low acid anion concentrations, distorting the relationship between SBC and  $\Sigma\text{acids}$ . As a result, simple regression lines fitted to this relationship misrepresent the underlying  $\Sigma\text{acids}$  dependence of SBC (Figure 5c).

Because SBC is nonlinearly related to  $\log(q)$  at Harp 3A and Harp 4, the multiple linear regression analysis used above (for our hypothetical catchment) yields unevenly distributed residuals. This statistically confirms what Figure 5a visually suggests, namely, that a linear  $\log(q)$  trend is an inadequate description of the data. The data show that SBC shifts gradually between high- and low-flow concentrations that vary little with discharge. This observation suggests that the simple flow-mixing model shown in Figure 3b may adequately express the flow dependence of SBC. We therefore fit the data with a regression model that combines the nonlinear flow dependence of (4) with linear dependence on  $\Sigma\text{acids}$ :

$$y = f_1(\Sigma\text{acids}) + f_2(q) \quad (8)$$

$$f_1(\Sigma\text{acids}) = m_1(\Sigma\text{acids} - \overline{\Sigma\text{acids}})$$

$$f_2(q) = \frac{qC_{\text{high}} + q_{\text{ref}}C_{\text{base}}}{q + q_{\text{ref}}}$$

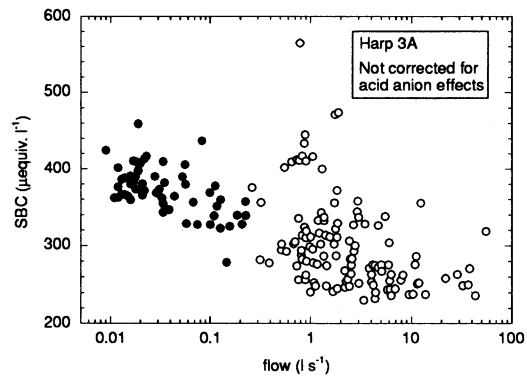
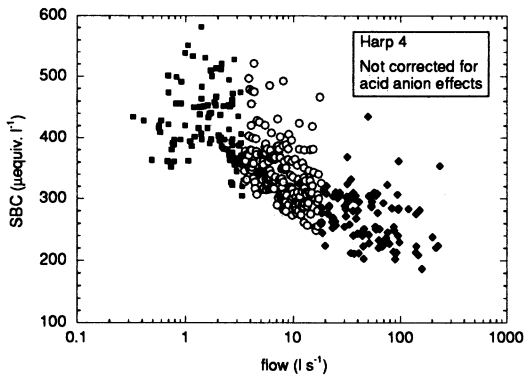
This model has four parameters.  $C_{\text{high}}$  and  $C_{\text{base}}$  are high-flow and base flow concentrations at the mean acid anion concentration,  $q_{\text{ref}}$  is the reference discharge at which  $C_{\text{high}}$  and  $C_{\text{base}}$  are mixed in equal proportions, and  $m_1$  is, as before, the slope of the linear  $\Sigma\text{acids}$  trend. These parameters are all identifiable in a least squares fit to the data. For Harp 4,  $C_{\text{high}} = 251 \pm 4 \mu\text{equiv/L}$ ,  $C_{\text{base}} = 506 \pm 9 \mu\text{equiv/L}$ ,  $q_{\text{ref}} = 3.8 \pm 0.4 \text{ L/s}$ , and  $m_1 = 0.80 \pm 0.04$ ; for Harp 3A,  $C_{\text{high}} = 269 \pm 3 \mu\text{equiv/L}$ ,  $C_{\text{base}} = 418 \pm 4 \mu\text{equiv/L}$ ,  $q_{\text{ref}} = 0.26 \pm 0.04 \text{ L/s}$ , and  $m_1 = 0.76 \pm 0.03$ . The fitted model explains 82% of the variance in SBC at Harp 4 and 90% at Harp 3A.

Using the fitted parameters, we can correct the data for flow effects yielding SBC as a function of  $\Sigma\text{acids}$  at the mean effect of flow as follows:

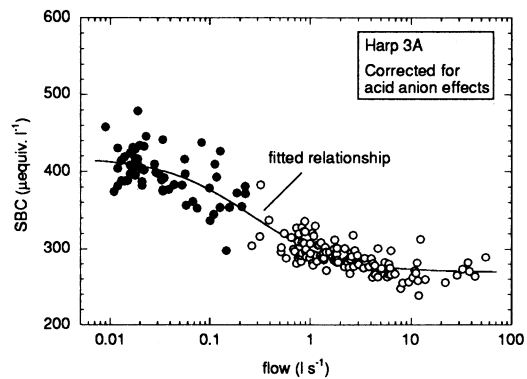
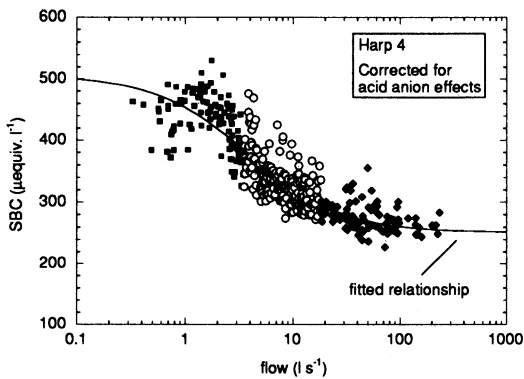
$$y_{\Sigma\text{acids}} \approx y - f_2(q) + \overline{f_2(q)} \approx f_1(\Sigma\text{acids}) + \overline{f_2(q)} \quad (9)$$

where, because  $\overline{f_2(q)}$  is a constant,  $y_{\Sigma\text{acids}}$  should be a linear function of  $\Sigma\text{acids}$  alone. Similarly, we can remove the linear acid anion trend, yielding SBC as a function of flow at the mean  $\Sigma\text{acids}$  as follows:

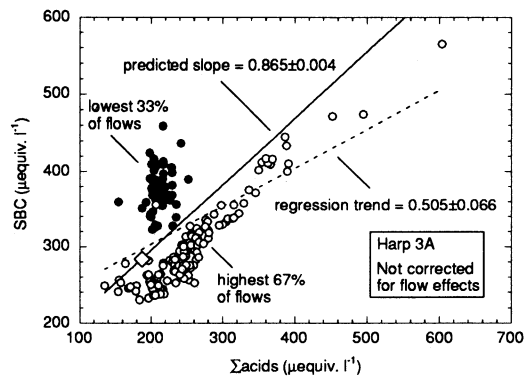
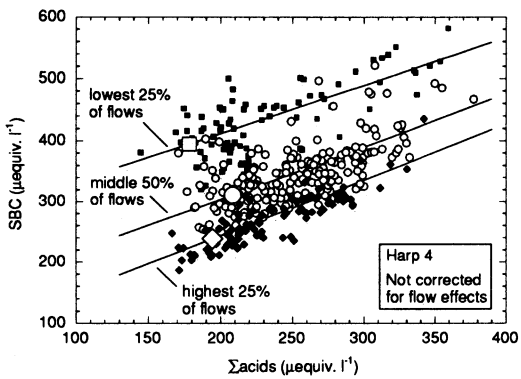
a. effect of flow variations (raw data)



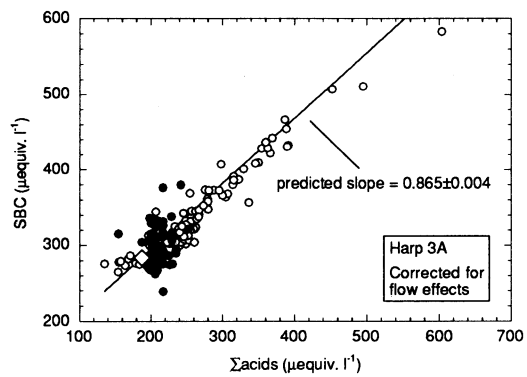
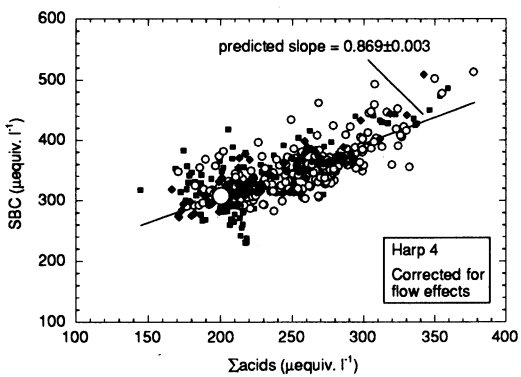
b. effect of flow variations (corrected for acid anion effects)



c. effect of acid anion variations (raw data)



d. effect of acid anion variations (corrected for flow effects)





$$y_q \approx y - f_1(\Sigma\text{acids}) + f_1(\overline{\Sigma\text{acids}}) \approx f_2(q) \quad (10)$$

Removing the linear acid anion trend reveals that our simple mixing model predicts the general shape of SBC's dependence on flow (Figure 5b). Correcting for this flow dependence makes the separate groups of data (representing different flow ranges) coalesce into a single relationship between SBC and  $\Sigma\text{acids}$  (Figure 5d).

The linear trends relating SBC to  $\Sigma\text{acids}$  have slopes (the  $m_1$  coefficients above) similar to the trends predicted by heterogeneous equilibrium. At Harp 4, the predicted slope is  $0.87 \pm 0.01$  ( $\mu\text{equiv SBC per } \mu\text{equiv } \Sigma\text{acids}$ ) and the observed slope is  $0.80 \pm 0.04$ , while at Harp 3A, the predicted slope is  $0.86 \pm 0.01$ , and the observed slope is  $0.76 \pm 0.03$ . Applying the nonlinear regression model in (8) to ANC data from these catchments yields similar results. At both Harp 4 and Harp 3A, the predicted slope is  $-0.13 \pm 0.01$  ( $\mu\text{equiv ANC per } \mu\text{equiv } \Sigma\text{acids}$ ); the observed slopes are  $-0.12 \pm 0.04$  at Harp 4 and  $-0.17 \pm 0.02$  at Harp 3A. Using only the average runoff chemistry before the first acid pulse as input, heterogeneous equilibrium correctly predicts these catchments' chemical responses to changes in acid anion concentrations (as revealed in the flow-corrected data), even though the underlying chemical relationships are utterly obscured in the uncorrected data.

#### DISCUSSION

Through what mechanism does catchment discharge affect runoff chemistry? Although our presentation is cast in terms of discharge altering the mixing ratios of different catchment runoff sources, our data do not prove that flow mixing is, in fact, the mechanism at work in our catchments (nor was this our purpose). The major point of our paper is not that discharge variations affect runoff chemistry in any particular way, or through any particular mechanism. Instead, our point is that whatever the effects of discharge fluctuations on runoff chemistry (and however those effects are created),

they can be factored out of catchment data to better illuminate the effects of other factors (such as variations in stream water acid anion concentrations).

In addition to the flow-mixing mechanism analyzed here, dilution effects [e.g., Johnson *et al.*, 1969] or contact time effects [e.g., Peters and Murdoch, 1985] could make runoff chemistry vary with discharge. These effects could be significant if the chemistry of runoff is not in geochemical equilibrium with the catchment, but instead is controlled by kinetically limited reactions that are far from equilibrium. Our analysis assumes that runoff chemistry (except for acid anions) is governed by geochemical equilibria. To the extent that our analysis explains the observed variations in runoff chemistry, contact time or dilution effects are not needed to explain the data presented here. However, the data do not exclude a possible role for these processes in the catchments we have analyzed.

Hydrologists have often viewed runoff as a mixture of chemically distinct waters and have used the chemical composition of runoff to infer the proportions from each source being mixed. Variations in runoff chemistry have been attributed to changes in the mixture of different types of waters, such as precipitation and groundwater [e.g., Johnson *et al.*, 1969] or "event" and "preevent" water [e.g., Sklash and Farvolden, 1979]. Recently, a more elaborate "end-member mixing analysis" has been used to interpret runoff chemistry as a conservative mixture of soil water solutions from various locations and horizons within the catchment [Christophersen *et al.*, 1990; Christophersen and Hooper, 1992; Hooper *et al.*, 1990]. Here, by contrast, the objective is not to infer flow path routing from runoff chemistry, but instead to isolate flow path changes and geochemical processes as separate causal factors in runoff chemistry time series. Our approach explicitly recognizes that both factors affect runoff chemistry, rather than attributing the observed chemical changes solely to changes in mixing ratios.

Hydrological analyses, like those cited above, often assume that each source of water has a fixed chemical signature. However, catchment time series data may reflect marked changes in chemical driving forces such as  $\Sigma\text{acids}$ , which can alter the chemistry of runoff even if flow path routing does not change. Large changes in  $\Sigma\text{acids}$  can obscure the role of hydrology in shaping runoff chemistry (e.g., Figure 4a). Just as our analysis shows that correcting for flow path effects can clarify geochemical influences on water quality, it also shows that correcting for geochemical effects (resulting from, for example, changes in  $\Sigma\text{acids}$ ) can clarify how runoff chemistry depends on catchment hydrological behavior.

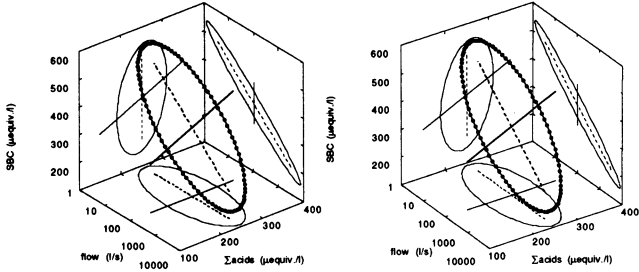
The extent to which variation in  $\Sigma\text{acids}$  obscures the effect of discharge (or, conversely, variation in discharge obscures the effect of  $\Sigma\text{acids}$ ) is controlled by several factors that can be illustrated graphically (see Figure 6). These factors can also be elucidated through simple statistical analysis if  $y$ , the water quality variable of interest, is assumed to be linearly dependent on  $\log(q)$  and  $\Sigma\text{acids}$  (see the appendix). Flow variations will obscure more of the relationship between  $y$  and  $\Sigma\text{acids}$  if either (1) the variance in  $\log(q)$  increases, (2) the variance in  $\Sigma\text{acids}$  decreases, (3) the slope of the causal relationship between  $\log(q)$  and  $y$  becomes steeper ( $m_1$  increases), or (4) the slope of the relationship between  $\Sigma\text{acids}$  and  $y$  becomes shallower ( $m_2$  decreases). Any of

Fig. 5. (Opposite) Effects of flow and acid anion concentrations ( $\Sigma\text{acids}$ ) on sum of base cations (SBC) at catchments 3A and 4, Harp Lake, Ontario. Effects of discharge variations are highlighted by plotting different flow ranges with different symbols. (a) Apparent relationship between SBC and flow, without correcting for acid anion effects. (b) Dependence of SBC on flow, clarified by removing linear acid anion trend as described in text. Line shown is simple mixing model (equation (8)) fitted by nonlinear least squares regression (see text). (c) Apparent relationship between SBC and acid anion concentrations, without correcting for flow effects. At Harp 4, SBC is a well-defined function of  $\Sigma\text{acids}$  in each of the flow ranges, although when all three flow ranges are taken together, the dependence on  $\Sigma\text{acids}$  is obscured. The straight lines show the catchment response to  $\Sigma\text{acids}$  predicted by heterogeneous equilibrium for each flow range from the mean runoff chemistry before the first acid pulse (large open symbols). As is hypothesized by Kirchner *et al.* [this issue], heterogeneous equilibrium predicts the observed  $\Sigma\text{acids}$  dependence of SBC in each flow range, although flow variations obscure the observed relationships when different flow ranges are plotted together. At Harp 3A, flow effects distort the relationship between  $\Sigma\text{acids}$  and SBC. (d) Dependence of SBC on acid anion concentrations, revealed by removing nonlinear discharge trend as described in text. Lines shown in Figures 5d and 5c for Harp 3A are relationships predicted by the heterogeneous equilibrium hypothesis from mean concentrations before the first acid pulse (including all flow ranges).

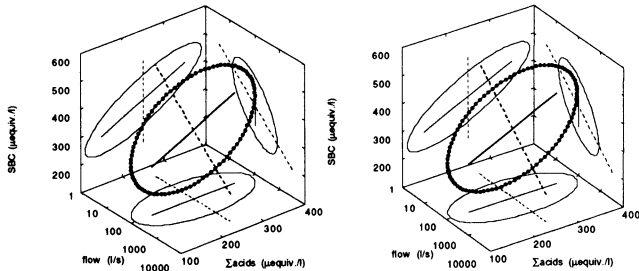
these four changes will decrease the correlation between  $y$  and  $\Sigma\text{acids}$  in the  $y$ - $\Sigma\text{acids}$  plane, but will make the correlation between  $y$  and  $\log(q)$  more distinct (equation (15); Figures 6a and 6b). Any conditions that clarify  $y$ 's dependence on one factor will obscure its dependence on the other;  $y$  cannot be closely correlated with both  $\log(q)$  and  $\Sigma\text{acids}$  simultaneously, as long as one views the data in only the  $y$ - $\log(q)$  plane and the  $y$ - $\Sigma\text{acids}$  plane.

Although it is widely (and correctly) understood that correlation does not prove causation, it is also widely (and incorrectly) believed that poor correlation proves that no causal relationship exists. The correlation between two variables (say,  $y$  and  $\Sigma\text{acids}$ ) does not directly measure the strength of the causal relationship between them [Sokal and Rohlf, 1981]. Instead, it combines several different elements: the strength of the relationship between  $y$  and  $\Sigma\text{acids}$  (that is, the slope  $m_1$ ), the amount of variation in  $\Sigma\text{acids}$ , the amount of variation in other factors, and the strength of their relationships to  $y$ . Comparing Figures 2a, 6a, and 6b shows that the degree of correlation between  $y$  and either  $\log(q)$  or  $\Sigma\text{acids}$  can vary greatly, even though the causal relationship between  $y$ ,  $\log(q)$ , and  $\Sigma\text{acids}$  remains exactly the same

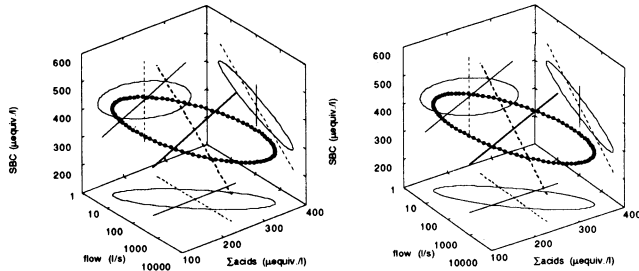
a. greater variance in flow, smaller variance in  $\Sigma\text{acids}$



b. greater variance in  $\Sigma\text{acids}$ , smaller variance in flow



c. positive correlation between  $\Sigma\text{acids}$  and flow



d. negative correlation between  $\Sigma\text{acids}$  and flow

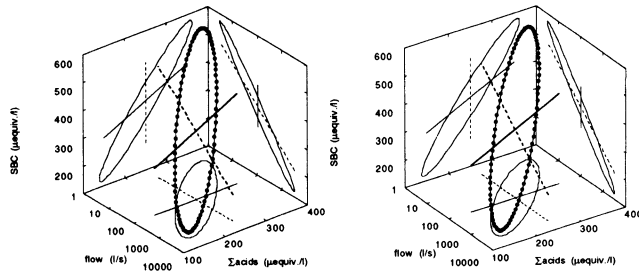


Fig. 6. (Opposite) Three-dimensional perspective diagrams (in stereo pairs) illustrating how the apparent relationships between base cations, acid anions, and flow are altered if (a) flow varies more and  $\Sigma\text{acids}$  varies less, (b)  $\Sigma\text{acids}$  varies more and flow varies less, (c) flow and  $\Sigma\text{acids}$  are positively correlated, or (d) flow and  $\Sigma\text{acids}$  are negatively correlated. In all four plots, the dependence of SBC on  $\Sigma\text{acids}$  and flow (i.e., the plane in which the heavy ellipse lies) is the same as the functional relationship in Figure 2a. The solid and dashed straight lines, representing variation in  $\Sigma\text{acids}$  at constant flow and variation in flow at constant  $\Sigma\text{acids}$  are also in the same position and have the same length in all four plots as in Figure 2a. These lines provide a visual reference for the changes in shape and orientation of the ellipses, which indicate the potential range spanned by catchment runoff data under different conditions. Figures 6a and 6b illustrate how SBC may be poorly correlated with either  $\Sigma\text{acids}$  and flow, even if it is causally related to both. In Figure 6a the variance in flow has increased and the variance in  $\Sigma\text{acids}$  has decreased, obscuring the relationship between  $\Sigma\text{acids}$  and SBC in the SBC- $\Sigma\text{acids}$  plane (the back left wall of the coordinate cube) but sharpening the relationship between SBC and flow in the SBC flow plane (the back right wall of the coordinate cube). In Figure 6b the variance of flow is smaller and the variance of  $\Sigma\text{acids}$  is greater, which decreases the confounding flow effect in the SBC- $\Sigma\text{acids}$  plane and increases the confounding  $\Sigma\text{acids}$  effect in the SBC flow plane. Note that the degree of correlation between SBC and both  $\Sigma\text{acids}$  and flow varies greatly between Figures 6a, 6b and Figure 2a, although the causal relationship between the three variables remains precisely the same. In Figures 6c and 6d both  $\Sigma\text{acids}$  and flow have the same variance and the same causal relationship to SBC as in Figure 2a, but here they are correlated with one another. In Figure 6c flow and  $\Sigma\text{acids}$  are positively correlated, but have opposite effects on SBC. Thus increasing flow directly decreases SBC, but also indirectly increases SBC, by increasing  $\Sigma\text{acids}$ . In Figure 6d flow and  $\Sigma\text{acids}$  are negatively correlated with one another. Each factor's direct effect on SBC is reinforced by its indirect effect through its correlation with the other factor. For example, increasing flow decreases SBC, both as a direct effect, and indirectly by decreasing  $\Sigma\text{acids}$ . Note that in both Figure 6c and 6d the apparent relationships between  $\Sigma\text{acids}$  and SBC in the SBC- $\Sigma\text{acids}$  plane are very different from the actual causal effect of  $\Sigma\text{acids}$  on SBC (the solid straight line). Even though the apparent slopes are misleading, nonetheless the apparent relationships are much more distinct than in Figure 2a. Unless the confounding effect of flow were discovered, the strong correlation between SBC and  $\Sigma\text{acids}$  could lead to the incorrect conclusion that the apparent relationship is a causal one.

(i.e.,  $m_1$  and  $m_2$  in (5) do not change). Unless one can analyze the effects of confounding variables, as we have done above, poor correlation between two variables should not be interpreted as conclusive evidence that a causal relationship does not exist between them, or that such a relationship is weak. Poor correlation implies only that if a causal relationship exists, it accounts for a small fraction of the total variance.

The preceding discussion assumes that there is no correlation between  $\log(q)$  and  $\Sigma\text{acids}$  themselves. If, instead,  $\log(q)$  and  $\Sigma\text{acids}$  are strongly correlated, plotting  $y$  against either  $\log(q)$  or  $\Sigma\text{acids}$  alone can give an even more misleading picture of the underlying causal relationships. As Figures 6c and 6d show, strong correlation between  $\log(q)$  and  $\Sigma\text{acids}$  would make simple linear regression unreliable in estimating the slope of the underlying relationship between  $y$  and either causal factor (equation (18)). Furthermore, spurious correlation introduced by a close linkage between  $\Sigma\text{acids}$  and  $\log(q)$  could make either variable's relationship with  $y$  look quite well-defined, even though the apparent relationships are very different from the correct ones (equation (20); Figures 6c and 6d).

The point of this theoretical discussion (as well as the empirical examples presented earlier) is that when both flow and acid anion concentrations affect water quality, both factors must be taken into account so that the effect of each can be correctly identified. Simply plotting water quality as a function of flow, or as a function of acid anion concentrations, does not necessarily reveal its underlying dependence on either variable.

The two-compartment flow-mixing model used to generate the synthetic data in our hypothetical merged stream also describes the flow dependence observed in our real catchments. This invites the interpretation that runoff from Harp 4 and Harp 3A is, in fact, composed of a mixture from two such catchment sources: a small base flow source with high base cation concentrations and high alkalinity, and a variable high-flow source with much lower base cation concentrations and alkalinity. Our view is more cautious; the data are consistent with such an interpretation, but it is not clear that they require it. The good fit implies that Harp 4 and Harp 3A behave as if they were composed of flows from two such sources; whether these sites actually are primarily composed of two such flows is another matter, which requires additional research.

In the analysis presented here, the relationship between discharge and runoff chemistry is empirically determined. Does estimating the flow dependence of runoff chemistry require large data sets? The Harp 3A data set analyzed here consists of 180 paired flow readings and chemical analyses, and the Harp 4 data set contains 410 points, but data sets this large are probably not necessary. To explore how smaller data sets would behave, we randomly deleted half of the points from each data set, then refitted the parameters, then randomly deleted half the remaining points, and so forth. The parameters reported above remained close to their original values ( $C_{\text{high}}$  within 6  $\mu\text{equiv L}^{-1}$ ,  $C_{\text{base}}$  within 15  $\mu\text{equiv L}^{-1}$ ,  $q_{\text{ref}}$  within 37%, and  $m_1$  within 0.07), even when the data sets were shrunk to 1/8 of their original sizes (that is, 52 points at Harp 4 and 22 points at Harp 3A). Although this test is not exhaustive, it does indicate that where flow effects are pronounced, they can be estimated from relatively modest data sets.

The empirical approach outlined here is minimally parameterized, and seeks only to estimate how changes in discharge affect runoff chemistry. It does not try to predict what those changes in discharge will be, or when they will occur (given, for example, a particular precipitation time series). Such rainfall-runoff modeling is considerably more difficult than estimating the simple concentration-discharge relationships used here and requires much larger data sets, either for fitting empirical models or for calibrating mechanistic models.

Because our approach, unlike many catchment hydrogeochemical models, does not attempt to model the relationship between precipitation and discharge, its data requirements are much more modest. The data requirements are even more modest for predicting how water quality responds to acid anion concentrations in pore water or stream water, because the heterogeneous equilibrium analysis requires only catchment runoff chemistry data as input, and only a few samples are needed for robust predictions [Kirchner, 1992; Kirchner *et al.*, 1992]. Runoff chemistry does not need to be corrected for flow effects to yield accurate predictions, although, as Figure 5a shows, the runoff chemistry samples must be representative of the flow regimes (and thus mixtures of sources) for which predictions are desired [Kirchner *et al.*, this issue].

In all the cases presented here, we predicted catchment acid buffering behavior directly from runoff chemistry measurements, without correcting them for flow effects or manipulating them in any other way. We only corrected for flow effects to test the predictions, by statistically removing the confounding effects of flow variations and thus revealing catchment response to acid anion changes. Large data sets, like those used here, are not required by the heterogeneous equilibrium method, but they are useful for testing its reliability.

Many catchment acidification analyses seek to predict how changes in acid deposition will affect runoff chemistry. To the extent that changes in runoff acid anion concentrations can be predicted from changes in deposition, heterogeneous equilibrium provides an efficient method for predicting catchment response to changes in acid loading. Heterogeneous equilibrium itself, however, does not directly predict how acid deposition affects runoff acid anion concentrations.

However, in the heterogeneous equilibrium approach, empirical descriptions or mechanistic models of anion processes (e.g., deposition/runoff relationships or adsorption isotherms) can be used to link changes in atmospheric deposition to shifts in runoff acid anion concentrations, and thus to changes in various water quality variables. Sulfate is the anthropogenic acid anion of primary concern in most catchments; data from Norway and much of North America [Wright and Henriksen, 1983; Sullivan *et al.*, 1988] suggest that shifts in runoff sulfate concentrations are often proportional to changes in concentrations in precipitation. This is not the case in some areas (such as the Southern Blue Ridge province) where highly weathered soils may adsorb significant quantities of sulfate; as their sulfate adsorption capacity becomes increasingly saturated, sulfate concentrations in runoff may rise even without changes in sulfate deposition [Church *et al.*, 1990]. Nitrate deposition is largely offset by biomass uptake, keeping nitrate concentrations low in porewaters and runoff [Reuss and Johnson, 1986], although there is evidence that in some areas the capacity of the biota to

take up nitrate is becoming saturated, raising nitrate concentrations in surface waters [Henriksen and Brakke, 1988; Dillon and Molot, 1990; Aber, 1992].

In addition to the shifts in equilibrium considered here, long-term acidification can occur if base cation leaching exceeds resupply by mineral weathering, leading to depletion of bases from catchment soils. As exchangeable base cations become depleted, the plane of the data in Figure 2 will shift downward over time. Kirchner [1992] showed that this rate of "progressive" acidification and its effects on runoff chemistry can be calculated straightforwardly under the heterogeneous equilibrium hypothesis, if the rate of soil base cation depletion is known. Results from these calculations [Kirchner, 1992] are quantitatively consistent with the 25-year trends in runoff chemistry at Hubbard Brook, New Hampshire [Driscoll et al., 1989].

Kirchner [1992] and Kirchner et al. [1992] showed that catchment response to changes in acid anion concentrations could be predicted mechanistically, directly from the chemistry of catchment runoff, without direct measurements of the hydrological or geochemical properties of the catchment itself. Our companion paper [Kirchner et al., this issue] shows that the same method can predict the acid buffering behavior of spatially heterogeneous catchments, without direct measurements of the properties of individual geochemical regions within them. Here, we have further extended this analysis, showing that even in catchments where runoff chemistry varies with discharge, heterogeneous equilibrium still accurately predicts how catchments respond to changes in acid anion concentrations. Thus the response of such catchments to acid anion loading can be predicted, without modeling or measuring the hydrologic properties and processes that link discharge variations to changes in runoff chemistry.

Catchment monitoring data typically span a relatively small range in  $\Sigma\text{acids}$  and a relatively large range in discharge; they therefore will often reflect discharge effects more than acid anion effects. Under these conditions, catchment response to acid anions will likely be obscured or distorted by flow effects (e.g., Figure 5c). Therefore empirical estimates of the effect of acid anion concentrations on water quality may be misleading; they may understate the strength of the underlying correlation (e.g., Figure 6a) or the slope of the underlying relationship (e.g., Figures 6c and 6d). In such cases, mechanistic predictions, such as those derived here, may be more accurate than empirical correlations in predicting how catchments will respond to changes in acid anion concentrations.

#### CONCLUSIONS

Catchment runoff combines flows from geochemically diverse sources, in proportions that may vary with discharge. As a result, catchment runoff chemistry is often correlated with discharge (Figure 1). Where runoff chemistry is discharge-dependent, discharge variations can obscure catchment response to changes in acid anion concentrations. Likewise, fluctuations in acid anion concentrations can obscure the relationship between runoff chemistry and catchment discharge. Although water quality variables may be well-defined functions of both discharge and acid anion concentrations, these functional relationships may not be apparent when the variables are simply plotted against one

another (Figures 2 and 6). If the two causal factors (acid anion concentrations, and discharge) are uncorrelated, each can blur the effect of the other (Figures 6a and 6b). If, however, they are strongly correlated, each can distort the apparent role of the other in shaping runoff chemistry (Figures 6c and 6d).

Simple statistical techniques can be used to isolate discharge and acid anion concentrations as separate factors controlling runoff chemistry, in order to analyze each without the confounding effects of the other. We tested this approach in a hypothetical catchment where flows from an acidic stream and a circumneutral stream were mathematically mixed in a ratio that varied with the assumed catchment discharge. In runoff chemistry data from this hypothetical catchment, there were no clear relationships between acid anion concentrations and alkalinity, total inorganic aluminum, or hydrogen ion concentrations (Figure 4c). However, multiple regression clearly revealed the effects of both discharge and acid anion variations in these data (Figure 4). Similar techniques also dramatically clarified catchment geochemical response to both discharge fluctuations and acid anion concentrations in data from two real catchments where runoff chemistry is strongly discharge-dependent (Figure 5).

In each case, catchment response to changes in acid anion concentrations, after correcting for discharge variations, mirrored a priori predictions derived by heterogeneous equilibrium from average catchment runoff chemistry (Table 1 and Figures 4 and 5). Thus bulk runoff chemistry can be used to predict catchment response to changes in acid anion concentrations, even though that response may be obscured by the confounding effects of discharge fluctuations.

The chemical measurements used in predicting catchment response to  $\Sigma\text{acids}$  were not corrected for flow effects, or mathematically manipulated in any other way. The predictions, made without knowing how flow variations affect runoff chemistry, agree well with the acid anion response observed after flow effects are removed from the data. The success of such "naive" predictions (naive, that is, of hydrological influences on catchment runoff chemistry) indicates that catchment response to acid anions can be predicted, even when the hydrological properties of the catchment are unknown.

#### APPENDIX

Consider the chemical variable of interest  $y$  (for example,  $y = \text{SBC}$  or  $y = \text{ANC}$ ) to be a linear function of two variables  $x_1$  and  $x_2$ :

$$y = m_1x_1 + m_2x_2 + b + \varepsilon \quad (11)$$

where  $x_1 = \Sigma\text{acids}$ ,  $x_2 = \log(q)$ ,  $m_1$ ,  $m_2$ , and  $b$  are constants, and  $\varepsilon$  is an error term expressing random deviations from the linear relationship. If  $x_1$  and  $x_2$  are uncorrelated with one another the variance of  $y$ ,  $\sigma_y^2$  is simply the sum of the variances due to each factor:

$$\sigma_y^2 = m_1^2\sigma_{x_1}^2 + m_2^2\sigma_{x_2}^2 + \sigma_\varepsilon^2 \quad (12)$$

In the  $y$ - $\Sigma\text{acids}$  plane, the variance in  $y$  explained by  $\Sigma\text{acids}$  is simply the corresponding term of (12) ( $m_1^2\sigma_{x_1}^2$ ). The coefficient of determination  $r^2$  of a simple linear regression

in the  $y$ - $\Sigma$ acids plane is the ratio of the variance explained by  $\Sigma$ acids to the total variance in  $y$ , or

$$r_{x_1y}^2 = \frac{m_1^2 \sigma_{x_1}^2}{m_1^2 \sigma_{x_1}^2 + m_2^2 \sigma_{x_2}^2 + \sigma_\varepsilon^2} \quad (13)$$

Flow variations add to the total variance in  $y$  without increasing the variance explained by  $\Sigma$ acids, and thus dilute the correlation between  $y$  and  $\Sigma$ acids. The size of this effect depends on how much influence  $\log(q)$  has on  $y$ , relative to  $\Sigma$ acids. We can conveniently express this as the dimensionless ratio of the two factors' standard deviations and the slopes of  $y$ 's dependence on them:

$$\beta = \frac{m_2 \sigma_{x_2}}{m_1 \sigma_{x_1}} \quad (14)$$

We can then rewrite (13) as

$$r_{x_1y}^2 = \frac{1}{1 + \beta^2 + \frac{\sigma_\varepsilon^2}{m_1^2 \sigma_{x_1}^2}} \quad (15)$$

As (15) shows, the greater the influence of  $\log(q)$  on  $y$ , relative to  $\Sigma$ acids (the higher the value of  $\beta$ ), the lower the apparent correlation in the  $y$ - $\Sigma$ acids plane (Figures 6a and 6b).

The foregoing assumes that  $\log(q)$  and  $\Sigma$ acids are themselves uncorrelated. If, instead,  $\log(q)$  and  $\Sigma$ acids are correlated, we can use path analysis [Li, 1975; Sokal and Rohlf, 1981] to express the correlation between  $\Sigma$ acids and  $y$  in the  $y$ - $\Sigma$ acids plane as

$$r_{x_1y} = m_1 \frac{\sigma_{x_1}}{\sigma_y} + r_{x_1x_2} m_2 \frac{\sigma_{x_2}}{\sigma_y} \quad (16)$$

where  $r_{x_1x_2}$  is the correlation between  $\Sigma$ acids and  $\log(q)$ . If we estimated the slope of  $y$ 's dependence on  $\Sigma$ acids by simple linear regression in the  $y$ - $\Sigma$ acids plane, we would obtain

$$\hat{m}_1 = r_{x_1y} \frac{\sigma_y}{\sigma_{x_1}} = m_1 + r_{x_1x_2} m_2 \frac{\sigma_{x_2}}{\sigma_{x_1}} \quad (17)$$

where  $\hat{m}_1$  is the regression estimate of the true slope  $m_1$ . From (17) it is obvious that if  $\Sigma$ acids and  $\log(q)$  are correlated,  $\hat{m}_1$  can diverge substantially from the true slope  $m_1$  (Figures 6c and 6d). We can express the fractional deviation of  $\hat{m}_1$  from  $m_1$  in terms of  $r_{x_1x_2}$  and our relative influence ratio  $\beta$ :

$$\frac{\hat{m}_1 - m_1}{m_1} = r_{x_1x_2} \frac{m_2}{m_1} \frac{\sigma_{x_2}}{\sigma_{x_1}} = r_{x_1x_2} \beta \quad (18)$$

Note that as long as  $\Sigma$ acids and  $\log(q)$  are uncorrelated ( $r_{x_1x_2} \approx 0$ ), the linear regression slope  $\hat{m}_1$  in the  $y$ - $\Sigma$ acids plane will be an accurate estimator of the true slope  $m_1$ , even though large values of  $\beta$  may substantially dilute the regression coefficient  $r^2$  in (15). When  $\Sigma$ acids and  $\log(q)$  are correlated, however, the apparent slope in the  $y$ - $\Sigma$ acids plane will reflect both the direct dependence of  $y$  on  $\Sigma$ acids, and the artifactual relationship between  $\Sigma$ acids and  $y$  that

arises because  $\log(q)$  is related to both  $y$  and  $\Sigma$ acids. The distortion thus introduced into  $\hat{m}_1$  will be proportional to both  $r_{x_1x_2}$  and  $\beta$ , and can be either positive or negative depending on the signs of  $m_1$ ,  $m_2$ , and  $r_{x_1x_2}$  (equation (18)). Although  $r_{x_1x_2}$  is bounded,  $\beta$  is not, and thus the distortion of  $\hat{m}_1$  could be very large indeed, if  $\log(q)$  has much more influence on  $y$  than  $\Sigma$ acids does, and if  $\log(q)$  and  $\Sigma$ acids are highly correlated (Figures 6c and 6d). If  $\log(q)$  and  $\Sigma$ acids are correlated, their underlying causal effects on  $y$  can only be revealed through techniques that can treat all three variables simultaneously, such as multiple linear regression (equation (5)) or multivariate nonlinear models like (8).

Correlation between  $\log(q)$  and  $\Sigma$ acids can increase the correlation between  $\Sigma$ acids and  $y$ , even while it distorts the apparent slope of the relationship between them. The coefficient of determination for regression of  $y$  on  $\Sigma$ acids in the  $y$ - $\Sigma$ acids plane is

$$r_{x_1y}^2 = \frac{m_1^2 \sigma_{x_1}^2 + r_{x_1x_2}^2 m_2^2 \sigma_{x_2}^2 + 2r_{x_1x_2} m_1 m_2 \sigma_{x_1} \sigma_{x_2}}{m_1^2 \sigma_{x_1}^2 + m_2^2 \sigma_{x_2}^2 + 2r_{x_1x_2} m_1 m_2 \sigma_{x_1} \sigma_{x_2} + \sigma_\varepsilon^2} \quad (19)$$

which is the same as (13) in the limiting case of  $r_{x_1x_2} = 0$ . Using our relative influence ratio  $\beta$ , we can simplify (19) to

$$r_{x_1y}^2 = \frac{(1 + r_{x_1x_2} \beta)^2}{(1 + r_{x_1x_2} \beta)^2 + \beta^2 (1 - r_{x_1x_2}^2) + \frac{\sigma_\varepsilon^2}{m_1^2 \sigma_{x_1}^2}} \quad (20)$$

If the artifactual correlation between  $\Sigma$ acids and  $y$  through  $\log(q)$  reinforces the direct dependence of  $y$  on  $\Sigma$ acids (i.e., if  $r_{x_1x_2}$  and  $\beta$  have the same sign), increasing the correlation between  $\Sigma$ acids and  $\log(q)$  will raise the regression coefficient  $r^2$  in the  $y$ - $\Sigma$ acids plane (equation (20)), even while it drives the regression slope  $\hat{m}_1$  farther and farther from the true slope  $m_1$  (equation (18, Figure 6d)). Even if the artifactual correlation between  $\Sigma$ acids and  $y$  through  $\log(q)$  counteracts the direct dependence of  $y$  on  $\Sigma$ acids, large enough values of  $r_{x_1x_2}$  will increase the regression coefficient  $r^2$ .

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## REFERENCES

- Aber, J. D., Nitrogen cycling and nitrogen saturation in temperate forest ecosystems, *Trends Ecol. Evol.*, 7, 220-224, 1992.
- Beck, M. B., F. M. Kleissen, and H. S. Wheeler, Identifying flow paths in models of surface water acidification, *Rev. Geophys.*, 28, 207-230, 1990.
- Bergstrom, S., B. Carlsson, and G. Sandberg, Integrated modelling of runoff, alkalinity, and pH on a daily basis, *Nord. Hydrol.*, 16, 89-104, 1985.
- Bishop, K. H., H. Grip, and A. O'Neill, The origins of acid runoff in a hillslope during storm events, *J. Hydrol.*, 116, 35-61, 1990.
- Christophersen, N., and R. P. Hooper, Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem, *Water Resour. Res.*, 28, 99-107, 1992.

- Christophersen, N., H. M. Seip, and R. F. Wright, A model for streamwater chemistry at Birkenes, Norway, *Water Resour. Res.*, **18**, 977–996, 1982.
- Christophersen, N., C. Neal, R. P. Hooper, R. D. Vogt, and S. Andersen, Modelling streamwater chemistry as a mixture of soilwater end-members—A step towards second-generation acidification models, *J. Hydrol.*, **116**, 307–320, 1990.
- Church, M. R., P. W. Shaffer, K. N. Eshleman, and B. P. Rochelle, Potential future effects of current levels of sulfur deposition on stream chemistry in the Southern Blue Ridge Mountains, U.S., *Water Air Soil Pollut.*, **50**, 39–48, 1990.
- Dillon, P. J., and L. A. Molot, The role of ammonium and nitrate retention in the acidification of lakes and forested catchments, *Biogeochemistry*, **11**, 23–43, 1990.
- Driscoll, C. T., G. E. Likens, L. O. Hedin, J. S. Eaton, and F. H. Bormann, Changes in the chemistry of surface waters: 25-year results at the Hubbard Brook Experimental Forest, NH, *Environ. Sci. Technol.*, **23**, 137–143, 1989.
- Genereux, D. P., H. F. Hemond, and P. J. Mulholland, Spatial and temporal variability in streamflow generation on the West Fork of Walker Branch watershed, *J. Hydrol.*, **142**, 137–166, 1993.
- Gherini, S., L. Mok, R. J. M. Hudson, G. F. Davis, C. Chen, and R. Goldstein, The ILWAS model: Formulation and application, *Water Air Soil Pollut.*, **26**, 95–113, 1985.
- Henriksen, A., and D. F. Brakke, Increasing contributions of nitrogen to the acidity of surface waters in Norway, *Water Air Soil Pollut.*, **42**, 183–201, 1988.
- Hooper, R. P., A. Stone, N. Christophersen, E. de Grosbois, and H. M. Seip, Assessing the Birkenes model of stream acidification using a multisignal calibration methodology, *Water Resour. Res.*, **24**, 1308–1316, 1988.
- Hooper, R. P., N. Christophersen, and N. E. Peters, Modelling streamwater chemistry as a mixture of soilwater end-members—An application to the Panola Mountain catchment, Georgia, U.S.A., *J. Hydrol.*, **116**, 321–343, 1990.
- Johnson, N. M., G. E. Likens, F. H. Bormann, D. W. Fisher, and R. S. Pierce, A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire, *Water Resour. Res.*, **5**, 1353–1363, 1969.
- Kirchner, J. W., Heterogeneous geochemistry of catchment acidification, *Geochim. Cosmochim. Acta*, **56**, 2311–2327, 1992.
- Kirchner, J. W., P. J. Dillon, and B. D. LaZerte, Predicted response of stream chemistry to acid loading tested in Canadian catchments, *Nature*, **358**, 478–482, 1992.
- Kirchner, J. W., P. J. Dillon, and B. D. LaZerte, Predictability of geochemical buffering and runoff acidification in spatially heterogeneous catchments, *Water Resour. Res.*, this issue.
- Li, C. C., *Path Analysis: A Primer*, 347 pp., The Boxwood Press, Pacific Grove, Calif., 1975.
- Mulder, J., N. Christophersen, M. Hauhs, R. D. Vogt, S. Andersen, and D. O. Andersen, Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts, *Water Resour. Res.*, **26**, 611–622, 1990.
- Nikolaidis, N. P., H. Rajaram, J. L. Schnoor, and K. P. Georgakakos, A generalized soft water acidification model, *Water Resour. Res.*, **24**, 1983–1996, 1988.
- Peters, N. E., and P. S. Murdoch, Hydrogeologic comparison of an acidic-lake basin with a neutral-lake basin in the west-central Adirondack mountains, New York, *Water Air Soil Pollut.*, **26**, 387–402, 1985.
- Reuss, J. O., and D. W. Johnson, *Acid Deposition and the Acidification of Soils and Waters*, 119 pp., Springer-Verlag, New York, 1986.
- Schofield, C. L., J. N. Galloway, and G. R. Hendry, Surface water chemistry in the ILWAS basins, *Water Air Soil Pollut.*, **26**, 403–423, 1985.
- Sklash, M. G., and R. N. Farvolden, The role of groundwater in storm runoff, *J. Hydrol.*, **43**, 45–65, 1979.
- Sokal, R. R., and F. J. Rohlf, *Biometry*, 859 pp., W. H. Freeman, New York, 1981.
- Sullivan, T. J., J. M. Eilers, M. R. Church, D. J. Blick, K. N. Eshleman, D. H. Landers, and M. S. DeHaan, Atmospheric wet sulphate deposition and lakewater chemistry, *Nature*, **331**, 607–609, 1988.
- Wright, R. F., and A. Henriksen, Restoration of Norwegian lakes by reduction in sulphur deposition, *Nature*, **305**, 422–424, 1983.

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