

Controls Over Base Cation Concentrations in Stream and River Waters: A Long-Term Analysis on the Role of Deposition and Climate

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ABSTRACT

Significant concern has emerged over the past decades regarding decreases in available base cations (that is, calcium, magnesium, potassium, and sodium) in forest soils and surface waters. Base cations (BCs) are important for buffering against changes in soil and water acidity, and their concentrations can be indicative of environmental management problems such as those linked to acid deposition and land use. Climate variability is also a potentially large factor influencing the dynamics of BCs in soils and surface waters, but our understanding of these interactions at broad scales remains elusive. We used a hierarchical Bayesian model to evaluate the long-term (1990–2010) patterns and drivers of BC concentrations for 60

stream and river monitoring stations across Sweden. Results indicated that the long-term trends in concentration, and the associated environmental drivers, differed among individual BCs and geographical regions. For example, we found that concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ have decreased in southern Sweden since 1990 and that this is strongly related to concurrent declines in sulfate (SO_4^{2-}) over the same period of record. In contrast, concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in northern Sweden did not exhibit significant directional trends, despite declines in SO_4^{2-} , nitrate (NO_3^-), and chloride (Cl^-) over the same period. Instead, BC dynamics in the north are characterized by inter-annual variability that is most closely linked to climate variables. Results suggest that the interaction between climatic variability and historical acid deposition determines the regional pattern and long-term trends of BC concentrations across streams and rivers of Sweden. Understanding the strength of the interaction between climate features and historic deposition will greatly improve our ability to predict long-term trends of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ and their inter-annual dynamics in the future.

Key words: hierarchical Bayesian model; calcium; magnesium; potassium; Sweden; acid deposition; recovery; stream water chemistry.

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INTRODUCTION

Decreases in available base cations (that is, calcium, magnesium, potassium, and sodium) in soils and waters have emerged as a significant concern in forest ecology over the past 20–30 years (Adams and others 2000; Berthrong and others 2009). Base cations (BCs) are macrominerals critical for some of the most basic biological processes such as photosynthesis, energy storage, stomatal pore closure, and cell signaling (McLaughlin and Wimmer 1999). In addition, these minerals are important for buffering against changes in the acidity of soils and surface waters (Fernandez and others 2003). Strong acid anions in soils mobilize BCs, which are preferentially displaced from exchange sites in the soil matrix by hydrogen or aluminum ions (Fölster and Wilander 2002; van Breeman 2002; SanClements and others 2010). Upon release, BCs are transported hydrologically through the soil matrix, accompanying dominant anions to maintain charge neutrality (Fölster and Wilander 2002; Finér and others 2004; Molot and Dillon 2008). Vertical and lateral transport of these solutes ultimately leads to adjacent aquatic environments, where they continue to play important biogeochemical roles (Stuanes and Kjønaas 1998; Edwards and others 2002). Because the primary source of BCs to ecosystems is the long-term weathering of parent materials (Sverdrup and Warfvinge 1988; Likens and others 1998), rapid losses of these elements can deplete soil pools and detrimentally affect ecological processes and acid buffering capacity for many years (SanClements et al. 2010).

Base cation depletion from soils and accelerated leaching into surface waters has been associated with trends in atmospheric acid deposition (Fernandez and others 2003; Sullivan and others 2006). Early observations linking acid deposition with declining BC status in lake waters (Almer and others 1974; Dillon and others 1987) motivated large-scale international collaboration oriented toward mitigating further deposition increases (Bull and others 2001). Important international agreements and legislation (UN/ECE 2005) have been successful in bringing down levels of acid deposition, particularly that of sulfur (S), in many parts of Europe and North America (Forsius and others 2001; Mitchell and others 2011). Although temporal records of BC concentrations in some regions are consistent with ecosystem recovery in response to these reductions in deposition (Evans and others 2001; Fölster and Wilander 2002; Skjellkvåle and others 2005), this is not true in all areas (Stoddard and others 1999; Fölster and Wilander 2002; Martinson and others 2005; Sullivan and others 2006) suggesting that acid

inputs continue to be important in determining BC availability in soils and surface waters.

Climate variability is also a key regulator of BC concentrations and dynamics in soils and surface waters (Campbell and others 2009; Lucas and others 2011). Indeed, temperature and precipitation govern basic biological and physical processes in soils (Cable and others 2011), the strength of hydrologic routing, and the rates of forest productivity (Drake and others 2011; Toledo and others 2011)—all of which contribute to the export of BCs from terrestrial ecosystems to surface waters (Laudon and others 2011). Despite the obvious importance of these climatic factors, we lack sufficient understanding to reliably predict how changes in air temperature and precipitation will affect the suite of processes which interact to control the delivery of BCs to aquatic systems. Although some studies have examined how recovery from acidification will be affected by climate variability (Watmough and others 2005; Aherne and others 2006; Hardekopf and others 2008; Molot and Dillon 2008), there has been less work examining the basic relationships between climate variability and spatial and temporal trends in the concentration of different BCs in streams and rivers (Mitchell and Likens 2011).

The primary objective of this study was to evaluate the patterns and drivers of the long-term changes in stream and river chemistry across Sweden. The long-term sustainability of ecosystem BC pools is of particular interest in Sweden, where surface waters have already been heavily impacted by historical atmospheric deposition of S and nitrogen (N) (Taylor and others 1989; Eriksson and others 1992; Fölster and Wilander 2002). Furthermore, currently available biogeochemical modeling tools indicate Swedish streams and rivers could re-acidify if land management decisions allow forest soils to become depleted of BCs faster than they can be replenished by weathering (Akselsson and others 2007). Here, we use regional monitoring data in conjunction with variation in potential covariates as a means to understand the factors governing broad-scale and long-term patterns of BCs in streams and rivers. More specifically, we evaluate the degree to which long-term trends in BCs are linked to changes in anion chemistry versus inter-annual climate variability.

METHODS

Study Sites, Water Chemistry, and Covariate Data

We analyzed water chemistry data collected from 1990 to 2010 at 60 monitoring sites maintained by

the Swedish Environmental Protection Agency, and distributed broadly across Sweden (Figure 1; Table 1). Monitoring sites were assigned to different geographical regions (that is, south, central, and north) and represent a wide range of watershed sizes, elevations, mean annual temperatures, vegetation covers, and land-use histories (Table 1). Samples for water chemistry were collected from the central part of each channel, generally at semi-weekly intervals during periods of high flows (for example, every 2 weeks during snow melt) and monthly during periods of low flow. Samples were collected in clean polyethylene bottles and kept cool as they were transported to the lab for processing, in compliance with international standards for sampling and handling (ISO 5667-1:2007, ISO 5667-3, ISO 5667-6: 2005). Analytical methods for solutes considered in this study followed protocols as defined by the International Organization for Standardization. Spatial and temporal patterns of dissolved organic carbon (DOC) were estimated from absorbance at 420 nm (Abs420) on filtered samples in a 5 cm cuvette (filter size 0.45 μm), which is a commonly used proxy for DOC (Erlandsson and others 2008). For further information on methods and for stream chemistry data, see <http://www.slu.se/vatten-miljo>. For this analysis, we focused on inter-annual variation in solute concentrations and

thus used annual means to describe variables of interest. Because reliable discharge data were not available for every watershed, water chemistry data were not volume-weighted.

Atmospheric deposition data are from the Swedish Environmental Research Institute (IVL; www.ivl.se). For this analysis, we used deposition data collected as part of the throughfall network for the years 1990–2010. Deposition data were collected on a county-by-county basis by the Swedish Environmental Protection Agency and county administration boards. The throughfall network estimates wet deposition and a portion of dry deposition from samples collected monthly within 30 \times 30 m square plots distributed throughout the country. Annual deposition estimates for each watershed were obtained by calculating an area-weighted mean of interpolated deposition splines generated using the spline function in ArcMap version 10.0 (ESRI, Redlands, CA, USA).

Mean annual temperature and precipitation data were obtained from meteorological stations maintained by the Swedish Meteorological and Hydrological Institute (SMHI; www.smhi.se). Annual precipitation estimates for each watershed were determined by calculating an area-weighted mean of interpolated precipitation splines created using the spline function in ArcMap. Annual temperatures were calculated and included in our model (described below) as regional means only. Regional means were obtained by calculating the average mean temperature for each of the 150 available monitoring sites, and then calculating a regional mean from sites in the appropriate region.

Statistical Analyses

To standardize stream and river base cation concentrations and other covariates (that is, sulfate [SO_4^{2-}], chloride [Cl^-], nitrate [NO_3^-], Abs420, total annual precipitation, and mean annual temperature) between watersheds with such large differences in drainage size, discharge, and background concentrations (Table 1), all calculations were performed on data that had been transformed to z scores (Snelick and others 2005). Z-scores for annual average base cation concentrations (and covariates) were calculated separately for each watershed by subtracting the value of interest from the long-term watershed mean divided by the long-term watershed standard deviation. This centers all concentration and covariate data for each watershed on zero, and z score values represent the number of standard deviations away from the watershed mean.

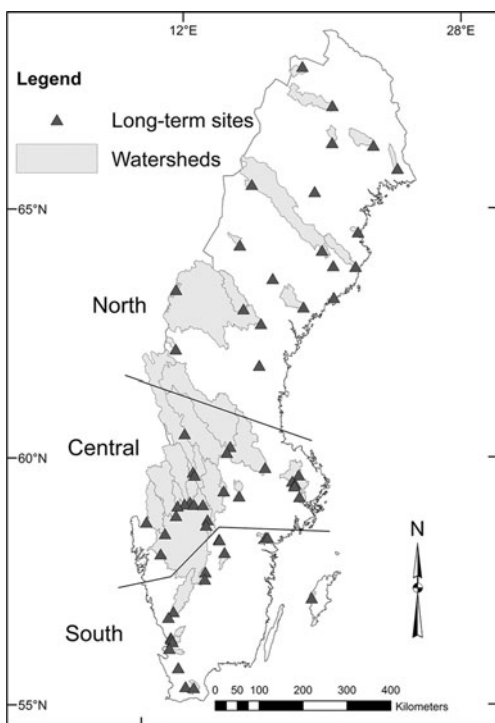


Figure 1. Locations of 60 Swedish long-term monitoring sites used in this analysis, their associated watersheds, and corresponding regions.

Table 1. Regional Medians and Ranges of Watershed Characteristics and All Measurement Data in Southern, Central, and Northern Sweden

Parameter	South (<i>n</i> = 20)		Central (<i>n</i> = 24)		North (<i>n</i> = 16)	
	Median	Range	Median	Range	Median	Range
Latitude	57°9'N	55°38'N–58°43'N	59°34'N	58°21'N–60°51'N	64°26'N	62°13'N–68°11'N
Longitude	13°35'E	12°54'E–18°17'E	14°1'E	11°49'E–17°56'E	18°40'E	12°36'E–23°59'E
Elevation (m)	85	3–193	54	5–465	245	20–614
Size (km ²)	118	1–2340	1432	2–46883	391	1–23842
Agriculture (%)	14	0–50	5	0–31	0	0–6
Lake (%)	2	0–9	6	0–18	4	0–13
Wetland (%)	9	0–37	9	2–17	16	0–43
Ca ²⁺ (mg l ⁻¹)	10.6	0.6–115.6	4.1	0.4–78.9	3.6	1.2–20.0
Mg ²⁺ (mg l ⁻¹)	2.4	0.3–13.3	1.1	0.1–11.7	0.9	0.3–1.9
K ⁺ (mg l ⁻¹)	1.3	0.2–6.5	0.8	0.1–6.3	0.5	0.2–1.9
Na ⁺ (mg l ⁻¹)	7.7	1.9–45.0	3.2	0.8–37.7	1.3	0.8–4.9
SO ₄ ²⁻ (mg l ⁻¹)	11.2	1.5–71.1	5.2	1.1–89.9	2.6	0.9–22.5
NO ₃ ⁻ (µg l ⁻¹)	662	12–6574	158	8–2512	44	7–142
Cl ⁻ (mg l ⁻¹)	11.9	2.2–42.7	4.1	0.5–55.8	1.1	0.3–5.7
Absorbance (@420 nm)	0.16	0.05–0.56	0.13	0.03–0.53	0.09	0.01–0.59
Stream water pH	6.9	4.2–8.1	6.8	4.3–7.8	6.8	4.6–7.7
Air temperature (°C)	6.8	4.3–9.1	5.2	-0.9–7.9	1.0	-4.0–4.7
Precipitation, 1990–2010 (mm)	817	564–1435	778	449–1337	761	445–1328
N deposition (kg ha ⁻¹)	7.0	0.7–44.1	3.9	0.3–14.9	1.2	0.1–7.9
Cl deposition (kg ha ⁻¹)	19.6	2.0–179.0	6.9	1.4–37.8	2.9	0.6–54.8
S deposition (kg ha ⁻¹)	6.5	1.3–40.0	4.0	0.7–17.2	1.8	0.4–6.8

The significance of long-term trends for *z* scores was assessed using the nonparametric Mann–Kendall test which is well suited to distinguish between random fluctuations and monotonic trends in nonnormally distributed datasets (Hirsch and Slack 1984). When Mann–Kendall tests indicated a significant trend, the rate of change and *y* intercepts were estimated by calculating Sen's slope robust line fit over the 21-year time series (Sen 1968) using the *mblm* package available for R (Komsta 2007). We tested for correlations between base cations concentrations in stream and river waters and all potential covariates data using the nonparametric Spearman's rank correlation. All calculations were done using R version 2.13.1 (R Development Core Team 2011).

The determinants of long-term change for calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺), and sodium (Na⁺) concentrations were explored within a hierarchical Bayesian (HB) framework (Clark 2005; Ogle and others 2012). An HB approach was taken because it allows us to estimate response parameters regionally, and it is easily structured to the nested and unbalanced sampling design associated with this large data set. The HB approach is particularly advantageous with complicated data sets because it allows the incorporation of multiple sources of variation into a

consistent model framework from which inferences can be drawn using accepted rules of probability (Clark 2005). The analysis we conducted is analogous to a non-linear mixed model, but such a model would be difficult to implement in a classical framework because data are unbalanced and collected at different scales. What is unique about our analysis is that it incorporates parameters that account for differences among regions in Sweden, as well as of multiple sources of uncertainty that are included in posterior probability distributions. Posterior probability distributions explicitly quantify uncertainty in all quantities of interest and represent an alternative to conventional *p* values by providing a direct measure of the probability of a parameter estimate which we report as a credible interval (Ellison 2004). Credible intervals are analogous to confidence intervals from traditional analyses. Such HB approaches are becoming more common and proving to be useful in a variety of ecological and biogeochemical fields (Patrick and others 2009; Cable and others 2011; Ogle and others 2012).

The HB model has three components: the data model that describes the likelihood of the observed concentration, the process model that describes base cation concentrations and related uncertainty, and the parameter model that specifies prior

distributions for all parameters (that is, a quantitative model that summarizes the information available before a study is conducted). The three components are combined to generate posterior probability distributions (Gelman 2004; Clark 2005) that lend insight in the factors driving variation in the concentrations of base cations in streams and rivers.

The data model, or the likelihood function of the observed concentration of a given base cation (bc), was specified by assuming each observation was normally distributed such that for observation i ($i = 1, 2, \dots, 1224$):

$$bc_i \sim Normal(\overline{bc}_i, \sigma^2) \quad (1)$$

where \overline{bc}_i is the mean (or expected) base cation concentration and σ^2 describes the variability or uncertainty associated with the observations.

The process model, or the model describing \overline{bc}_i from Eq. 1, was specified as a function of the concentrations of anions (estimated using SO_4^{2-} , NO_3^- , and Cl^- concentrations), and dissolved organic carbon (estimated by Abs420; Erlandsson and others 2008) measured at each monitoring station, as well as total annual precipitation in each watershed ($precip$), and the regional mean annual temperature (mat). Also included in the model was uncertainty introduced due to inter-site random variation ϵ_{site} . Thus, for a given observation of base cation concentration i made in region r in a given year:

$$\begin{aligned} \overline{bc}_i = & a_{1r} * [SO_4^{2-}]_i + a_{2r} * [NO_3^-]_i + a_{3r} * [Cl^-]_i \\ & + a_{4r} * abs_i + a_{5r} * precip_i + a_{6r} * mat_i + \epsilon_{site} \end{aligned} \quad (2)$$

where the a parameters represent the relative contributions of each covariate. The a parameters were modeled hierarchically as a function of a latent region index ($Rind$) which enabled improved parameter estimation by data pooling and borrowing strength across all regions. Where $a_{k,r}$ is the k th parameter from Eq. 2 in the r th region,

$$a_{k,r} = b_{0,k} + b_{1,k} * Rind_{1,r} + b_{2,k} * Rind_{2,r} \quad (3)$$

The latent $Rind_1$ and $Rind_2$ were modeled as independent 3×3 vectors coming from multivariate normal distributions centered on 0 but with each vector having a separate covariance matrix (Σ_1 or Σ_2 , respectively). Elements i, j of the m th covariance matrices ($m = 1$ or 2) were estimated by an exponential covariance function (Diggle and others 2002):

$$\sum_m (i,j) = \rho_m^{S_{mi,j}} \quad (4)$$

where ρ_m represents the estimated correlation coefficients and $S_{1i,j}$ and $S_{2i,j}$ represent similarity indices based on regional differences in mean annual temperature or the total annual precipitation, respectively. Similarity indices were computed as the relative differences between the mean annual temperatures or the mean annual precipitation between the i th and j th regions functions as follows:

$$S_{1i,j} = \frac{mat_i - mat_j - 2\overline{mat}}{sd_{mat}} \quad (5)$$

$$S_{2i,j} = \frac{map_i - map_j - 2\overline{map}}{sd_{map}} \quad (6)$$

where \overline{mat} and \overline{map} are the mean annual temperature and mean annual precipitation for all watersheds and sd_{mat} and sd_{map} are the standard deviations for all watersheds (Cable and others 2011).

We specified noninformative prior distributions for all terminal parameters. All b parameters were assigned noninformative, normal priors varying around a mean of 0 with a diffuse variance (that is, variance = 100000, or precision = 0.00001). The ρ parameters were assigned noninformative Beta(1, 1) priors. The uncertainty terms ϵ_{site} were specified such that each term was centered around a mean of 0 with a regionally specific standard deviation assumed to arise from a uniform distribution between 0 and 10,000. Finally, we assigned a uniform prior between 0 and 10,000 to the observation standard deviation (Gelman 2006).

The HB model was implemented in OpenBUGS version 3.1.2 (Lunn and others 2009) interfacing with the ‘‘R2WinBUGS’’ package (Sturtz and others 2005) of R version 2.13.1 (R Development Core Team 2011). The OpenBUGS code is provided in online Appendix 1. We ran three parallel MCMC (Markov chain Monte Carlo) chains for 30,000 iterations each, discarding the first 5,000 as a burn-in sample. The Brooks–Gelman–Rubin (BGR) diagnostic tool was used to evaluate convergence (Brooks and Gelman 1998).

Initial versions of the model included estimates of BC deposition, SO_4^{2-} deposition, elevation, percentage of each watershed with agricultural land cover, lake, and wetland coverage (%), regional stream flow, and a regional estimate of base cation uptake by plants. These potential covariates, however, did not improve the performance of the model in terms of the deviance information criterion (DIC) or the ability to match observed and predicted data, and consequently were not included in the final analysis.

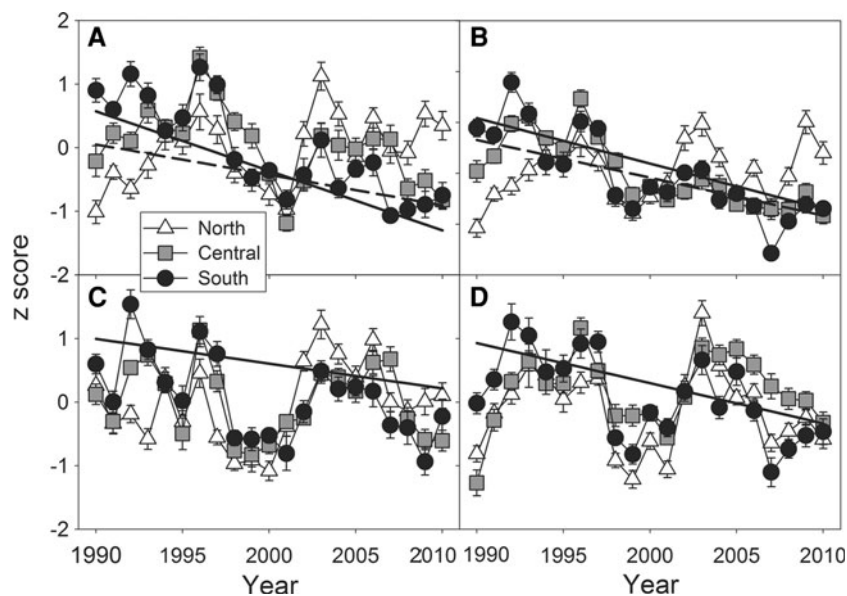


Figure 2. Regional mean z scores showing trends from 1990–2010 of base cation concentrations in stream and river waters of 60 watersheds throughout Sweden. *Trend lines* are calculated using Sen's slope robust line fit and are only shown for significant trends for **A** calcium, **B** magnesium, **C** potassium, and **D** sodium. *Solid lines* represent trends in southern Sweden, *dashed* regression lines represent central Sweden. Sen's slopes reported in Table 2. *Error bars* are standard errors ($N = 20, 24,$ and 16 for southern, central, and northern Sweden, respectively).

RESULTS

Median concentrations of nearly all solutes between 1990 and 2010 varied among streams and rivers in southern, central, and northern regions of Sweden. Anion concentrations were generally an order of magnitude greater in southern compared to northern Sweden (Table 1). Similarly, concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ decreased with increasing latitude, and were three to five times greater in the south than in the north (Table 1). In all cases, the concentrations of anions and cations in central Sweden were intermediate relative to southern and northern watersheds. In addition to the differences in water chemistry, other important regional distinctions included the median annual air temperature, the extent of agricultural presence in the watersheds, and the amount of atmospheric deposition received—all of which increased from north to south (Table 1).

Long-term trends in riverine chemistry from 1990 to 2010 also varied by region. In southern Sweden, concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ all exhibited significant declining trends (Figure 2; Table 2). In central Sweden, only Ca^{2+} and Mg^{2+} declined over this time period (Figure 2; Table 2). In contrast, there were no significant directional trends in any of the BC concentrations observed in the northern Sweden (Table 2), despite concurrent and significant declines in SO_4^{2-} , NO_3^- , and Cl^- in

this region (Figure 3; Table 2). In the southern and central regions, riverine SO_4^{2-} and NO_3^- also declined over the period of record (Figure 3; Table 2). Riverine Cl^- showed a significant declining trend in southern Sweden, but not in central Sweden (Figure 3; Table 2). Finally, Abs420 increased significantly in southern and central Sweden during this period but not in northern Sweden (Figure 3D; Table 2). In addition, inter-annual variation in BC concentrations was often correlated with other anions and environmental variables. The correlation strengths of these relationships tended to be greatest in the southern region and weakest in the northern region (Table 3).

There were also clear trends and regional differences in atmospheric deposition from 1990 to 2010 across Sweden. Principle among these was a dramatic decline in SO_4^{2-} deposition (Figure 4; Table 2), which was significant in all regions of Sweden, but greatest in the southern region where rates decreased from approximately 14 to 4 kg S ha year⁻¹ between 1990 and 2010. The greater rate of decline may be because total annual atmospheric inputs of SO_4^{2-} in the southern and central regions of Sweden were approximately four and two times greater than that observed in the north, respectively (Figure 4A). Inorganic N and Cl^- deposition were also much higher in southern than in central or northern Sweden (Figure 4C, E).

Table 2. Long-term Regional Trends (from 1990 to 2010 Except Where Indicated) of Deposition, Climatic Variables, and Stream and River Water Chemistry using Kendall's Tau Statistic to Test for the Presence of a Significant Monotonic Trend and the Sen's Slope to Estimate the Rate of Change

Element	South			Central			North		
	Kendall's tau	<i>P</i> value	Sen's slope	Kendall's tau	<i>P</i> value	Sen's slope	Kendall's tau	<i>P</i> value	Sen's slope
Deposition									
Absolute SO ₄ ²⁻	-0.91	0.00	-0.34	-0.88	0.00	-0.23	-0.62	0.00	-0.07
SO ₄ ²⁻	-0.91	0.00	-0.13	-0.88	0.00	-0.11	-0.62	0.00	-0.03
Absolute N	-0.41	0.01	-0.10	-0.29	0.07	-0.05	-0.11	0.54	-0.02
N	-0.41	0.01	-0.10	-0.29	0.07	-0.04	-0.11	0.54	-0.01
Absolute Cl	-0.03	0.88	-0.05	-0.25	0.12	-0.07	0.28	0.09	0.11
Cl	-0.03	0.88	-0.01	-0.25	0.12	-0.03	0.28	0.09	0.01
Climatic variables (1961–2010)									
Precip	0.04	0.71	0.00	0.00	1.00	0.00	0.18	0.06	0.01
MAT	0.28	0.00	0.00	0.28	0.00	0.00	0.22	0.02	0.00
Anions in stream water									
SO ₄ ²⁻	-0.75	0.00	-0.13	-0.82	0.00	-0.12	-0.49	0.00	-0.06
NO ₃ ⁻	-0.68	0.00	-0.07	-0.37	0.02	-0.04	-0.37	0.02	-0.05
Cl ⁻	-0.47	0.00	-0.08	0.08	0.65	0.01	-0.38	0.02	-0.05
Cations in stream water									
Ca ²⁺	-0.60	0.00	-0.10	-0.40	0.01	-0.04	0.30	0.06	0.04
Mg ²⁺	-0.65	0.00	-0.10	-0.64	0.00	-0.08	0.24	0.14	0.03
K ⁺	-0.37	0.02	-0.06	-0.07	0.69	-0.01	0.19	0.24	0.03
Na ⁺	-0.38	0.02	-0.06	0.01	0.98	0.01	-0.09	0.61	-0.02
DOC and pH in stream water									
Absorb. 420 nm	0.50	0.00	0.08	0.58	0.00	0.10	0.27	0.10	0.04
pH	0.53	0.00	0.07	0.41	0.01	0.05	0.35	0.03	0.07

Tests were performed on the transformed z score values for all components except for SO₄²⁻ and inorganic N deposition where tests were also performed on the absolute values. Entries in bold highlight the significant trends. Precip precipitation, MAT mean annual temperature, Absorb 420 nm absorbance at 420 nm.

In the case of N deposition, however, there was only a significant declining trend observed in southern Sweden (Table 2). Moreover, atmospheric Cl⁻ deposition did not show any significant trends from 1990 to 2010 (Table 2).

Posterior parameter means from the Bayesian model indicated important regional differences in the drivers of inter-annual variation in concentrations of Ca²⁺, Mg²⁺, K⁺, and Na⁺ (Figure 5). The predictive strength of the final models varied among cations, with the *r*² of model predictions versus observed data being 0.45, 0.55, 0.48, and 0.64 for Ca²⁺, Mg²⁺, K⁺, and Na⁺, respectively. Concentrations of SO₄²⁻ were a strong positive covariate in the models describing the inter-annual variation in Ca²⁺ and Mg²⁺ for all regions, but particularly for southern and central Sweden. In contrast, SO₄²⁻ was only weakly associated with variation in K⁺ and Na⁺, which were instead more closely linked to changes in Cl⁻. Overall, Cl⁻ was a strong positive correlate of BCs, except for Ca²⁺ in

northern Sweden. The importance of riverine NO₃⁻ as a predictor of BCs was more variable in comparison to SO₄²⁻ and Cl⁻, but was a positive correlate in all regions for K⁺. Finally, Abs420 was significant, but negatively related to Ca²⁺, Mg²⁺, and Na⁺ in southern Sweden, as well as and K⁺ in central Sweden.

The predictive strength of climate variables in the Bayesian models also varied regionally (Figure 5). Mean annual precipitation was a significant negative covariate of Ca²⁺, Mg²⁺, K⁺, and Na⁺ in northern and central Sweden. Precipitation was only significant in southern Sweden for Mg²⁺ and Na⁺. Mean annual temperature was a significant covariate of Mg²⁺, K⁺, and Na⁺ in central and northern Sweden, but was never an important variable in southern Sweden. Posterior parameter estimates of σ^2 from Eq. 1, the regional standard deviation of ϵ_{site} from Eq. 2, and the latent R_{ind} variables from Eq. 3 are reported in online Appendix 2.

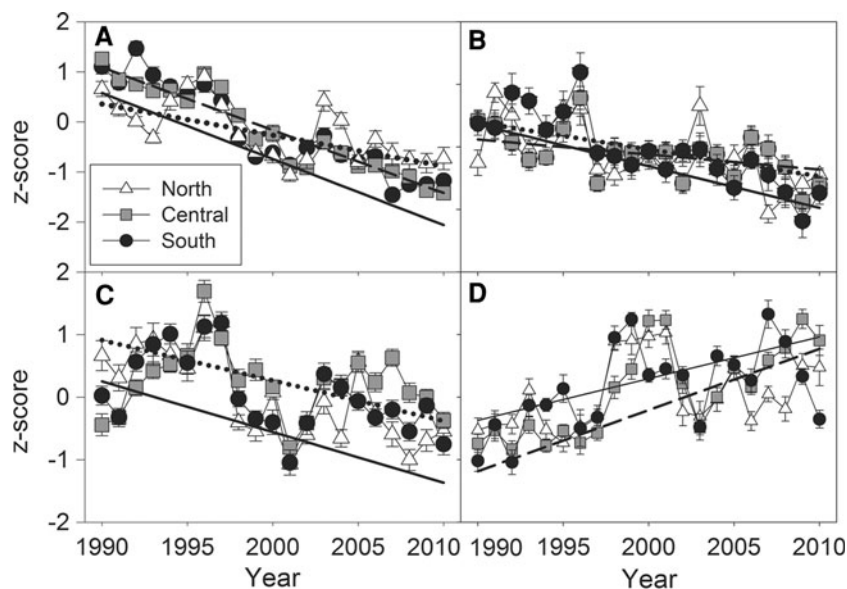


Figure 3. Trends of the regional mean z scores of major anions from 1990–2010 in 60 Swedish streams and rivers for **A** SO_4^{2-} , **B** NO_3^- , **C** Cl^- , and **D** absorbance of filtered samples at wavelength 420 nm (a proxy for the concentration of dissolved organic carbon). *Trend lines* are Sen's slope robust line fit. Sen's slopes reported in Table 2. *Solid lines* represent trends in southern Sweden, *dashed* regression lines represent central Sweden, and *dotted lines* represent northern Sweden. *Error bars* are standard errors ($N = 20, 24,$ and 16 for southern, central, and northern Sweden, respectively).

DISCUSSION

Results from this study highlight important regional differences in the patterns and drivers of BC concentrations in streams and rivers across Sweden. Overall, our analysis indicated that concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in southern, and Ca^{2+} and Mg^{2+} in central Sweden have declined significantly from their high points in the early 1990s to present day values (Figure 2). Because the transport of BCs into stream waters adheres to principles of physical chemistry, such as the requirement to maintain charge neutrality (Stumm and Morgan 1996), we can expect changes in riverine BCs to be closely coupled to variation in strong acid anions (Kirchner and Lydersen 1995). This expectation is supported in southern Sweden, and for the most part in central Sweden, where significant declines in concentrations of strong acid anions were concurrent to, and highly correlated with, observed declines in Ca^{2+} and Mg^{2+} .

Declining concentrations of Ca^{2+} , Mg^{2+} , and K^+ in southern and Ca^{2+} and Mg^{2+} in central Sweden are consistent with recovery from atmospheric acid deposition. Total acid deposition has decreased across Sweden, as it has for the rest of Europe and North America (Dentener and others 2006), but decreases of SO_4^{2-} have been the most dramatic in the southern part of the country (Figure 4). The observation that the sum of the long-term median

concentrations of BCs is roughly equivalent to the sum of the strong acid anions in southern and central regions suggests chemical exchanges between catchment soils and porewaters, which consequently affect stream and river concentrations, are closely matched over the time scale of this study. This observation is consistent with the early stage of a recovery from soil acidification (Galloway and others 1983; Evans and others 2001), as reduced concentrations of mobile acid anions lead to decreased leaching of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ from soils. Longer-term recovery requires that as the relative importance of SO_4^{2-} diminishes, decreased BC leaching will lead to increases in the base saturation of soils as Ca^{2+} , Mg^{2+} , K^+ , or Na^+ replace H^+ and Al^{3+} anions on exchange sites in soils (Galloway and others 1983). Consequently, BC leaching into stream waters will reach a new steady state in equilibrium with natural anions such as Cl^- and HCO_3^- , primarily sourced from sea salt deposition in equilibrium with respired CO_2 and as a byproduct from mineral weathering (Wilson 2004; Klaminder and others. 2011). Concentrations of Na^+ may be most closely associated with variations in sea salt deposition. Although not necessary to produce the observed pattern of declining BCs in southern Sweden, data from the Swedish Nation Forest Inventory suggest the base saturation of soils in southern and central

Table 3. Table of Spearman Rank Correlations Between Regional Stream Water Concentrations of Base Cations, Anions, Absorbance at 420 nm (abs420; a Proxy for the Concentration of Dissolved Organic Carbon), and Mean Annual Precipitation (precip.)

	[Ca ²⁺]	[Mg ²⁺]	[K ⁺]	[Na ⁺]	[SO ₄ ²⁻]	Abs420	[Cl ⁻]	[NO ₃ ⁻]
Northern Sweden (<i>n</i> = 601)								
[Ca ²⁺]	–							
[Mg ²⁺]	0.85	–						
[K ⁺]	0.49	0.44	–					
[Na ⁺]	0.52	0.55	0.47	–				
[SO ₄ ²⁻]	0.35	0.34	0.29	0.33	–			
Abs420	–0.27	–0.25	–0.34	–0.33	–0.50	–		
[Cl ⁻]	0.21	0.23	0.22	0.66	0.43	–0.27	–	
[NO ₃ ⁻]	0.17	0.23	0.15	0.33	0.32	–0.23	0.23	–
Precip.	–0.35	–0.30	–0.37	–0.32	–0.25	0.45	–0.32	–0.06
Central Sweden (<i>n</i> = 501)								
[Ca ²⁺]	–							
[Mg ²⁺]	0.71	–						
[K ⁺]	0.34	0.38	–					
[Na ⁺]	0.49	0.40	0.54	–				
[SO ₄ ²⁻]	0.46	0.67	0.32	0.18	–			
Abs420	–0.41	–0.55	–0.41	–0.27	–0.72	–		
[Cl ⁻]	0.53	0.47	0.37	0.75	0.31	–0.34	–	
[NO ₃ ⁻]	0.14	0.28	0.20	0.13	0.35	–0.14	0.19	–
Precip.	–0.29	–0.33	–0.33	–0.35	–0.27	0.43	–0.35	–0.01
Southern Sweden (<i>n</i> = 406)								
[Ca ²⁺]	–							
[Mg ²⁺]	0.80	–						
[K ⁺]	0.59	0.59	–					
[Na ⁺]	0.61	0.77	0.56	–				
[SO ₄ ²⁻]	0.75	0.84	0.56	0.59	–			
Abs420	–0.64	–0.76	–0.49	–0.63	–0.70	–		
[Cl ⁻]	0.59	0.66	0.54	0.80	0.63	–0.55	–	
[NO ₃ ⁻]	0.53	0.49	0.47	0.33	0.55	–0.37	0.36	–
Precip.	–0.34	–0.44	–0.31	–0.47	–0.34	0.48	–0.47	–0.14

Entries in bold indicate a significant correlation. *n* = 1,508.

Sweden has remained unchanged or may have slightly increased from 1983 to 2002 (Stendahl 2007), further suggesting a nascent recovery may be underway. The widespread recovery of riverine concentrations of Ca²⁺, Mg²⁺, and K⁺ from acid deposition in Sweden is noteworthy, given that many areas have not recovered as expected following the decline of S deposition (Stoddard and others 1999; Fölster and Wilander 2002; Martinson and others 2005; Sullivan and others 2006).

It is possible that concurrent declines in concentrations of Ca²⁺, Mg²⁺, and K⁺ and anions in southern Sweden could be linked to a decrease in the hydrologic forcing and subsequent transport of mobile solutes from soil porewaters into streams (Lutz and others 2012). Sweden, however, has not had significant long-term changes in total annual

discharge, based on an analysis of regional means from 1990–2010 (online Appendix 3). Neither has southern or central Sweden had significant long-term trends in precipitation (Table 2). Thus, although the inter-annual variation of precipitation emerged as an important covariate for some of the water chemistry patterns observed in this study, we find it unlikely that hydrologic patterns were responsible for the directional trends in riverine BCs and anions presented here.

Unlike patterns observed in southern and central Sweden, we did not find significant long-term directional changes (increases or decreases) in concentrations of Ca²⁺, Mg²⁺, K⁺, or Na⁺ in the north, which represented the largest area of the three regions considered here. We can infer from the necessity of waters to maintain charge

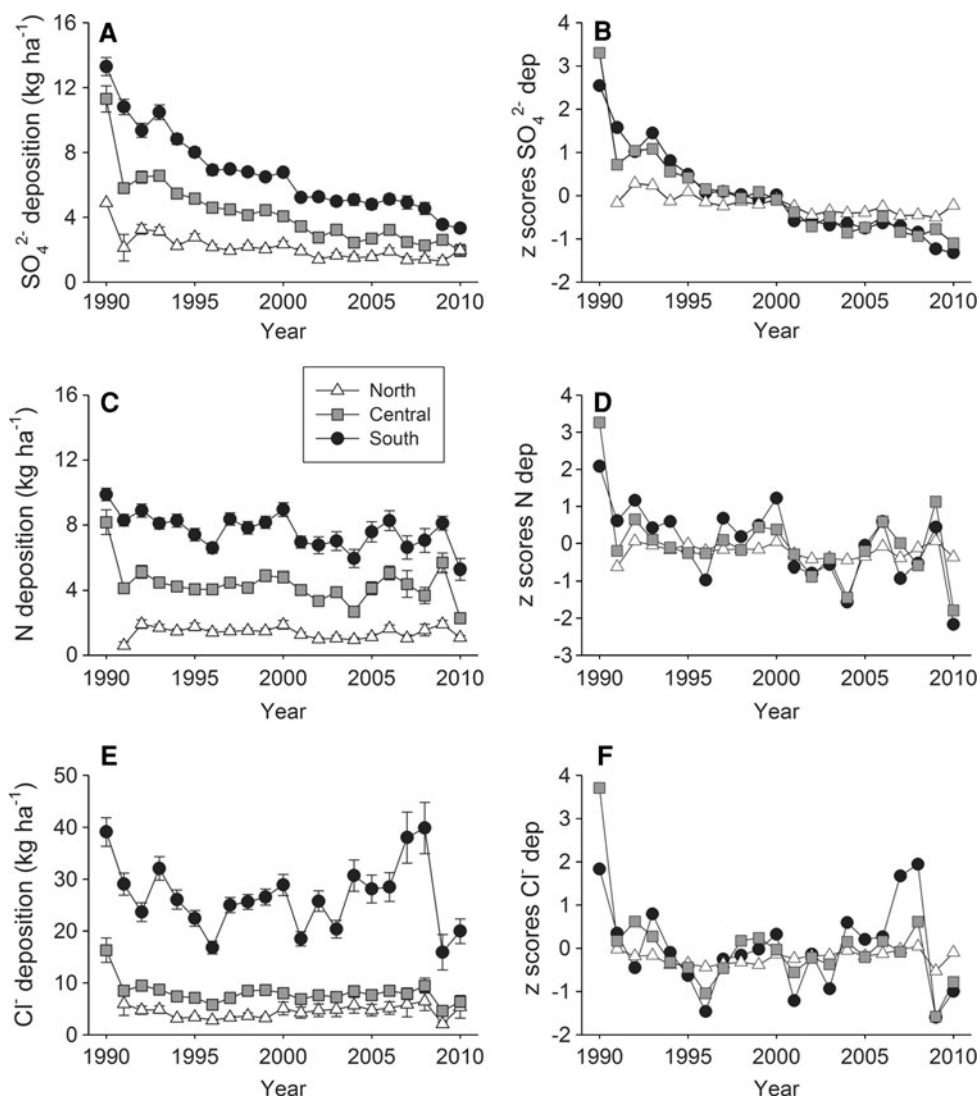


Figure 4. Regional means of **A** total atmospheric SO₄²⁻ deposition, **B** z score of SO₄²⁻ deposition, **C** the total atmospheric inorganic N deposition, **D** trend of N deposition using z scores, **E** total Cl⁻ deposition, and **F** trend of Cl⁻ deposition using z scores. For clarity, standard error bars included only for absolute deposition. In some cases error bars are smaller than the symbol.

neutrality (Stumm and Morgan 1996) that unchanged concentrations of Ca²⁺, Mg²⁺, K⁺, and Na⁺, despite concurrently declining concentrations of SO₄²⁻, NO₃⁻, and Cl⁻, must be matched by and become more sensitive to increases in other negatively charged ions such as HCO₃⁻ or organic acids. In this study we do not have data on HCO₃⁻ in Swedish stream waters, but an increase in HCO₃⁻ is consistent with the observed increasing trend in pH from 1990 to 2010 (Table 2). It is possible organic acidity has increased also, despite the increase in pH. Increasing trends of organic acidity since 1990 have been suggested as being common throughout Sweden and may be sufficiently high in some areas to counteract increases in lake water pH due to declines in acid deposition (Erlandsson and others 2011). Given the putative links between recovery from acid deposition and trends in water chemistry described above, the lack of significant directional

change in BCs in northern Sweden is not surprising. Historically, rates of deposition in northern Sweden have been comparatively low. For example, mean S deposition has been at or below the suggested critical load for northern Sweden of 3 kg S ha⁻¹ y⁻¹ (Sverdrup and Warfvinge 1995) for 20 of the last 21 years (Figure 4). Moreover, N has been well below the suggested critical load of 10–15 kg N ha⁻¹ y⁻¹, as well as the more strict critical load suggested to be 6 kg N ha⁻¹ y⁻¹ (Nordin and others 2005). Given this history of low acid deposition, the patterns of Ca²⁺, Mg²⁺, K⁺, and Na⁺ concentrations in northern Sweden were less closely linked to trends of atmospheric inputs and instead were more strongly associated with variation in climate variables.

Although there were no long-term directional changes in concentrations of Ca²⁺, Mg²⁺, K⁺, and Na⁺ in northern Sweden, there were large

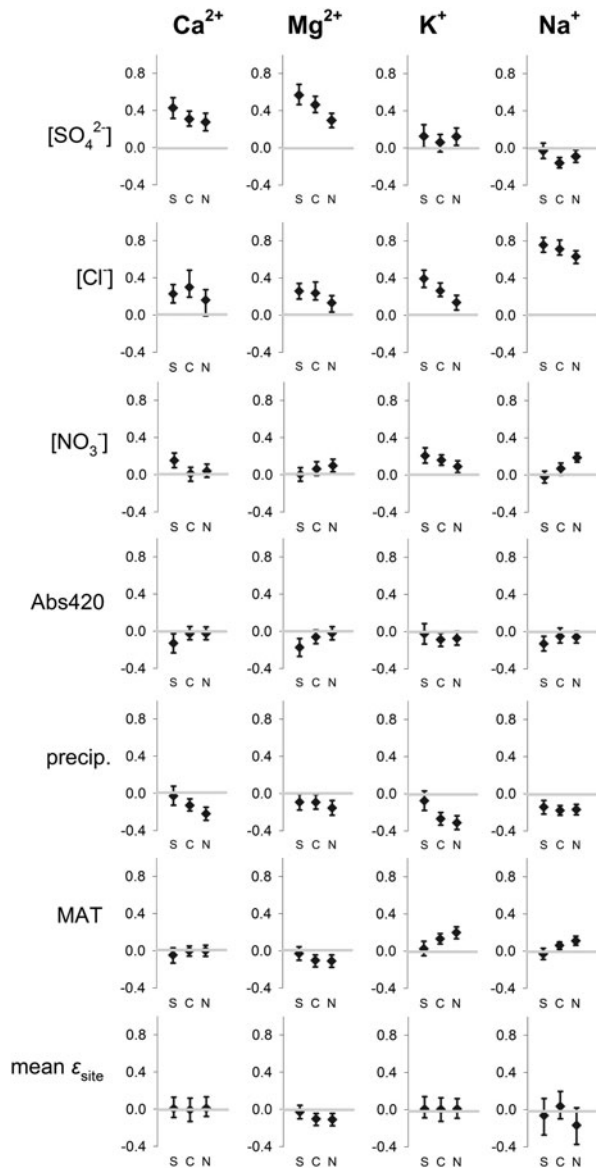


Figure 5. Selected posterior parameter means and 95% credible intervals for each region of Sweden. If credible intervals overlap, parameters are not significantly different from each other. S, C, and N denote southern, central, and northern regions of Sweden. Abbreviations are the same as those listed in Table 2. Mean ϵ_{site} represents the regional means of the ϵ_{site} from Eq. 2.

inter-annual variations throughout the period of record (Figure 2), with multi-year phases of both high and low concentrations observed for each solute. Results from our hierarchical Bayesian models indicated that in general, mean annual temperature, and mean annual precipitation assumed a larger role as drivers of the inter-annual dynamics of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in northern than in southern and central Sweden. In fact, neither mean annual temperature nor

precipitation were significant contributors to inter-annual patterns in southern Sweden, except for variation in Na^+ in the south, in which precipitation was a significant contributor.

It is well known that temperature can strongly influence all major biogeochemical processes. Relevant to this study, variation in temperature may affect the local availability of Ca^{2+} , Mg^{2+} , and K^+ in soils and surface waters indirectly through a stimulation of plant growth and increased rates of uptake (McMahon and others 2010). This is germane to Ca^{2+} , Mg^{2+} , and K^+ in Swedish surface waters as 70% of Sweden is covered by forests or forest plantations (Skogsstyrelsen 2009). Moreover, standing tree volumes have increased by 21, 35, and 19% from 1987 to 2010 in southern, central, and northern Sweden, respectively (NFI 2010), and therefore represent a potentially important and increasing sink for Ca^{2+} , Mg^{2+} , and K^+ in the landscape (Jobbagy and Jackson 2004; Johnson 2006). However, this mechanism should give rise to a negative statistical relationship between temperature and Ca^{2+} , Mg^{2+} , and K^+ concentrations in streams and rivers, which was only observed in our model of Mg^{2+} . Instead, increases in temperature could positively affect Ca^{2+} , Mg^{2+} , and K^+ by stimulating decomposition (Kirschbaum 1995; Knorr and others 2005) or weathering processes (Klaminder and others 2011), thereby resulting in greater BC availability in soils. This may be particularly important in colder areas, such as northern Sweden, which are most sensitive to changes in temperature (Hartley and Ineson 2008).

Modeling results also suggested inter-annual variation in BC dynamics was more strongly related to mean annual precipitation in northern when compared to southern Sweden. Negative model coefficients for mean annual precipitation, indicating that BC concentrations went down with increasing precipitation, can be explained by dilution—wet years being linked to lower BC concentrations. In addition to total rainfall, which clearly influences stream flow, the timing of precipitation events can have particularly strong impacts on soil and surface water biogeochemistry, and may have contributed to the observed inter-annual variability in water chemistry. During prolonged dry periods, lower water tables expose soil horizons that are normally saturated to oxic conditions. In oxic soils, reduced sulfides can be re-oxidized (Eimers and Dillon 2002; Mayer and others 2010), and thereby represent a large source of SO_4^{2-} in soil and stream waters during subsequent re-wetting of these deeper soil horizons. This mechanism may help explain short-term episodes and inter-annual

variability in the concentration of SO_4^{2-} in stream and river waters (Mörth and others 1999; Laudon and Hemond 2002; Laudon 2008). In fact, in our analysis, the driest years in the record for northern Sweden (1996 and 2003; online Appendix 4), were associated with the highest observed concentrations of riverine SO_4^{2-} . Given there were no corresponding peaks in S deposition, the transient increase in SO_4^{2-} concentrations were presumably from re-oxidation of reduced sulfides during the dry period and export during a re-wetting period (Mayer and others 2010). Consistent with the idea that SO_4^{2-} is an important driver of BC dynamics, concentrations of all BCs in northern Swedish streams and rivers rose dramatically in 1996, and were particularly high in 2003.

Finally, our data also indicate there has been a general decline in the concentrations of NO_3^- throughout Swedish stream waters (Figure 3B), but, other than for K^+ , this does not appear to be a strong driver of long-term BC trends or inter-annual dynamics. Although this region-wide decline is relevant to our models describing the drivers of BC dynamics, it is more broadly significant because N is a strongly limiting nutrient across the Swedish landscape (Binkley and Högberg 1997), and because NO_3^- loading remains of concern from the standpoint of eutrophication in Baltic ecosystems (Futter and others 2010). Our observation of NO_3^- decline is noteworthy because such trends have not been previously documented across such a large spatial extent, for watersheds that span a broad range in size, or with such different land-use patterns and histories. Low order streams in New Hampshire (Aber and others 2002; Bernhardt and others 2005; Bernal and others 2012) and watersheds with aggrading forests (Oulehle and others 2008) are among the few studies that have reported similar declines in NO_3^- concentration. In some instances, decreases in the stream NO_3^- have been related to environmental variables such as reduced atmospheric N deposition (Kothawala and others 2011). In other cases, however, the declining NO_3^- concentrations have occurred despite stable or rising N deposition (Bernhardt and others 2005) and cannot be satisfactorily explained with current ecosystem models (Aber and others 2002). Instead, NO_3^- declines have been linked to the history of forest management (for example, Bernal and others 2012). In Sweden, the importance of different natural and anthropogenic drivers are likely to vary regionally, with long-term trends in atmospheric deposition and agricultural fertilizer use potentially important to NO_3^- declines observed in the south. In northern Sweden, more subtle declines observed

in the absence of either historically high N-deposition rates, or widespread agricultural activity, point to changes in climate, hydrology, and forest growth and management as potential-driving mechanisms. Resolving the relative importance of these mechanisms merits further study.

In conclusion, concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in streams and rivers have declined significantly in southern Sweden but have shown no directional change in the north. The drivers behind these biogeochemical patterns differ regionally. Although model results indicate that dissolved anions are key drivers of BCs across all regions, in southern and central Sweden, these interactions are primarily governed by trends in atmospheric deposition, and are therefore directional in nature. In northern Sweden, where ecosystems have been comparatively less affected by acid deposition (Laudon and Bishop 2002), the fundamental connections between anions and BCs appear mediated through climate drivers, potentially through changes in soil properties that influence inter-annual changes in SO_4^{2-} production and release. It is clearly important to understand the strength of climate influences on the inter-annual variability of soil and water biogeochemistry. If extreme weather events continue to become more common as hypothesized (IPCC 2007), hydrologic variability and the frequency of dry years, both of which influence the delivery of SO_4^{2-} to surface waters and the associated release of re-oxidized sulfides (Mayer and others 2010), may emerge as an increasingly important control on peak concentrations of base cations in surface waters.

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