*Biogeochemistry* **47:** 335–353, 1999.

# Watershed- and plot-scale tests of the mobile anion concept

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Received 8 December 1998; accepted 14 January 1999

**Key words:** base cations, calcium, forest ecosystem, mobile anions, soil acidification, surface-water acidification

**Abstract.** Anion fluxes from a forest soil are usually correlated with those of base cations (BC). Declines in base cation deposition or long-term depletion from the soil may change these relationships. We used multiple regression to identify biogeochemical variables predicting annual volume-weighted concentrations of BC in streamwater draining a forested watershed, and analysis of variance to compare the effects of Ca and Cl inputs on BC fluxes out of soil horizons in irrigated plots. For the watershed, anion concentrations in streamwater predicted BC export most precisely ($R^2 = 0.84$). The best two-variable model (adjusted $R^2 = 0.91$) also included BC concentration in bulk deposition. Consistent with predictions from equations governing exchange chemistry, the proportion of charge contributed by $Ca^{2+}$ increased with increasing total anion concentration, while that of $Na^+$ decreased. At the plot scale, $Cl^-$ concentrations in treatment solutions had a stronger effect ($p = 0.06$) on BC concentration in Oa-horizon solutions than did $Ca^{2+}$ concentrations ($p = 0.33$). In individual horizons of individual plots, BC and total ion concentrations were correlated, but cation composition was not consistent within horizons from different plots. This study detected no evidence of long-term cation depletion in the soils controlling streamwater, but did detect extremely base-poor plots. Because acid deposition affects surface horizons first, streamwater chemistry may not be an adequate way to assess nutrient supply of forest soils.

**Abbreviations:** AD – anion deficit; BC – base cations; HBEF – Hubbard Brook Experimental Forest

## Introduction

Base cations (BC), particularly Ca, Mg, K and Na, play several essential roles in preserving forest health and the quality of surface water. High ratios of Al/Ca in the rooting zone can stress plant roots (Cronan & Grigal 1995). Imbalances of N and Mg can cause needle yellowing and loss of older needle cohorts (Schulze 1989). Deficiencies of Mg have been documented in high deposition areas in Europe (Schulze 1989), and of Ca in a high-elevation spruce forest in the U.S. (Van Miegroet & Johnson 1993). Deficient foliar Mg concentrations have also been found in sugar maple forests in Canada (Bernier & Brazeau 1988). Low levels of exchangeable bases in mineral soil can lead to the leaching of $H^+$ or $Al^{3+}$ to aquatic ecosystems (van Breemen et al. 1984; Reuss & Johnson 1986). Recent investigations have identified long-term changes in BC biogeochemistry, including widespread decreases in their inputs from atmospheric deposition (Hedin et al. 1994), and in exchangeable pools in forest soils (Knoepp & Swank 1994; Lawrence et al. 1995).

The mobile anion concept (Nye & Greenland 1960; Johnson & Cole 1980; Reuss & Johnson 1986) is a model for understanding BC biogeochemistry. According to that concept, in a soil with limited capacity for anion exchange or adsorption, the concentration of anions in solution will control the total concentration of cations, while the composition of cations in solution should be controlled by equilibration with a usually large cation pool adsorbed to a solid phase. Departures from linear relationships are consistent with ionic strength effects, but should be small over small changes in anion concentration (Kirchner et al. 1992). Phenomena that would contradict this concept would include increases in other cation concentrations (e.g., $H^+$, $Al^{n+}$ or $NH_4^+$) while BC concentrations remained the same or declined.

Several criticisms about both the accuracy and usefulness of the mobile anion concept have been brought forward (e.g., Hendershot et al. 1991). Several of these criticisms, such as the role of organic acids, may depend on the space and time scales of the phenomena under investigation. Organic acids, for example, accompany cations in water draining from surface horizons, but adsorption to mineral soil usually removes organic anions from solution, so that they are not important mobile anions at a watershed scale. On the other hand, little adsorption may occur in areas with shallow soil, or after several millennia of soil development.

The objective of this paper is to test the ability of the mobile anion concept to predict BC fluxes at two scales: that of annual watershed fluxes from a watershed, and that of responses to individual rain events within a soil profile. In both cases, we tested (1) whether BC concentrations were related linearly to anion concentrations, (2) whether other factors, particularly BC deposition, influence BC concentrations in soil solution or streamwater, (3) whether BC compositions are constant for waters from the same source, and (4) whether the slope of the relationship between BC and anion concentrations is the same for each anion. Variability in anion concentrations in streamwater is a result of changes in deposition and ecosystem behavior over time. In the soil profile study, we caused variability in anion concentrations in soil solutions by irrigating plots with solutions containing high and low Cl concentrations. By varying $Ca^{2+}$ concentrations independently, we also tested the alternative hypothesis that BC deposition affects BC leaching.

## Procedures

### *Site description*

Both investigations took place at the Hubbard Brook Experimental Forest (HBEF), New Hampshire, U.S.A. (43°56′ N, 71°45′ W). Its climate includes short, cool summers and long cold winters, with rainfall, which is evenly distributed throughout the year, exceeding potential evapotranspiration by 2–3 fold (Federer et al. 1990). The soils, acidic, coarse-loamy, typic Haplorthods, developed in locally-derived glacial till derived from base-poor bedrock. Northern hardwoods, predominantly sugar maple (Acer saccharum), beech (Fagus grandifolia) and yellow birch (Betula alleghaniensis), account for most of the tree biomass (Bormann et al. 1970). The watershed study uses biogeochemical data from watershed 6, which occupies approximately 13 ha between the elevations of 550 and 800 m. Northern hardwoods cover most of the area, but patches of boreal species, including balsam fir (Abies balsamea), red spruce (Picea rubens) and paper birch (Betula papyrifera), occupy shallow-to-bedrock areas in the higher-elevation region (Bormann et al. 1970). Plot studies took place in a beech-dominated northern hardwood forest at a lower elevation (300–350 m) in the Norris Brook watershed (Christ et al. 1995; see Likens & Bormann 1995 for map).

### *Experimental section*

#### *Watershed 6 study*

The dataset for the test of the mobile anion concept at the watershed scale consisted of 30 water-year measurements (1 June 1965–31 May 1995) of volume-weighted concentrations of solutes in bulk deposition and streamwater. Data from water year 1964 were available but were excluded (see discussion). Water-year concentrations in bulk deposition were estimated using concentrations in weekly rain samples, weighted by precipitation volume, which was measured using standard rain gages (Likens & Bormann 1995). Water-year concentrations in streamwater were estimated using concentrations in weekly grab samples from the stream draining the watershed, weighted according to continuous stage measurements at a v-notch weir (Likens & Bormann 1995). Chemical analyses are described in Likens and Bormann (1995). Further descriptions of the hydrometeorological methods are found in Federer et al. (1990).

*Table 1.* Composition of treatment solutions used in plot experiment.

| Treatment name | $Cl^-$ level | $Ca^{2+}$ level | Concentrations (meq $m^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $Cl^-$ | $Ca^{2+}$ | $H^+$ | $SO_4^{2-}$ | $K^+$ | $NO_3^-$ |
| Control | Low | Low | 0 | 0 | 100 | 100 | 50 | 50 |
| Neutral | Low | High | 0 | 100 | 0 | 100 | 50 | 50 |
| Acid | High | Low | 100 | 0 | 200 | 100 | 50 | 50 |
| Salt | High | High | 100 | 100 | 100 | 100 | 50 | 50 |

### *Soil profile study*

Lysimeter plots (1 m × 2 m) were used to test the mobile anion concept on the soil-horizon scale. In the fall of 1990, 12 plots were equipped with a pair of zero-tension lysimeters (Driscoll et al. 1988) within or under each of three soil horizons, Oa, Bhs, and Bs2 (approximately 8, 28 and 48 cm, respectively). Plots were assigned at random to one of four treatments, and treated four times (24 July, 1, 10 and 12 August) with ~5 cm (~100 L) of the corresponding solution. Treatment solutions differed in concentrations of $Cl^-$, $Ca^{2+}$, and $H^+$ (Table 1). Solutions were prepared by adding one liter of concentrated solution to a 100 L reservoir of deionized streamwater located upslope from each plot (vertical distance ~2 m), and were siphoned via a garden hose to two pieces of black, 3/4" diameter polyethylene tubing, one along each 2-m side of the plot, into which several pinholes had been poked. Reservoirs emptied in approximately four hours. Patterns of wetness during and after treatment indicated that water was spread evenly within the plot and that little landed outside the plot. We sampled lysimeters 27 July, and 8 and 15 August, and analyzed the major constituents using standard methods (Table 2).

The second phase took place after 15 August. Eight plots which had dependably yielded solutions in Bs2-horizon lysimeters (at least one sample $\geq$50 ml from two of the three sampling dates) were selected for further treatments. All eight plots were irrigated 16 and 18 August with a single solution ("Control", Table 1), and then 20 and 22 August with one of the four treatment solutions. We sampled lysimeters two days after each irrigation (before additional irrigations), and analyzed the solutions for major constituents.

*Table 2.* Methods used for chemical analyses.

| Category | Solute | Method | Reference |
|---|---|---|---|
| *Base cations* | Na, K | Atomic emission spectrophotometry | USEPA 1987 |
| | Mg, Ca | Atomic absorption spectrophotometry | USEPA 1987 |
| *Inorganic anions* | $Cl^-$, $NO_3^-$, $SO_4^{2-}$ | Ion chromatography | Tabatabai & Dick 1983 |
| *Acid cations* | $H^+$ | Potentiometry with glass electrode | |
| | $Al^{n+}$ | Automated colorimetry[1] | McAvoy et al. 1992 |
| *Other ions* | $NH_4^+$ | Automated colorimetry | Technicon 1969 |

[1] Charge on Al ions was calculated by subtracting organic monomeric Al concentrations from total monomeric concentrations, distributing Al concentrations among the $Al^{3+}$, $Al(OH)^{2+}$, and $Al(OH)_2^+$ components using measured pH and pKa1 and pKa2 of 4.99 and 10, respectively (Schecher & Driscoll 1987). Ionic strength effects were taken into consideration using the Debye–Hückel rule. An amount equal to the typical concentration of $F^-$ in these solutions (1 meq $m^{-3}$; Driscoll et al. 1985) was then subtracted from the charge of $Al^{n+}$ in solution to account for the strong interaction of $F^-$ ligands with Al.

## *Calculations and statistics*

### *Definition of variables*

Base cation concentrations are defined for this study as the sum of $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$ concentrations, expressed as meq $m^{-3}$. "Total cations" denotes the sum of BC, $NH_4^+$, $H^+$ and, in the soil-horizon study, $Al^{n+}$. Aluminum concentrations are not available for water years 1970 to 1976 in the watershed study. Total anions denotes the sum of $SO_4^-$, $NO_3^-$ and $Cl^-$, and, in the plot study, organic anion concentration, which is defined here as the anion deficit (AD), or the difference between total cations and the sum of $SO_4^-$, $NO_3^-$ and $Cl^-$. The "charge contribution" of each cation is the concentration of that cation divided by the total cation concentration.

### *Regression analysis of watershed scale data*

Stepwise linear regression (SAS 1994) was used to obtain the best 1-, through 3-variable models for predicting base-cation concentrations and cation charge contributions in streamwater from W6. Models were evaluated using the adjusted $R^2$ statistic. Autoregressive terms for lags of 1 to 5 years were tested for significance using the Durbin–Watson statistic (SAS 1994). If autoregressive terms were significant, the significance of variables already in the model was reevaluated. Candidate variables included concentrations in bulk deposition and streamwater of $SO_4^{2-}$, $NO_3^-$, $Cl^-$, and total anions, BC concentration in bulk deposition, year, total precipitation, total streamflow, volume-weighted streamflow, and proportion of streamflow during the growing season. Individual anions as well as sums were included to determine whether a single variable was sufficient to capture the effect of all anions. The variable year was introduced to account for any gradual change in the watershed, such as a gradual removal of BC from available pools. Johnson et al. (1969) found that certain solute concentrations changed in systematic ways with streamflow. We introduced volume-weighted streamflow to distinguish years in which large or small proportions of water left the watershed during large storm or melting events. Volume-weighted streamflow was calculated as the sum over a year of the squares of daily streamflow, divided by total annual streamflow. Johnson et al. (1969) also documented differences in streamwater chemistry during growing and dormant seasons. Proportion of streamflow occurring from 1 June through 30 September was introduced to account for the annual effect of that difference. An additional multiple regression using each individual anion as an independent variable was used to compare the slopes due to each anion.

*Plot study*

To make the plot-scale test of the mobile-anion concept as sensitive as possible, we used concentration data from 15 August, after each plot had received, and possibly equilibrated with, the same treatment four times. The effects of $Cl^-$ and $Ca^{2+}$ levels were compared using $p$ values from a two-way classification ANOVA. The effect of $H^+$ concentration was treated as an artifact of the $Cl^-$ and $Ca^{2+}$ levels.

Concentration data from the eight plots that were treated after 15 August were used for additional tests of the relationship between BC and anion concentrations. The tests used a model where base cation concentration, $BC_{ij}$, in plot $i$ following the $j$th treatment, was determined using the following model:

$$BC_{ij} = \alpha(TC) + \beta_i + \gamma_j + \varepsilon_{ij},$$

where $\alpha$ is a coefficient for the concentration of total cations (a surrogate for anion concentration), $\beta_i$ is a constant effect for each plot i, $\gamma_j$ is a multiplier for the number of times the plot had been irrigated, and $\epsilon_{ij}$ is an error term. Charge contributions of individual cations were analyzed using the same model. In an additional analysis, the term $\alpha$(TC) was replaced by terms for the effects of individual anions ($\alpha_1(SO_4^{2-})$, $\alpha_2(NO_3^-)$, $\alpha_3(Cl^-)$, and $\alpha_4$(AD)).

*Table 3.* Models chosen by stepwise regression for predicting the volume-weighted concentration of base cations from a forested watershed.

| Model | Intercept ($p$ value) | Regressors | Coefficient ($p$ value) | $R^2$ |
|---|---|---|---|---|
| One-variable | 14.3 (0.10) | Stream anions[1] | 0.702 (0.0001) | 0.84 |
| With autoregression | 10.1 (0.39) | Stream anions | 0.736 (0.0001) | 0.90 |
| | | $R_{n-1}$[3] | 0.53 | |
| Two-variable | 15.3 (0.03) | Stream anions | 0.58 (0.0001) | 0.91 |
| | | Bulk dep. BC | 1.34 (0.0001) | |
| Three-variable | 32.2 (0.03) | Stream anions | 0.609 (0.0001) | 0.92 |
| | | Bulk dep. BC | 1.11 (0.0009) | |
| | | Precipitation | −0.013 (0.04) | |

[1] Volume-weighted concentration of acid anions, $SO_4^{2-}$, $NO_3^-$, and $Cl^-$, in meq $m^{-3}$.
[2] Probability of attaining a lower Durbin–Watson statistic.
[3] Actual – predicted BC concentration from the previous year.

## Results

### *Watershed 6 study*

The best single-variable model for the annual volume-weighted concentration of BC in streamwater included the total acid anion concentration in streamwater, and had an $R^2$ of 0.84 (Table 3). The pattern showed significant autocorrelation (probability of a smaller Durbin–Watson statistic = 0.0001), and correction for deviation of the model in the previous year caused an increase in $R^2$ to 0.90. The best two-variable model included the volume-weighted concentration of BC in bulk deposition, and had an $R^2$ of 0.91. The best three-variable model also included annual precipitation, and had an $R^2$ of 0.93. There was no significant autocorrelation in the 2- or 3-variable models. All models traced the general features of the pattern of BC concentrations, including a decline from approximately 140 meq $m^{-3}$ in the late 1960s to approximately 90 meq $m^{-3}$ by 1992, and concentration peaks in 1974, 1979 and 1980, and in 1988 or 1989 (Figure 1). The one-variable model with autocorrelation predicted the approximate maximum BC concentration for water year 1970, but the maximum actually occurred in 1969. The two- and three-variable models were both more accurate for BC concentrations in the late 1960s than either the one-variable model, or the one-variable model with autocorrelation.

The slope for the effect of anion concentrations on BC concentrations was 0.7 for the one-variable model, was higher for the model including autoregression, and was smaller for the 2- and 3-variable models. The regression

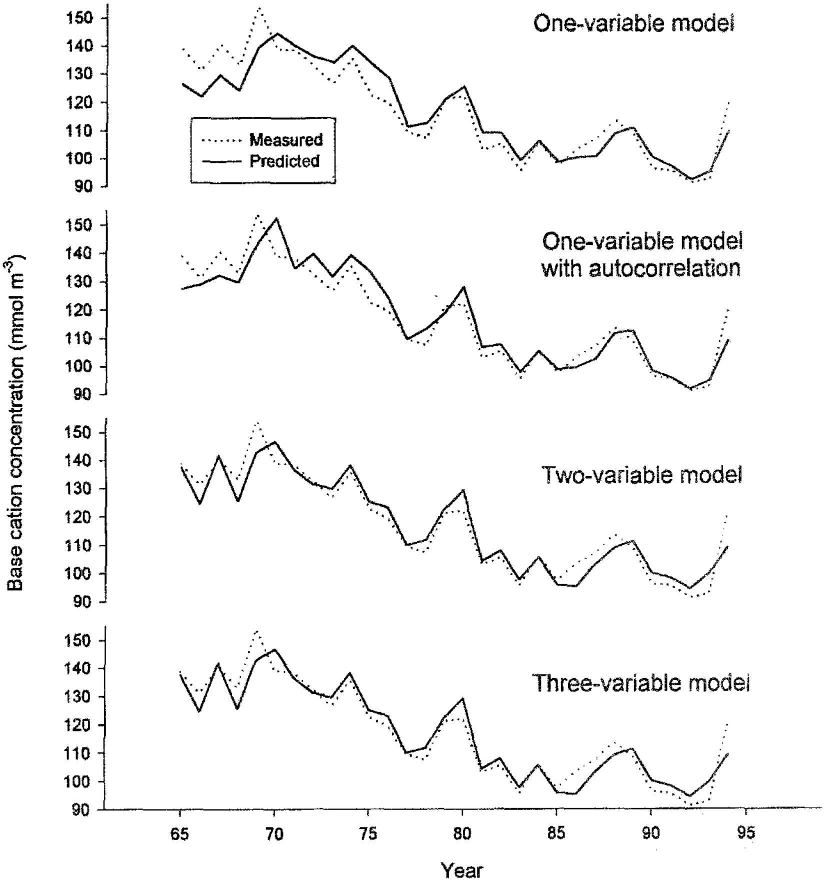

*Figure 1.* Comparison of modeled and measured volume-weighted mean BC concentrations from watershed 6 at HBEF for water years 1965 to 1994. All models include the effect of volume-weighted concentrations of the sum of $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ in streamwater. The two- and three-variable models also include the effect of the concentration of BC in bulk deposition, and the three-variable model includes an effect of precipitation. The model with an autoregressive term subtracts a fraction of the previous year's error from the prediction for the current year.

procedure always included the effect of the total anion concentration rather than the concentrations of individual anions. The slopes of the regression of BC concentrations against individual anion concentrations were within the confidence intervals of one another (Figure 2).

Contributions of $Ca^{2+}$ and $Na^+$ were inversely correlated ($r = 0.94$), and varied more (standard deviation ~3%) than those of Mg and K (standard deviation ~1%). Furthermore, regression models explained larger proportions of the variability in their contributions to total cation charge (Table

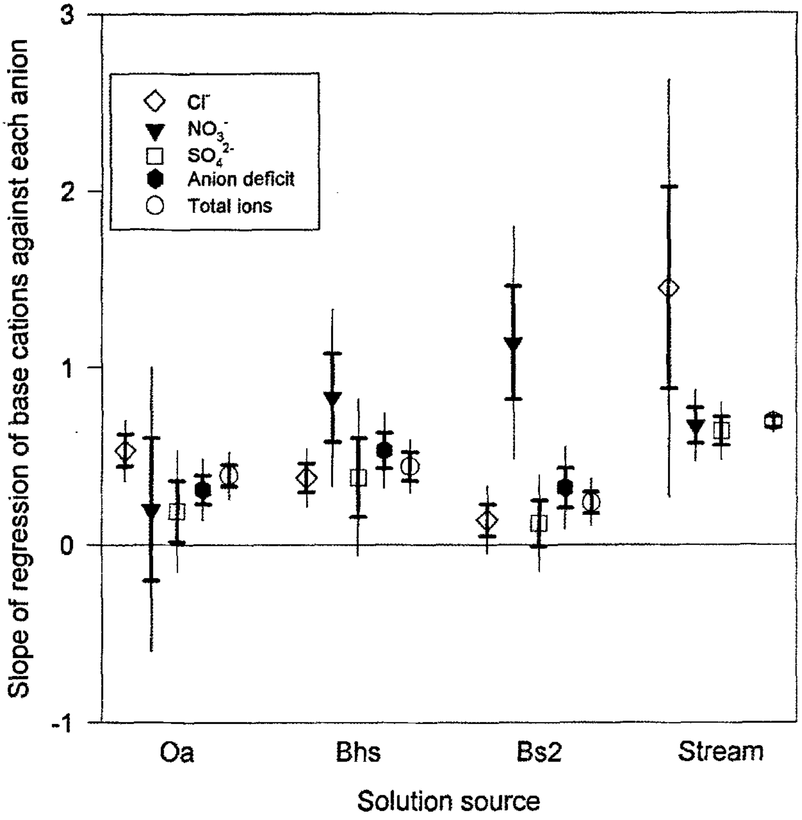

*Figure 2.* Parameters fitted for the slopes of the regressions between BC concentrations and those of individual anions, with standard error of estimates (heavy bars) and 95% confidence intervals (lines). Regressions for the soil horizons (Oa, Bhs and Bs2) included effects of plot and cumulative water additions as well as those of the individual anions or total ion concentrations. The regression for the watershed included only the anions, or the sum of the anions.

4). The charge contribution of $Ca^{2+}$ increased with higher streamwater total anion concentration (Figure 3). Other significant factors included higher $Ca^{2+}$ charge contributions with higher $Cl^-$ concentrations in bulk deposition, and during the earlier years of the study. In contrast, the contribution of $Na^+$ increased during the later years of the study, decreased with higher streamwater $NO_3^-$ concentrations, and increased with greater concentrations of BC in bulk deposition. Models for the contributions of $Mg^{2+}$ and $K^+$ were weaker (Table 4). Three-variable models for $Mg^{2+}$ and $K^+$ had adjusted $R^2$ of 0.27 and 0.38, respectively.

*Table 4a.* Models chosen by stepwise regression predicting charge contributions of Ca$^{2+}$ and Na$^{+}$.

| Variables | Ca$^{2+}$ | | | Na$^{+}$ | | |
|---|---|---|---|---|---|---|
| | Regressors | Coefficient ($p$ value) | $R^2$ | Regressors | Coefficient ($p$ value) | $R^2$ |
| 1 | Stream anions | 0.00125**** | | Year | 0.00283*** | 0.66 |
| 2 | Stream anions | 0.00149**** | 0.87 | Year | 0.00197**** | 0.77 |
| | Stream Cl$^-$ | −0.00465**** | | Stream NO$_3^-$ | −0.00093** | |
| 3 | Stream anions | 0.00116**** | 0.90 | Year | 0.00276**** | 0.85 |
| | Stream Cl$^-$ | −0.00478**** | | Stream NO$_3^-$ | −0.00085*** | |
| | Year | −0.00106** | | Bulk dep. BC | 0.00277*** | |

*Table 4b.* Models chosen by stepwise regression predicting charge contributions of Mg$^{2+}$ and K$^{+}$.

| Variables | Mg$^{2+}$ | | | K$^{+}$ | | |
|---|---|---|---|---|---|---|
| | Regressors | Coefficient ($p$ value) | $R^2$ | Regressors | Coefficient ($p$ value) | $R^2$ |
| 1 | Bulk dep. BC | 0.00082* | 0.18 | Bulk dep. SO$_4^{2-}$ | −0.00036** | 0.22 |
| 2 | Bulk dep. SO$_4^{2-}$ | 0.00027* | 0.22 | Bulk dep. SO$_4^{2-}$ | −0.00037** | 0.27 |
| | Ppt. | −0.00001* | | GSSF[1] | −0.027 | |
| 3 | Bulk dep. BC | 0.00113** | 0.27 | Bulk dep. SO$_4^{2-}$ | −0.00044** | 0.38 |
| | Streamflow | −0.00001 | | Stream Cl$^-$ | 0.00123* | |
| | Stream Cl$^-$ | −0.00111 | 0.27 | VWSF[2] | 0.00055* | |

[1] Growing season streamflow fraction.

[2] Volume-weighted streamflow.

## *Lysimeter plot experiment*

### *Results of ANOVA experiment*

The addition of 100 meq Cl m$^{-3}$ in simulated throughfall caused significant increases in soil solution Cl and total inorganic anion concentrations in all three horizons (Table 5). Average concentrations of Cl in high-Cl plots were 62, 56 and 52 meq m$^{-3}$ greater than in low-Cl plots in Oa, Bhs and Bs2 horizons, respectively. The Ca$^{2+}$ factor also contributed weakly to differences in Cl$^-$ concentrations in Oa horizon solutions, but plots under the high-Ca treatment contained only 3 meq m$^{-3}$ more Cl$^-$ than those under low-Ca throughfall. There were no significant treatment effects on NO$_3^-$ or SO$_4^{2-}$ in any horizon. High Cl treatments increased total strong acid anion concentrations by 63, 58 and 52 meq m$^{-3}$ in Oa, Bhs and Bs2 horizon solutions, respectively.

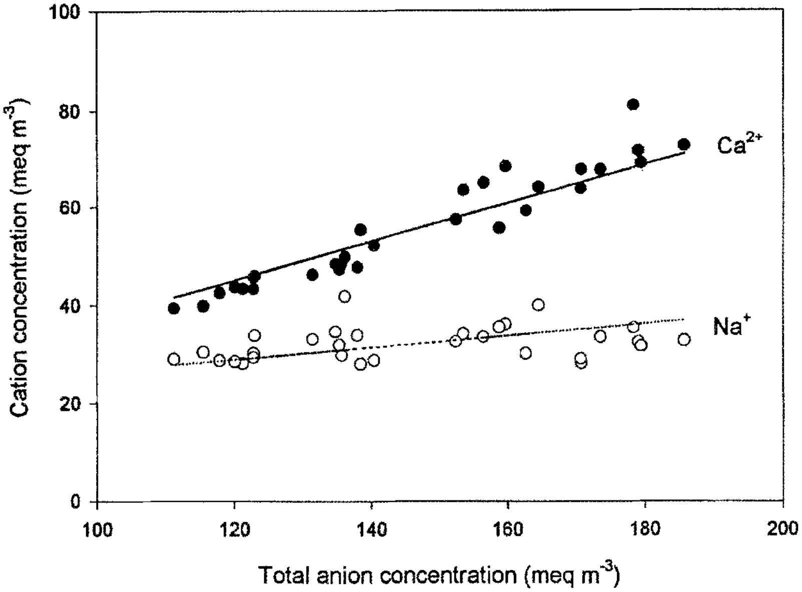

*Figure 3.* Annual volume-weighted concentrations of $Ca^{2+}$ and of $Na^+$ plotted against annual volume-weighted concentrations of anions ($Cl^-$, $NO_3^-$ and $SO_4^{2-}$). Lines illustrate the predicted relationship for each cation based on heterogeneous equilibrium calculations (Kirchner 1992).

Effects of the $Cl^-$ factor on total BC concentrations were weakly significant in the Oa horizon, but were not significant in either mineral horizon. The $Ca^{2+}$ factor had no significant effect on BC concentrations in any horizon (Table 5). High levels of either $Cl^-$ or $Ca^{2+}$ caused weak increases in Mg concentrations in Oa-horizon solutions. High levels of $Cl^-$ in the treatment solution were associated with higher concentrations of total cations in the Oa- and Bs2-horizon solutions, and with lower concentrations of $Na^+$ in Bhs-horizon solutions.

### *Lysimeter experiment: Regression analysis*

Variables for plot and sampling date, as well as total cation concentration, contributed significantly to the model predicting BC concentrations (Table 6). In all horizons, there was an increase in BC with increasing total ion concentration, and a decrease in BC concentration of about 3 meq $m^{-3}$ with each successive sampling. Plots varied widely in BC concentrations, even when the statistical model was used to correct values for a common sampling date and total cation concentration (Table 6).

Regression analysis of BC fluxes using individual anion concentrations as independent variables suggested that equivalents of $SO_4^{2-}$ and of organic

*Table 5.* Concentrations (meq $m^{-3}$) affected ($p \leq 0.1$) by either treatment factor.[1]

| Solute | $Cl^-$ treatment means | | | $Ca^{2+}$ treatment means | | |
|---|---|---|---|---|---|---|
| | High | Low | *P* value | High | Low | *P* value |
| Oa horizon: *n* = | 5 | 6 | | 5 | 6 | |
| $Cl^-$ | 67 | 5 | 0.0001 | 35 | 32 | 0.06 |
| Anions[2] | 163 | 100 | 0.001 | 133 | 125 | 0.29 |
| $Mg^{2+}$ | 25 | 14 | 0.06 | 26 | 14 | 0.05 |
| BC | 126 | 80 | 0.06 | 117 | 97 | 0.33 |
| Total cations | 269 | 214 | 0.05 | 224 | 251 | 0.36 |
| Bhs horizon: *n* = | 6 | 5 | | 5 | 6 | |
| $Cl^-$ | 60 | 4 | 0.0001 | 41 | 29 | 0.34 |
| Anions | 133 | 75 | 0.004 | 118 | 97 | 0.31 |
| $Na^+$ | 7 | 14 | 0.05 | 10 | 11 | 0.89 |
| Bs2 horizon: *n* = | 4 | 5 | | 5 | 4 | |
| $Cl^-$ | 56 | 4 | 0.0001 | 35 | 17 | 0.63 |
| Anions | 128 | 76 | 0.0006 | 107 | 89 | 0.98 |
| Total cations | 171 | 106 | 0.01 | 147 | 119 | 0.70 |

[1] Data from solutions taken 15 August 1992, after four treatments under a single treatment.
[2] Sum of concentration of $Cl^-$, $NO_3^-$ and $SO_4^{2-}$.

*Table 6.* Effects of total cation concentration, sample set, and plot on total base cation concentrations in the entire lysimeter plot dataset.

| Horizon | Model including total ion concentration, amount of water added, and plot | | | |
|---|---|---|---|---|
| | $R^2$ | Total ions[1] | Number of irrigations[2] | Range of plot effects[3] |
| Oa | 0.83 | 0.39***[5] | −2.9**[4] | 15–137***[4] |
| Bhs | 0.95 | 0.45*** | −2.5*** | 17–115*** |
| Bs2 | 0.98 | 0.23*** | −3.2*** | 37–180*** |

[1] Sum of measured cation concentrations.
[2] Number of 5-cm irrigation events preceding sample.
[3] Minimum and maximum BC concentrations in each plot assuming total ion concentrations of 240, 138 and 135 meq $m^{-3}$ for Oa, Bhs and Bs2 horizons, respectively (see Table 6), after 4 irrigation events. Significance level is for effect of plot.
[4] Effects of total ion concentration are dimensionless. Those of irrigation and plot are meq $m^{-3}$ irrigation$^{-1}$ and meq $m^{-3}$, respectively.
[5] Effects followed by *, ** or *** are significant at 0.05, 0.01 and 0.001 levels, respectively.

anions were associated with similar amounts of BC in each horizon (Figure 2). At increasing depths in the profile, however, $NO_3^-$ fluxes were associated with larger BC fluxes than with those of other anions. Fluxes of $Cl^-$ were associated with smaller fluxes of BC at increasing depth. Confidence intervals for the effects of each individual anion were large, especially for $NO_3^-$.

The contributions of individual base cations were not constant within an individual horizon, but were affected strongly by plot ($p = 0.0001$). For example, plot means for the contribution of $Ca^{2+}$ to total charge ranged from 4–32%, from 7–41% and from 8–43% in the Oa, Bhs and Bs2 horizons, respectively. The charge contribution of $Na^+$ declined with successive sample sets in all horizons ($p = 0.0001$). Total cation concentration had no effect on BC composition in the Oa and Bhs horizons ($p > 0.1$) but contributions of $Na^+$ and $K^+$ in the Bs2 horizon declined with increasing total ion concentration by 0.04 ($p = 0.0001$) and 0.06% (meq $m^{-3}$)$^{-1}$ ($p = 0.04$), respectively.

## Discussion

The mobile anion concept was accurate at both scales in that anion concentrations were correlated with BC concentrations. Other factors, however, also affected BC concentrations. At the watershed scale, the concentration of BC in bulk deposition and the amount of precipitation had a significant effect on BC concentration in streamwater. The plot-scale test demonstrated wide variation among plots in BC concentrations in a particular horizon, and decreases in BC concentrations with successive irrigations. At the watershed scale, the composition of base cations varied in a manner that was quantitatively consistent with predictions based on models of cation exchange (Kirchner 1992): higher ionic concentrations caused ions with a higher valence to increase their contribution to total cation charge (Figure 3). At the plot scale, variability among the plots accounted for the most variation in cation composition, although there were also decreases in $Na^+$ after more irrigations, and a decline in monovalent cations with higher total ion concentrations in the Bs2 horizon. Regressions of BC concentrations against individual anions had similar slopes within individual horizons, and for the stream draining the watershed (Figure 2), with the exception that the effect of $NO_3^-$ was greater than that of other ions in the Bhs and Bs2 horizons.

An additional objective of this study was to reconcile the discrepancy between the mobile anion concept, and the observation that BC concentrations in a stream at the Hubbard Brook Experimental Forest are correlated with those in bulk deposition over time. This objective had two parts: first to determine whether the relationship between BC concentrations in bulk deposition and streamwater is an artifact of other correlations, and second, to test whether the mobile anion concept holds true within soil profiles at the Hubbard Brook Experimental forest.

The watershed study confirmed that BC concentration in bulk deposition plays a role in a parsimonious model for BC concentrations in streamwater. After factoring out the effect of total anion concentrations in streamwater on BC concentrations, no variable made as strong a contribution as BC concentration in bulk deposition (Table 3), although accounting for autocorrelation made the 1-variable model almost as precise. Nevertheless, the plot study confirmed that the mobile anion concept operates in the soil profiles in this ecosystem. The factorial experiment indicated that even large variations in BC concentrations in rain do not cause appreciable changes in soil solution BC concentrations, even in the uppermost horizon. A reconciliation between the data and the mobile anion concept, therefore, lies outside the scope of the soil profile test. The datasets here support some thoughts about the role of long-term soil changes, of spatial heterogeneity, and of hydrology in explaining the observations.

Understanding long-term changes in soil chemistry is important for managing both forests and streams. The transfer of BC and $Al^{n+}$ from soils to streamwater increases with increasing total anion concentration in soil solution, and with decreasing base saturation in the soil (Reuss & Johnson 1986). Decreases in $SO_2$ emissions in some industrialized regions have led to declines in atmospheric $SO_4^{2-}$ deposition, declines in soil solution and streamwater $SO_4^{2-}$ concentrations (Driscoll et al. 1989), and may lead to declines in BC and $Al^{n+}$ transport as well. Concentrations of $Al^{n+}$, however, may fail to decline, and BC levels in soils and streams may fail to recover if continued $SO_4^{2-}$ leaching depletes BC from the soil, and reduces base saturation (Christophersen et al. 1990; Kirchner & Lydersen 1995).

Effects of long-term soil changes at Hubbard Brook would be masked by many variables that change somewhat monotonically with time, and are therefore correlated with time variables, such as year. For example, for water years 1965 to 1994, concentrations of $SO_4^{2-}$ in bulk deposition and streamwater are negatively correlated with year ($p = 0.0001$), as are those of BC in bulk deposition and streamwater ($p = 0.0006$ and 0.0001, respectively), of $Cl^-$ in bulk deposition and streamwater ($p = 0.0001$ and 0.02, respectively), and those of $NO_3^-$ in streamwater ($p = 0.0003$). Therefore, although multiple regression analysis can identify the best models for certain dependent variables, those models may not be significantly better than those based on correlated variables. For example, although the best model for $Ca^{2+}$ contribution to streamwater cation charge depended on the total anion concentration in streamwater (adjusted $R^2 = 0.78$), models based on $NO_3^-$ concentration ($R^2$

= 0.68) or on year ($R^2 = 0.69$) explained approximately the same amount of variance.

Previous studies have concluded that the record at Hubbard Brook does indeed reflect long-term declines BC availability in the soil. Likens et al. (1996) observed that the residuals of a regression of BC concentrations in streamwater against the sum of $SO_4^{2-}$ and $NO_3^-$ concentrations in streamwater were generally high in the late 1960s, then declined rapidly, and may be recovering slowly. That study speculated that high $SO_4^{2-}$ deposition rates in the late 1960s were removing the last of a relatively labile pool of base cations, which consisted of cations cycling in the system before the onset of acid deposition, in addition to cations supplied in deposition. The current study is consistent with that speculation in that the importance of the addition of BC concentration in bulk deposition decreases the error sum of squares more in the first 10 years of the record (from 767 to 309) than in the last 20 years of the study (556 to 441).

Kirchner (1992) calculated the response in BC concentrations in streamwater to changes in $SO_4^{2-}$ concentrations using equilibrium principles, and concluded that the decline in BC concentrations was consistent with long-term soil depletion. That analysis, however, did not account for changes in other anions concentrations. Figure 4 modifies the analysis given by Kirchner (1992). In this figure, base cation concentrations from water years 1965 to 1994 (connected symbols) are compared with lines with slopes that correspond to (1) the predicted decline in base cation concentrations due to the decline in the sum of acid anion concentrations, and (2), the predicted decline in base cation concentrations assuming negligible weathering. In contrast to the conclusions of either Kirchner (1992) or Likens et al. (1996), this analysis does not indicate any consistent decline in base cation availability, but instead only variation about the line predicted by average declines in anion concentrations.

This study supported a role for the influence of base cation deposition in controlling base cation leaching, that may or may not be associated with changes in the exchangeable cations in the soil. This influence is secondary to a primary influence of anion leaching. The appearance of rainfall as the third variable in the empirical model for BC concentrations in streamwater and the decrease in BC concentrations with successive irrigations in the plot experiment suggest that the link between BC in bulk deposition and streamwater may depend on hydrology, rather than stream chemistry.

Hydrology may also be related to the extreme year, 1964. Precipitation and volume-weighted concentrations for water-year 1964 differed substantially from the rest of the dataset. For example, precipitation in that year was 2.6 standard deviations below the 1965–1994 average, and the volume-weighted

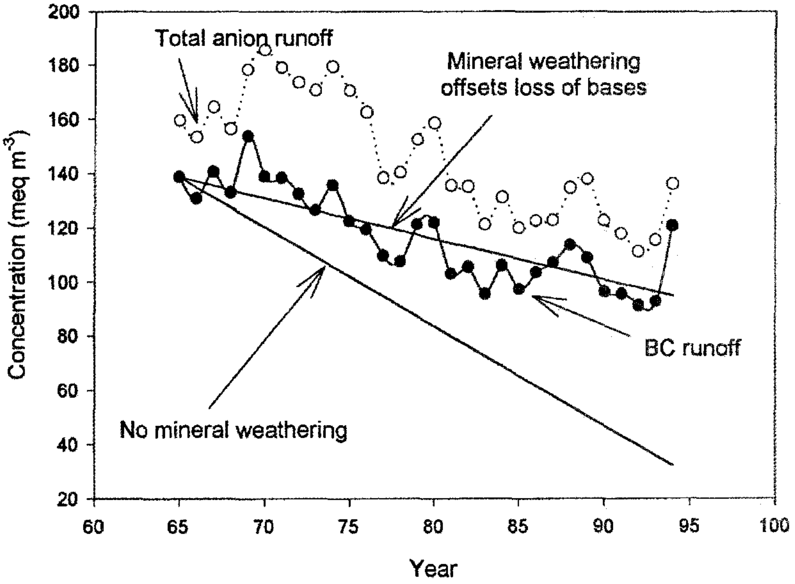

*Figure 4.* Test for long-term depletion of BC from soils regulating streamwater concentration, following the reasoning of Kirchner (1992). Volume-weighted concentrations of BC (filled circles) and of anions (open circles) are superimposed on lines predicting declines in BC concentration under two scenarios: 1. weathering offsets BC losses so that there is no decline in availability in the soil (upper lines); and 2. weathering is negligible (lower lines). The slope for scenario 1 is the long-term decline in anion concentrations (2.10 meq m$^{-3}$ y$^{-1}$) times an *F*-factor relating BC and anion concentrations (=0.72, Kirchner 1992), and equals −1.51 meq m$^{-3}$ y$^{-1}$. The slope for scenario 2 is 3.67 meq m$^{-3}$ y-1, which is calculated from Kirchner's (1992) estimate of 3.45 meq m$^{-3}$ y$^{-1}$, corrected for the actual decline in anion concentration, rather than a decline in $SO_4^{2-}$ concentrations of 1.8 meq m$^{-3}$ y$^{-1}$.

concentrations of $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$ were 5.8,10, 6.5 and 4.5 standard deviations above average. Charge contributions of $Ca^{2+}$ in streamwater that year were 2.5 standard deviations below average, while those of $Mg^{2+}$ were 2.2 standard deviations above average. Because the strong influence of this single year on the regressions could not be confirmed with data from similar years, the datapoint was omitted. It is possible that the 1964 data is typical for periods of extreme drought, such as the one HBEF witnessed in the early 1960's (Whittaker et al. 1979).

The analysis of the long-term watershed dataset did not indicate any long-term change in the chemistry of the soil with which streamwater equilibrates. That lack of an effect, however, does not rule out the possibility that individual patches of soil are being depleted of base cations, particularly in surface horizons. The plot study detected a wide range in base cation concentrations, and some plots with very low values. For example, even after receiving two applications (10 cm) of simulated throughfall containing 100 meq $m^{-3}$ $Ca^{2+}$, Oa-horizon lysimeters from one plot yielded solutions containing only 10–20 meq $m^{-3}$ $Ca^{2+}$. Likens et al. (1998) have compiled evidence that surface soils have been depleted in Ca by a combination of acid deposition and sequestration in biomass.

## Conclusions

Fluxes of mobile anions predicted BC movement from a watershed accurately, and contributed to models of BC flux from individual soil horizons. Spatial variability affected BC exports strongly at the plot scale. Base cation import had an effect on BC export at the watershed scale, especially during the first 10 years of the study. At the plot scale, our experiment detected no effect of BC input on soil solution fluxes of BC. The effects of individual anions in moving BC were similar in a single horizon, with the exception of $NO_3^-$ in the Bs2 horizon, but were greater at the watershed scale than at the soil horizon scale. Sodium was easily depleted from surface soils. According to this study, declining BC inputs during continued deposition of mobile anions could deplete surface horizons of BC without changing surface water quality. Certain patches already have very low BC reservoirs available to soil solution.

## Acknowledgements

This paper is a contribution to the Hubbard Brook Experimental Study. Logistical support as well as meteorologic and hydrologic data have been provided by the USDA Forest Service, Radnor, Pennsylvania, which operates and maintains the Hubbard Brook Experimental Forest. The Forest Service, has not, however, reviewed this paper. Travis McEwen assisted with field and laboratory work, especially treating and sampling soil solution from the lysimeter plots. Don Buso assisted with the analysis of the long-term chemistry dataset.

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