

# Long-term and seasonal variations in CO<sub>2</sub>: linkages to catchment alkalinity generation

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## Abstract

As atmospheric emissions of S have declined in the Northern Hemisphere, there has been an expectation of increased pH and alkalinity in streams believed to have been acidified by excess S and N. Many streams and lakes have not recovered. Evidence from East Bear Brook in Maine, USA and modelling with the groundwater acid-base model MAGIC (Cosby *et al.* 1985a,b) indicate that seasonal and yearly variations in soil PCO<sub>2</sub> are adequate to enhance or even reverse acid-base (alkalinity) changes anticipated from modest decreases of SO<sub>4</sub> in surface waters. Alkalinity is generated in the soil by exchange of H<sup>+</sup> from dissociation of H<sub>2</sub>CO<sub>3</sub>, which in turn is derived from the dissolving of soil CO<sub>2</sub>. The variation in soil PCO<sub>2</sub> produces an alkalinity variation of up to 15 meq L<sup>-1</sup> in stream water. Detecting and relating increases in alkalinity to decreases in stream SO<sub>4</sub> are significantly more difficult in the short term because of this effect. For example, modelled alkalinity recovery at Bear Brook due to a decline of 20 meq SO<sub>4</sub> L<sup>-1</sup> in soil solution is compensated by a decline from 0.4 to 0.2% for soil air PCO<sub>2</sub>. This compensation ability decays over time as base saturation declines. Variable PCO<sub>2</sub> has less effect in more acidic soils. Short-term decreases of PCO<sub>2</sub> below the long-term average value produce short-term decreases in alkalinity, whereas short-term increases in PCO<sub>2</sub> produce short-term alkalization. Trend analysis for detecting recovery of streams and lakes from acidification after reduced atmospheric emissions will require a longer monitoring period for statistical significance than previously appreciated.

**Keywords:** CO<sub>2</sub>, alkalinity, acidification, recovery, soils, climate change

## Introduction

In the last two decades, European and North American countries have adopted various protocols for control of atmospheric emissions of S (e.g. the U. S. Clean Air Act and Amendments of 1970 and 1990). Implementation of these protocols is underway. As a consequence of reduced emissions of S (NADP, 1998; UN ECE, 1994), atmospheric concentrations and deposition of SO<sub>4</sub> have declined substantially. Surface waters have responded with decreased SO<sub>4</sub> (e.g. Kopáček *et al.*, 1998; Stoddard *et al.*, 1999). In the northeastern U.S., the pH of precipitation has increased concurrently, even as NO<sub>3</sub> concentrations in precipitation have remained essentially constant. Scientists and policy makers expected that the pH of surface waters would increase as SO<sub>4</sub> declined and the pH of precipitation rose (Reuss *et al.*, 1987). Monitoring studies indicate that most streams and lakes have lower SO<sub>4</sub> but many surface waters have not

responded with higher pH. For example, Clair *et al.* (1995) identified many lakes and streams from Ontario to Newfoundland, Canada, that continued to acidify, even as SO<sub>4</sub> declined in precipitation and surface waters. Driscoll *et al.* (1989) believed that the lack of response of stream pH to higher pH and decreased SO<sub>4</sub> in precipitation at Hubbard Brook Experimental Forest, New Hampshire, USA, related to decreases in the concentrations of neutralizing base cations in precipitation. Similarly, in the Catskill Mountains of New York, USA, although some streams had increased pH as stream SO<sub>4</sub> declined over the last decade, some streams have continued to acidify (Stoddard *et al.*, 1998a,b). Across the northeastern USA, Clow and Mast (1999) found declining SO<sub>4</sub> in precipitation and streams, but not a ubiquitous decline in alkalinity. They suggested that the delayed response of alkalinity may have been caused by recovering soil base-saturation levels. In Maine, USA, Kahl *et al.* (1993) found

that a group of lakes increased in alkalinity through the 1980s in response to decreasing  $\text{SO}_4$ . Some of these lakes, however, have experienced declines in pH and alkalinity since 1990, in spite of continued decline in atmospheric  $\text{SO}_4$  and relatively constant  $\text{NO}_3$ . These declines in pH were accompanied in many cases by decreases in the concentration of base cations in the lake water.

The enigma is that, on a regional scale, many surface waters have experienced declines in the concentration of  $\text{SO}_4$ , some have had significant declines in  $\text{NO}_3$  (Mitchell *et al.*, 1996; Stoddard *et al.*, 1999), but not all surface waters have responded with increasing pH and alkalinity. This lack of clear response to air pollution controls is of interest to policy makers, as well as to scientists.

Many studies (e.g. Castelle and Galloway, 1993) demonstrate strong seasonality for stream alkalinity and soil  $\text{PCO}_2$ . Spring and fall alkalinity are low compared to summer alkalinity; these temporal relationships are linked to higher respiration during warmer months, and dilution of groundwater by surface runoff in the spring and fall (e.g. Stoddard, 1987). East Bear Brook in Maine (BBWM) (Norton and Fernandez, 1999) is an intensively studied system where decreasing  $\text{SO}_4$  atmospheric deposition has not produced an increase in stream pH and alkalinity. BBWM is a paired catchment study underway since 1987. From 1987 to 1999, the volume-weighted mean annual alkalinity of East Bear Brook declined from about 8 meq  $\text{L}^{-1}$  to 0 meq  $\text{L}^{-1}$ . We present empirical data from East Bear Brook on a soil  $\text{PCO}_2$  mechanism that may partially control this longer-term decline in the stream water alkalinity, occurring independently of anthropogenic acidification, chemical weathering, seasonality, and hydrological variation.

## Methods

### SITE DESCRIPTION AND COLLECTIONS

The Bear Brook Watershed in Maine (BBWM) is a paired catchment investigation of the effects of artificial acidification on stream water chemistry, soils, and vegetation. East Bear Brook, the reference catchment, has an area of 10 ha, an average slope of 30%, and is underlain predominantly by Spodosols developed on till. Monitoring since 1987 includes weekly precipitation chemistry and volume, chemistry of approximately 250 stream samples per year with high frequency sampling during high discharge, and discharge measurements at five minute intervals. The headwater stream has low alkalinity (*ca.* 0 meq  $\text{L}^{-1}$  in 1999) and low dissolved organic carbon (DOC) (*ca.* 2 mg  $\text{L}^{-1}$ ). A detailed description of the catchment, methods and results of chemical analysis have been presented by Norton and

Fernandez (1999) and Norton *et al.* (1999).

We measured the concentration of soil air  $\text{CO}_2$  in BBWM soil profiles for two years (1988–1990), including both winters. Soil air tubes were established in East Bear to collect soil air at the base of the O horizon, mid-B, and bottom of the B. As many as 20 concurrent (one-day of collection) soil air samples were collected at several depths in the soil and at multiple sites. Nearly all the soils at BBWM are freely drained and thus we assume that most groundwater below the zone of saturation equilibrates with a  $\text{PCO}_2$  equivalent to that of the lower B horizon. Here we use data only from the lower B horizon. Fernandez *et al.* (1993) give details of the methods.

## Results

### SUMMARY OF THE CHEMISTRY OF RUNOFF

The pH and alkalinity of waters draining a forest are controlled by a number of factors including: supplies of strong acid anions ( $\text{SO}_4 + \text{NO}_3 + \text{Cl} + \text{F} = \text{SAA}$ ) and strong base cations ( $\text{Ca} + \text{K} + \text{Mg} + \text{Na} = \text{SBC}$ ) from the atmosphere; chemical weathering and net ion exchange; and production of the weak acid anions (WAA) from  $\text{H}_2\text{CO}_3$  and dissolved organic acids (from DOC). Changes in biomass may influence several SAAs and SBCs, as well as DOC through a variety of mechanisms. Change in alkalinity depends on changes in the concentrations of SAA, SBC, or WAA.

SAA: The concentration of  $\text{SO}_4$  in precipitation at BBWM declined gradually from 1988 to 1999, as it did in precipitation and in many surface waters in the northeastern USA (Stoddard *et al.*, 1999). The decline in atmospheric deposition has caused a decrease in  $\text{SO}_4$  concentration in East Bear Brook of approximately 15 meq  $\text{L}^{-1}$  (15%) over the same period (Norton *et al.*, 1999). The concentration of  $\text{NO}_3$  has been relatively unchanged in wet precipitation at BBWM during this period. Stream concentration and export of  $\text{NO}_3$  reached a peak at BBWM about 1990 but decreased in East Bear runoff over the next nine years, as it has in many headwater surface waters in the northeastern USA (Mitchell *et al.*, 1996). Volume-weighted concentration is now about 2 to 3 meq  $\text{L}^{-1}$ . Chloride at BBWM is apparently derived entirely from atmospheric deposition of marine aerosols. The concentration of Cl in precipitation varies seasonally, with lower concentrations in the May–September period. The outflow concentration is damped significantly as a consequence of mixing of “old” and “new” water. Stream Cl declined from 1978 to 1991, followed by an increase to 1999. The annual volume-weighted mean values range from about 60 to 70 meq Cl  $\text{L}^{-1}$ . Sulfate from marine aerosols is, on an equivalent basis, 10% of Cl. Thus, long-term variation

of the SO<sub>4</sub> in the marine aerosol component flux is only about 1 meq SO<sub>4</sub> L<sup>-1</sup> in stream water. Most of the stream F, about 1 meq L<sup>-1</sup>, is derived from weathering. In summary, concentrations of some individual SAA in East Bear runoff have remained relatively constant during the 11-year period of observation but the sum of SAA has declined approximately 40 meq L<sup>-1</sup>, primarily due to declines in stream NO<sub>3</sub> (15 meq L<sup>-1</sup>) and SO<sub>4</sub> (20 meq L<sup>-1</sup>) (Kahl *et al.*, 1999).

**SBC:** Concentrations of SBC in wet atmospheric deposition, corrected for marine salts, were only a few meq L<sup>-1</sup>. Thus total atmospheric SBC varied consistently with Cl. Rates of release of SBC from chemical weathering rates, normalised to the concentration of Si, appear to be relatively constant from year to year (Uddameri *et al.*, 1995). Although there is a seasonal variation in stream chemistry associated with ion exchange of Na and Mg (from marine aerosols) for Ca and K (Norton and Kahl, in press), there is little net change in the sum of SBC derived from marine aerosols. We have not quantified biomass accumulation rate (and thus storage of SBC) at BBWM. However, changes in net storage would not vary strongly on a yearly basis in the absence of harvesting, substantial defoliation, or fire. Overall, SBC have decreased about 40 meq L<sup>-1</sup> in East Bear Brook through the period of record (Norton *et al.*, 1999). This is comparable to the decline in SAA.

**WAA:** The concentration of DOC averaged close to 2 mg L<sup>-1</sup> over the 11 year record of stream chemistry with no long-term systematic change. Kahl *et al.* (1989) and David *et al.* (1992) estimated that the charge density for the organic anions was approximately 5 meq mg<sup>-1</sup> DOC L<sup>-1</sup>. Thus, total organic anions are typically <10 meq L<sup>-1</sup> and range up to 20 meq L<sup>-1</sup> during periods of high discharge. Changes in DOC (and related organic acidity) are likely not responsible for the modest decline in alkalinity at East Bear Brook.

**Alkalinity and pH:** The paradox at East Bear Brook and at some other localities in the northeastern USA is that as the

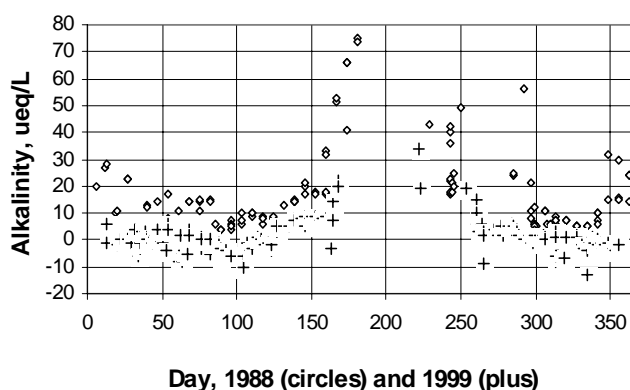


Fig. 1. Measured alkalinity (meq L<sup>-1</sup>) in East Bear Brook for 1988 (circles) and 1999 (crosses) for all stream samples.

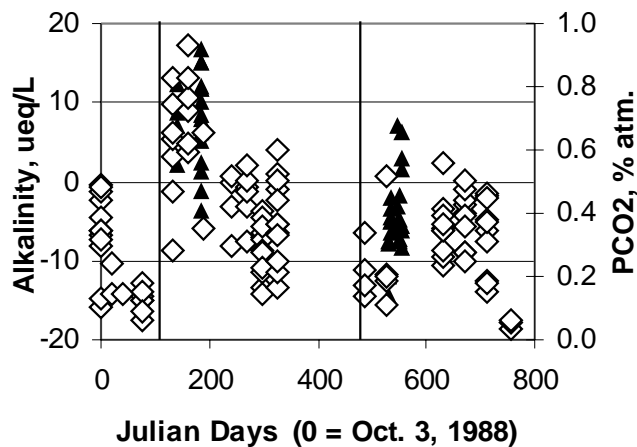


Fig. 2. (a) Percent CO<sub>2</sub> in soil air (diamonds) at 50 cm in the mineral soil (C horizon) at East Bear Brook in Maine. Julian time starts on October 3, 1988. January 1, 1989 and 1990 (vertical lines) are Julian Days 89 and 454. Synchronous data are from different air tubes on different plots. (b) Alkalinity (triangles) of East Bear Brook during high discharge (>0.5 ft<sup>3</sup> sec<sup>-1</sup>; >14 L sec<sup>-1</sup>) for January to April for 1989 and 1990. Synchronous data are from ISCO<sup>TM</sup> auto-samplers, typically taken every two hours on both sides of high discharge hydrographs.

concentrations of SAA, dominated by SO<sub>4</sub> and NO<sub>3</sub>, have declined in streams and lakes, the concentrations of SBC have declined as much or more, and alkalinity has declined, contrary to expectation (Fig. 1). Alkalinity at East Bear Brook has a strong seasonal pattern. It is typically low early in the year, declines to a minimum during snowmelt and early spring rains, climbs to a peak at very low flow (deep flow paths), and then declines during fall rains. In 1988, minimum alkalinity was approximately 0 meq L<sup>-1</sup> whereas by 1999 the pattern persisted but the minimum reached was -10 meq L<sup>-1</sup> (Fig. 2). East Bear had become more acidic.

#### SOIL PCO<sub>2</sub>

Synchronously collected samples of soil air from different soil depths revealed a concentration gradient for CO<sub>2</sub> from 0.1 to 1.0% from the O horizon to the C horizon. This depth trend for PCO<sub>2</sub> is opposite the trend in CO<sub>2</sub> generation in the soil from respiration, because CO<sub>2</sub> generated in the forest floor and uppermost mineral soil is readily lost to the atmosphere. Production of CO<sub>2</sub> decreases with depth in the soil but CO<sub>2</sub> is more efficiently retained in deeper soil pore space resulting in increasing PCO<sub>2</sub> with depth. The increase depends on season, soil texture, and soil moisture content. Fernandez *et al.* (1993) reported strong variations of PCO<sub>2</sub> between years, seasons, and from year to year for the same season. The highest PCO<sub>2</sub> at the base of the B horizon, approaching 1%, occurred in the winter of 1988/89. The snow

pack was particularly deep and continuous during that winter. In the 1989/90 winter which had an intermittent thin snow pack, the  $\text{PCO}_2$  was considerably lower, sometimes approaching 0.1%. Summer  $\text{PCO}_2$  in the B horizon was typically about 0.4% (Fig. 2).

Concurrent measurement of stream chemistry, stream discharge, and soil  $\text{PCO}_2$  throughout the 1988–1990 period enabled an evaluation of the relationships among these variables, especially controls on alkalinity. We compared the seasonality of alkalinity (including winter) and stratified the data by discharge. Figure 2 includes alkalinity data for only those times when discharge exceeded  $14 \text{ L s}^{-1}$ , approximately 1/10 of the maximum discharge over the 12-year record. We assume that similar discharge values correspond to similar flow paths. The high alkalinity that occurs in the summer period (Fig. 1) is caused by less acidic flow paths with a  $\text{PCO}_2$  of approximately 0.4% of an atmosphere. During the late 1988/89 winter period,  $\text{PCO}_2$  approached 1%, and alkalinity of the runoff (stratified by flow) was approximately  $10 \text{ meq L}^{-1}$  higher than the comparable period the following winter, when  $\text{PCO}_2$  was less than 0.2% (Fig. 2). The high  $\text{PCO}_2$  values of winter 1988/89 corresponded with a continuous and extensive snowpack and higher than normal alkalinity; the converse was true the next winter. The higher alkalinity was associated with an increase of SBC (Ca, Mg, and K), greater than the SAA decrease. Approximately half the annual runoff for East Bear is associated with the spring runoff (see Chen and Beschta, 1999, for detailed hydrology). Consequently, this spring period of higher than normal alkalinity influenced a considerable fraction of the volume-weighted mean alkalinity (and base cations) for the year.

## Discussion

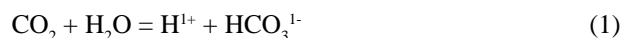
### $\text{CO}_2$ , WEATHERING, AND ALKALINITY PRODUCTION

The long-term role of  $\text{CO}_2$  in chemical weathering is well known. Through the dissolving of  $\text{CO}_2$  into water, the formation of carbonic acid ( $\text{H}_2\text{CO}_3$ ), and the dissociation of  $\text{H}_2\text{CO}_3$  into  $\text{H}^+$ ,  $\text{HCO}_3^{1-}$  and  $\text{CO}_3^{2-}$  in equilibrium amounts, chemical weathering and alkalinity generation are increased over what would occur in the absence of  $\text{H}_2\text{CO}_3$ . Respiration of heterotrophic microbial communities decomposing organic matter and root respiration in soils produce elevated concentrations of  $\text{CO}_2$ , further increasing the rates of chemical weathering (demonstrated empirically by Berner and Ji-Long, 1997, for example, and modelled by Neal and Whitehead, 1988). Weathering rates are also enhanced by the production of organic acidity.

In freely-drained forest Spodosols at BBWM, pH varies

dramatically with depth. Within the O horizon,  $\text{pH}_{\text{H}_2\text{O}}$  is commonly  $<4.0$ , controlled largely by weak organic acidity from partial decomposition of forest floor organic materials. Below the O horizon in these undisturbed Spodosols there is commonly a series of abrupt transitions between horizons. The E horizon, where present, is highly acidic but with a  $\text{pH} >4.0$ . This horizon is generally chemically inert, and extremely thin, intermittent, or absent. Below the O or E horizon is the B horizon, commonly with  $\text{pH} <4.5$  at its top, still below the pH at which soil  $\text{PCO}_2$  can affect pH significantly. Increased pH with depth occurs as the organic acid is precipitated, adsorbed, and metabolised, coincident with percolating solutions encountering increasingly less weathered aluminosilicate minerals. Lower B horizon soil pH at BBWM is commonly between pH 4.5 and 6.0. The higher pH with depth results in an increased role for  $\text{PCO}_2$  in controlling acid-base chemistry in soil solutions and groundwater.

Alkalinity is generated in the soil water by the formation of  $\text{HCO}_3^-$  from dissolved  $\text{CO}_2$  in soil water:



The  $\text{H}^+$  produced by reaction (1) reacts with an Al solid phase (e.g.,  $\text{Al}(\text{OH})_3$ ) in the soil:



Most soil cation exchange sites have a higher affinity for trivalent Al than for di- or monovalent base cations. Consequently an exchange of cations between dissolved and solid phases results:



where  $\text{BC}^{1+}$  represents a base cation and X represents the soil exchange complex. The net result of reactions (1), (2), and (3) is the production of bicarbonate alkalinity in the soil water (Fig. 3a,b). If soil air  $\text{PCO}_2$  decreases below long-term average values, less  $\text{CO}_2$  dissolves in the percolating soil water, the pH of the soil water tends to be higher than average (particularly if the soil pH approaches or is greater than 5), the soil solutions are less aggressive at chemical weathering and net adsorption of exchangeable cations occurs. A higher-than-average pH along any preferential flow path produces net adsorption of exchangeable cations (including SBC), decreasing the export of base cations (SBC). The alkalinity of the soil water is determined, in the short term, by this ion exchange equilibrium. As the groundwater emerges to a stream, excess  $\text{CO}_2$  is degassed partially (Norton and

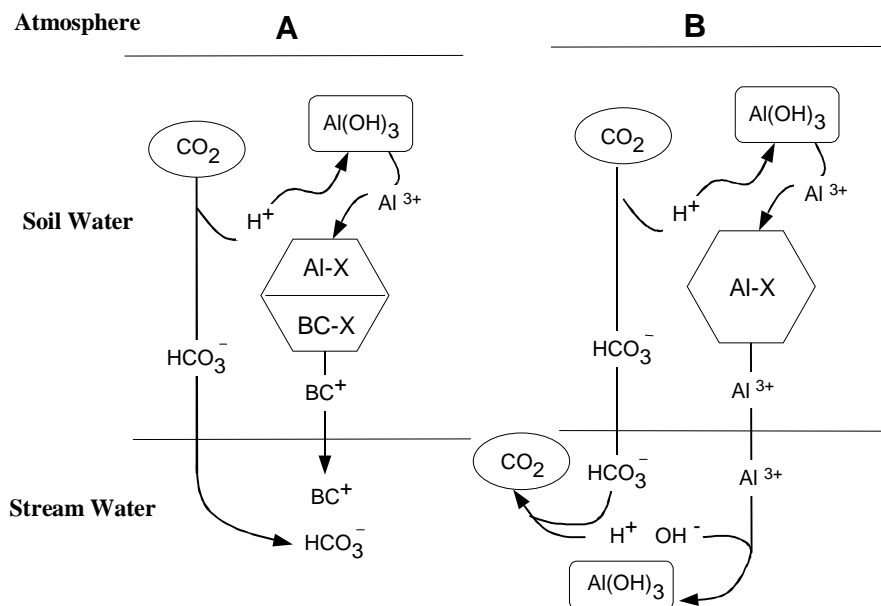


Fig. 3. Conceptual model of the influence of PCO<sub>2</sub> on (a) Export of exchangeable base cations (BC<sup>+</sup>) from soils with high base saturation and (b) Export of exchangeable Al (Al<sup>3+</sup>) from soils with very low base saturation. East Bear Brook is intermediate in base saturation.

Henriksen, 1983; Jones and Mulholland, 1998; Neal *et al.*, 1998). Virtually all headwater streams have overpressures of CO<sub>2</sub>, including East Bear Brook. During degassing, the pH increases but alkalinity is unaffected because the water is no longer in contact with soil. Modest alkalinity changes may occur because of interaction between the emergent groundwater and the stream substrate (Norton *et al.*, 2000) and precipitation of hydroxide phases (e.g. Fe and Mn) caused by increased oxidation potential. For lower than normal soil PCO<sub>2</sub>, the stream water would have lower SBC, accompanied by lower HCO<sub>3</sub><sup>-</sup>, i.e. lower alkalinity. If base saturation in the soil complex is very low, alkalinity variations are induced through interaction with the Al soil complex and soil water (Figure 3b). East Bear Brook responses include variation in the export of both SBC and Al. Degassing of CO<sub>2</sub> there results in the precipitation of Al in the stream (Roy *et al.*, 1999), with no net alkalinity production. David and Vance (1989) subjected B-horizon soil material from the BBWM site to leaching under PCO<sub>2</sub> ranging from atmospheric (10<sup>-3.5</sup> atm) to pure (100%) CO<sub>2</sub> (1 atm) and found that alkalinity ranged from -5 to 163 meq L<sup>-1</sup>, consistent with the mechanism described above. Their data also suggest that the soils are in equilibrium with a PCO<sub>2</sub> higher than 10<sup>-3.5</sup>, because the average alkalinity is higher than -5 meq L<sup>-1</sup>. It is concluded that episodic or short-term decreases in PCO<sub>2</sub> in the soil result in lower alkalinity in runoff at BBWM. Episodic or short-term increases in PCO<sub>2</sub> produce short-term higher alkalinity. This is somewhat counterintuitive because

long-term elevated PCO<sub>2</sub> produces long-term acidification of surface water.

Observed variations in soil air PCO<sub>2</sub> appear to affect alkalinity to the same quantitative extent as recent changes in SO<sub>4</sub> or NO<sub>3</sub> concentrations in streams and lakes, and thus obscure (or enhance) the expected alkalinity recovery as SO<sub>4</sub> concentrations decline. Although SO<sub>4</sub> concentrations in surface waters are generally declining, soil PCO<sub>2</sub> can vary concurrently and on a short time scale. The hypothesis was evaluated by estimating the magnitude of alkalinity changes expected to result from changes in SO<sub>4</sub> concentrations or from changes in soil PCO<sub>2</sub>. These estimates are derived using the process-based model of soil acid-base chemistry, MAGIC (Cosby *et al.*, 1985a, b).

#### MODELLING BBWM RESPONSE

Cosby *et al.* (1996) applied the MAGIC model to the Bear Brook catchments for the period 1987 to 1992. The lumped parameter model was calibrated to two years of pre-treatment data on the manipulated catchment (West Bear) as well as to four years of data from the reference catchment (East Bear). MAGIC reproduced fairly well the observed stream water chemistry trends in both the treatment and reference catchments for SO<sub>4</sub> and SBC. Residuals for the treated (predicted minus observed chemistry) were least if the West Bear data were used for the West Bear calibration. Both catchments had similar observed patterns (but different absolute values) of alkalinity, pH, and Al. The patterns

differed from some of the MAGIC prediction, suggesting that some process was occurring that was not correctly represented or parameterised in the model. The 1996 calibration of MAGIC for the East Bear catchment was modified for this paper by dividing the soil into an upper organic horizon and a lower inorganic horizon. The modified model was used to simulate the responses of stream water alkalinity to variations in observed  $\text{SO}_4$  concentrations and  $\text{PCO}_2$  in the soil air. As  $\text{SO}_4$  decreases in atmospheric deposition, MAGIC predicts a concurrent decrease in  $\text{SO}_4$  and increase in alkalinity of the stream water. However, episodically decreasing  $\text{CO}_2$ , can reduce or even reverse the increase in alkalinity.

Three different 20-year simulations were run:

- (1) The base case simulation assumed no changes in either  $\text{SO}_4$  concentrations (atmospheric input and stream values for 1991) or soil  $\text{PCO}_2$  (set at 0.25%).
- (2) Responses to altering  $\text{SO}_4$  concentrations in soil water, with soil  $\text{PCO}_2$  unchanged were examined and the resultant changes in simulated alkalinity relative to the base case simulation were calculated (Fig. 4).
- (3) Soil  $\text{PCO}_2$  in the lower horizon soil was varied while  $\text{SO}_4$  concentrations were held constant at 1991 values (Fig. 4).

The three simulations began with observed 1991 conditions. By the end of years 1, 10, and 20 of the base case simulation ( $\text{SO}_4$  and  $\text{PCO}_2$  unchanged), alkalinity of East Bear had

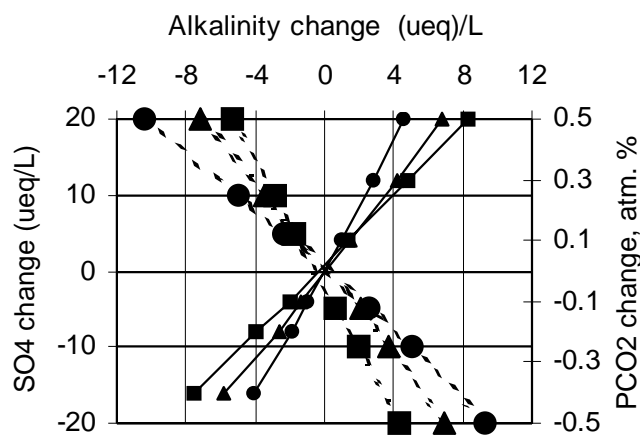


Fig. 4. Alkalinity change relative to the base case (1991 concentration of  $\text{SO}_4^{2-}$ ) expected at East Bear Brook from variations of stream  $\text{SO}_4$  and soil  $\text{PCO}_2$  for 1, 10, and 20 years. Dashed lines are for  $\text{SO}_4$ . Solid lines are for  $\text{PCO}_2$ . Squares are the 1-year response. Triangles are the 10-year response. Circles are the 20-year response. For example, if  $\text{SO}_4^{2-}$  decreased 20 meq  $\text{L}^{-1}$ , alkalinity would increase 4, 7, or 9 meq  $\text{L}^{-1}$  over 1, 10, and 20 years, respectively, relative to the base case.

declined to 6.9, 2.4, and  $-3.8$  meq  $\text{L}^{-1}$ , respectively (Fig. 5). That is, East Bear continued to acidify at 1991 levels of atmospheric S and N deposition and for a constant soil air  $\text{PCO}_2$  of 0.25% in the lower B horizon. This base case response for alkalinity is similar to the actual behavior of East Bear since 1987.

A step decrease in  $\text{SO}_4$  concentration of 20 meq  $\text{L}^{-1}$  resulted in a simulated alkalinity after the first year following the decrease that was 4 meq  $\text{L}^{-1}$  higher than the base case stream alkalinity for year one. Similarly, a decrease in soil  $\text{PCO}_2$  to 0.05% resulted in a simulated stream alkalinity in year one that was 4 meq  $\text{L}^{-1}$  lower than the base case alkalinity for year one. If the 0.2%  $\text{PCO}_2$  decrease and the 20 meq  $\text{SO}_4$   $\text{L}^{-1}$  concentration decrease occur simultaneously, there would be no detectable stream alkalinity (or pH) response to the  $\text{SO}_4$  concentration reduction in year 1 (Fig. 4). These simulations strongly support the hypothesis that “reasonable” changes in soil  $\text{PCO}_2$  can produce changes in stream alkalinity that are of the same magnitude as alkalinity changes expected from declining stream  $\text{SO}_4$  concentrations.

Ten years into the simulation, the base case stream alkalinity declined approximately 5 meq  $\text{L}^{-1}$  as East Bear continued to acidify from the excess  $\text{SO}_4$ . Relative to the base case alkalinity, the step decrease in  $\text{SO}_4$  of 20 meq  $\text{L}^{-1}$  resulted in an alkalinity increase of 7 meq  $\text{L}^{-1}$ . At 20 years, the decrease in  $\text{SO}_4$  produced an increase in alkalinity of 9 meq  $\text{L}^{-1}$  relative to the base case (the alkalinity of which had declined 11 meq  $\text{L}^{-1}$  since year 1). At 10 and 20 years, because of the low  $\text{PCO}_2$  of 0.25% for the base case, it is not possible to decrease  $\text{PCO}_2$  enough to compensate for the 20 meq  $\text{L}^{-1}$  decrease in  $\text{SO}_4$ . This change in response through time is caused by cation depletion in the soil to the point where changes in  $\text{SO}_4$  are accompanied by a nearly 1:1 response in acidic cations, largely  $\text{H}^+$ . At East Bear Brook, acidification or alkalization from changes in  $\text{PCO}_2$ , relative to the base case, could not be sustained for more than a few decades because of continued soil acidification.

The ratio of (the slope of the curve [D alkalinity:D  $\text{SO}_4$ ]) to (the slope of the curve [D alkalinity:D  $\text{PCO}_2$ ]) in any year can be used to establish a “compensation factor” for no net change in alkalinity for that year. This ratio expresses the increase (decrease) in  $\text{PCO}_2$  that offsets an increase (decrease) in  $\text{SO}_4$  concentration such that alkalinity does not change. Figure 4 shows that if  $\text{CO}_2$  is doubled for ten years, the alkalinity remains nearly constant relative to the base case. The opposite effects of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{CO}_3$  are caused by their appearance on opposite sides of the alkalinity relationship:

$$\text{SSBC} - \text{SSAA} = \text{alkalinity} = \text{SWAA} - \text{S}(\text{H}^+ + \text{Al}(\text{OH})_n^{+3-n}) \quad (5)$$

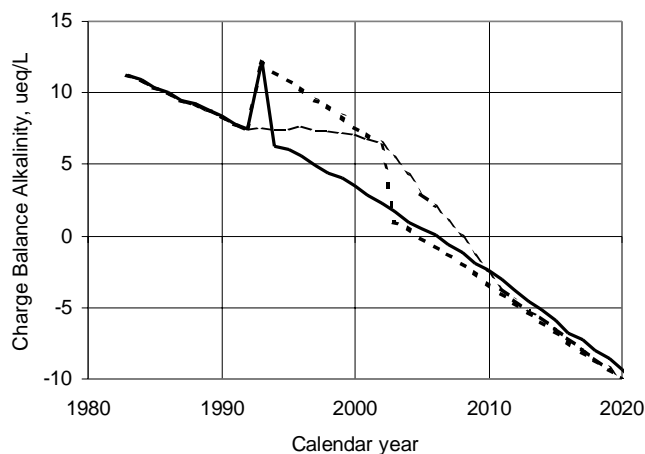


Fig. 5. Projected response in alkalinity of East Bear Brook to deposition of SO<sub>4</sub> atmospheric at 1991 values to (a) a one-year doubling of soil PCO<sub>2</sub> (solid line), (b) a doubling of soil PCO<sub>2</sub> for 10 years (dashed line), and (c) a 10-year ramp to doubled soil PCO<sub>2</sub> (dotted line).

Increased net cation adsorption because of decreased soil air PCO<sub>2</sub> is charge-compensated in the stream by decreased formation of HCO<sub>3</sub><sup>-</sup> and increased H<sup>+</sup>. However, as SO<sub>4</sub> from the input of H<sub>2</sub>SO<sub>4</sub> increases, the charge balance for the higher SO<sub>4</sub> is provided by higher concentrations of base cations and increased H<sup>+</sup>. Thus, changes in alkalinity from variations in soil PCO<sub>2</sub> and SO<sub>4</sub> may be additive or cancel each other.

The compensation factor is  $(\Delta \text{PCO}_2, \%) / (\Delta \text{SO}_4, \text{meq L}^{-1})$ ; the values for East Bear Brook are -0.013, 0.024 and -0.050 for the 1st, 10th, and 20th years, respectively. The increase with time indicates that the potential for changes of soil PCO<sub>2</sub> to offset changes of SO<sub>4</sub> concentration declines with time. For the conditions observed in East Bear Brook soils, the factors suggest that PCO<sub>2</sub> effects could obscure or delay alkalinity increases in response to SO<sub>4</sub> concentration. The impact of a doubling of PCO<sub>2</sub> (to 0.5%) for 1 and 10 years, or ramping the PCO<sub>2</sub> to 2× over ten years is shown in Fig. 5. By 20 years the alkalinity increases related to SO<sub>4</sub> reduction should be observed, in spite of any reasonable variation for soil PCO<sub>2</sub>.

#### IMPLICATIONS OF ALKALINITY CHANGES DRIVEN BY VARIABLE SOIL CO<sub>2</sub>

The increases in alkalinity expected from decreases in atmospheric deposition of strong mineral acid anions may be obscured by decreases in soil PCO<sub>2</sub>, a process that may persist for several years due to systematic climate change. Conversely, increased PCO<sub>2</sub> will cause enhanced alkalinity production. This would confuse documentation of recovery in surface water alkalinity associated with S emission reductions. Because of the effect of variable PCO<sub>2</sub>, long-

term monitoring is necessary to determine the efficacy of S emission control strategies. Surface water recovery from acidification will, most likely, not be monotonic, an extremely important consideration for evaluation of air pollution control policy.

The amount of short-term production of higher alkalinity due to higher PCO<sub>2</sub> is controlled by site characteristics prior to the changes. In systems that are more acidic than East Bear, the response of stream alkalinity to changes in CO<sub>2</sub> would be smaller. More alkaline systems would be more responsive and the effect would persist longer. These conclusions are consistent with the empirical findings of Stoddard *et al.* (1998a,b) who demonstrated that the magnitude of trends in acid/base variables (alkalinity and SBC) are related to the acidity of the system.

Is there evidence for annual decline in soil PCO<sub>2</sub>, other than that caused by strong seasonality? The authors are not aware of any regional or site-specific integrated programme of soil PCO<sub>2</sub> monitoring to demonstrate trends for this parameter. The northeastern U.S.A. has experienced some of the warmest years on record during the 1990s. Warmer summer conditions may *increase* both microbial and root respiration in the soil. Increased soil PCO<sub>2</sub> should result in an enhancement of the alkalinity recovery attributed (mistakenly) to SO<sub>4</sub>. However, Rustad and Fernandez (1998) found that experimental warming of spruce-fir soils in the snow-free period in Maine produced increased respiration and an increase in efflux of CO<sub>2</sub>, but PCO<sub>2</sub> in the lower soil horizon was not significantly higher, even though the temperature at 50 cm depth was increased by 5°C. The effect of such a temperature increase was investigated at the mini-catchment scale by Wright (1998). He found that the major result of increased air CO<sub>2</sub> (to two times atmospheric) plus warming of soil by 5°C was an increased mobilization of NO<sub>3</sub> to runoff. Nitrate *decreased* through the 1990s at East Bear Brook. A decline in soil PCO<sub>2</sub>, despite increased temperature and possibly increased soil respiration, could result from lower soil moisture content and greater efflux of soil CO<sub>2</sub>. For this reason, the O horizon of a forest rarely has high PCO<sub>2</sub>, despite high respiration rates, due to rapid exchange between forest floor gas phases and the open atmosphere. However, atmospheric warming in the winter period may cause a reduction in the temporal extent of the snow-pack, permitting loss of soil CO<sub>2</sub> and thereby reducing alkalinity of spring runoff from rain and snowmelt.

There are several alternative explanations for the continued decline in alkalinity at East Bear Brook concurrent with declining SO<sub>4</sub> in the stream water:

- (1) Perhaps the catchment is still acidifying from excess SO<sub>4</sub>, even as atmospheric loading of SO<sub>4</sub> has declined to produce stream concentrations 15 meq L<sup>-1</sup> below 1991

values. This explanation appears likely for East Bear. However, the BBWM soils adjust rapidly to changes in atmospheric deposition of  $\text{SO}_4$  and they should have been close to equilibrium at BBWM in 1991, having been subjected to higher loading prior to 1991. Under 1991 conditions, modelling suggests that East Bear apparently would slowly acidify, decreasing in alkalinity about  $0.5 \text{ meq L}^{-1} \text{ yr}^{-1}$ . If soil  $\text{CO}_2$  were increased by 0.4% to a long-term average of 0.65%, it would take approximately 40 years for alkalinity to decline to values achieved in the same period with the base case conditions (1991  $\text{SO}_4$  and  $\text{PCO}_2$ ). Thereafter, the system with elevated  $\text{CO}_2$  would be more acidic than for the base case conditions in the model simulation. Before that occurs, labile carbon for production of  $\text{CO}_2$  in soils might become limiting.

- (2) Dillon *et al.* (1997) suggested that drought affecting central Ontario lakes resulted in lowering of the water table and release of  $\text{SO}_4$ , oxidized from reduced S in organic matter. This mechanism would operate well in wetland-rich systems, but not at East Bear, which has no wetlands.
- (3) Webster *et al.* (1990) argued that acidification of some seepage lakes was strongly influenced by the moisture budget; lower water supply resulted in evaporative concentration of acidic components. At East Bear Brook, there have been no obvious changes in hydrology that parallel the decline in alkalinity from 1988 to 1999.
- (4) Driscoll *et al.* (1989) suggested that declines in atmospheric deposition of base cations may cause a decline in stream base cations, and thus alkalinity. Base cations have declined little, if at all, at BBWM from 1988 to 1999.
- (5) Lastly, as  $\text{SO}_4$  inputs to soil water decline, the rate of base saturation loss should decline. However, the implied net adsorption should be less than the decline in  $\text{SO}_4$ . At BBWM and at many other localities, the decline in base cations in stream waters exceeds the decline in  $\text{SO}_4$ .

## Summary

Variations in soil  $\text{PCO}_2$  at BBWM caused by variation in the snow pack appear to be responsible for variation of alkalinity production during the winter and early snow-melt period. The magnitude of variation ( $\pm 10 \text{ meq L}^{-1}$ ) is comparable to the increase in alkalinity expected by the reduction in atmospheric  $\text{SO}_4$  from 1990 to 1999. Soil  $\text{PCO}_2$  and surface water data with sufficient detail, and linked in space and time, are not available from appropriate catchments to determine the extent to which declines in soil  $\text{PCO}_2$  may cause declining stream and lake alkalinity in the northeastern USA and elsewhere. Theory, some field data, and limited

experiments, indicate that variations in soil  $\text{PCO}_2$  may introduce significant uncertainty into the interpretation of time series for acid-sensitive surface waters. It is important, therefore, that this mechanism not be overlooked, so that policy and evaluations of trends in air emissions, precipitation chemistry, and surface water chemistry are based on understanding.

## Acknowledgments

The helpful comments from Arne Henriksen, Richard Wright, and anonymous reviewers are appreciated. This research was supported by the U. S. Environmental Protection Agency through contracts CR813599 CR816261, CR821014, and R825762-01-0 to the University of Maine. The manuscript has been reviewed by the Agency but does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Research was also supported by grant (DEB9615199) from the National Science Foundation. This is contribution #2478 of the Maine Agricultural and Forest Experiment Station.

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