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Modeling preindustrial ANC and pH during the spring flood in northern Sweden

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Abstract. The natural preindustrial ANC and pH decline associated with 22 melt events from 11 streams during spring flood of 1997 and 1998 in Northern Sweden have been assessed using the Boreal Dilution Model (BDM). The results show that the spring flood pH decline of 0.5 to 2.5 pH units in the streams was largely caused by natural processes. The most important driving factors influencing pH were TOC increase in combination with ANC dilution. The study also demonstrates that pH in some streams can decline to pH values close to 4.5 as a result of natural processes alone. In general the anthropogenic component of the pH decline was between 0.1 and 0.3 pH units superimposed on the natural pH decline. Furthermore, the anthropogenic contribution to ANC and pH decline generally followed the gradient of anthropogenic S deposition in the region. The sites with the greatest inferred anthropogenic influence are also those for which the assumptions used in the BDM were most sensitive. Nevertheless, the results from this study suggest that the regional impact of anthropogenic acid deposition on the ANC and pH in northern Sweden is currently limited.

Introduction

The episodic decline of ANC (Acid Neutralization Capacity) and pH during hydrological events is an ubiquitous phenomenon in forested boreal watersheds (Wigington et al. 1992; Davis et al. 1992) which can be driven by both natural and anthropogenic mechanisms (Campbell et al. 1992; Wigington et al. 1996; Laudon & Bishop 1999). Rapid decline in pH and associated increase in toxic aluminum species can cause significant biological stress in acid sensitive catchments (Baker et al. 1996). It is generally thought that the pH decline in northern regions is due to acidic deposition. This belief has been an important factor in the decision to spend close to one billion Swedish crowns (>120 million US $) during the last decade to lime surface waters in northern Sweden in order to protect aquatic biodiversity. This investment, however, was made without an appropriate tool to separate the anthropogenic contribution to episodic acidity increases from natural mechanisms that increase acidity during hydrological episodes.

Despite the potential threat to biodiversity in northern Sweden (from both acidification as well as liming of naturally acid surface waters since tolerance against natural acid episodes is a competitive advantage for certain biota) and the large government subsidy for spring flood liming, surprisingly few episodic acidification studies have been conducted in the region. The isolated studies that have been carried out demonstrate that both anthropogenic (Jacks et al. 1986; Ahlström 1999) and natural factors (Bishop 1991; Jansson & Ivarsson 1994) can be the main source of the observed pH and ANC decrease during spring flood and rain events. The previous studies do not allow for a regional assessment of the impact of acid deposition on spring flood in northern Sweden because they are too few, too geographically circumscribed and lack a systematically testable evaluation methodology. The earlier studies do, however, demonstrate the need for both a more detailed understanding of the driving mechanisms of episodic acidification and a more regional overview of the problem in northern Sweden on which to base the ongoing investment in the liming.

In the last decade, much work has been carried out, particularly in North America, to identify and qualitatively estimate the importance of different mechanisms driving the ANC decline during rain storms and snow melt events (Molot et al. 1989; Campbell et al. 1992; Wigington et al. 1996). Several studies have also been conducted to predict the minimum episode ANC using empirical or semi-mechanistic approaches (Eshleman et al. 1995; Davies et al. 1999). Much less attention, however, has been paid to the separation and quantification of the anthropogenic and natural components of pH and ANC decline during episodes. For that reason, the Boreal Dilution Model (BDM) was designed to separate and quantify the natural ANC and pH decline from the anthropogenic decline during contemporary hydrological events. The model was recently presented and tested on one stream in the boreal region of northern Sweden (Bishop et al. 2000).

The BDM has been developed for use by national and regional environmental authorities in planning future liming activities in areas with episodic ANC and pH decline. The model and the stream sampling strategy on which it is based are constructed so that they can be used in environmental monitoring programs where it has previously been difficult to justify special sampling programs to evaluate hydrochemical variation during episodes despite their importance for aquatic biodiversity. The BDM is applied in this paper to 22 spring flood episodes on 11 streams during the 1997 and 1998 snow melt in northern Sweden. The data on these episodes was collected within the Episode Project financed by the Swedish EPA. The purpose of this paper is to provide a regional overview of the anthropogenic impact on stream water acidity during hydrological events in relation to the natural spring flood pH decline.

Study sites and methods

A detailed description of the sampling and analytical methodologies, pH modeling and characteristics of the field sites including anthropogenic acid deposition and geology was presented by Laudon et al. (2000).

The sampling locations were arranged along two east-west transects in northern Sweden (one more southerly, and one more northerly). Two of the streams in each transect were located in the mountains, two in the inland and two on the Baltic sea coast. (Data from Nyckelmyrbäcken was excluded since baseflow conditions were not observed.) Spring flood data for 1997 and 1998 from the remaining eleven streams are used in this paper (Figure 1).

The sampling program was based on weekly sampling of baseflow prior to the onset of spring flood and then daily sampling until the discharge returned to baseflow levels. All water samples were collected in acid washed 250 ml polyethylene bottles. The samples were stored cold and in the dark until analysis of major inorganic anions, cations, aluminum speciation, ambient pH (pH_{amb}), pCO_2 equilibrated pH ($pH_{aerated}$, pCO_2 380 ppm; Laudon et al. 2000) and total organic carbon (TOC). The TOC is analogous to dissolved organic carbon (DOC) in these streams during spring flood since 95% of TOC passes a 0.45 μm filter (H. Laudon, Unpublished data).

The spring flood episodes analyzed in this paper are separated into four phases in order to evaluate the sensitivity to anthropogenic acidification at different stages during the spring flood. These phases are;

> The *baseflow phase*, defined here as the period prior to the onset of the melt season. In most of the studied episodes the base flow phase is an average of two to four samples. In three of the 22 episodes, (Stopelebäcken 1997; Rukkebäcken 1997; Kälsbäcken 1997) the baseflow phase consists of only one sample. The baseflow chemistry is used as a ‘benchmark’ for natural conditions in the BDM.
>
> The *initiation phase* is the period between base flow and peak flow. The number of samples in this phase ranges between two and 20.
>
> The *peak flow phase* is an average of the three consecutive samples that were most acid.

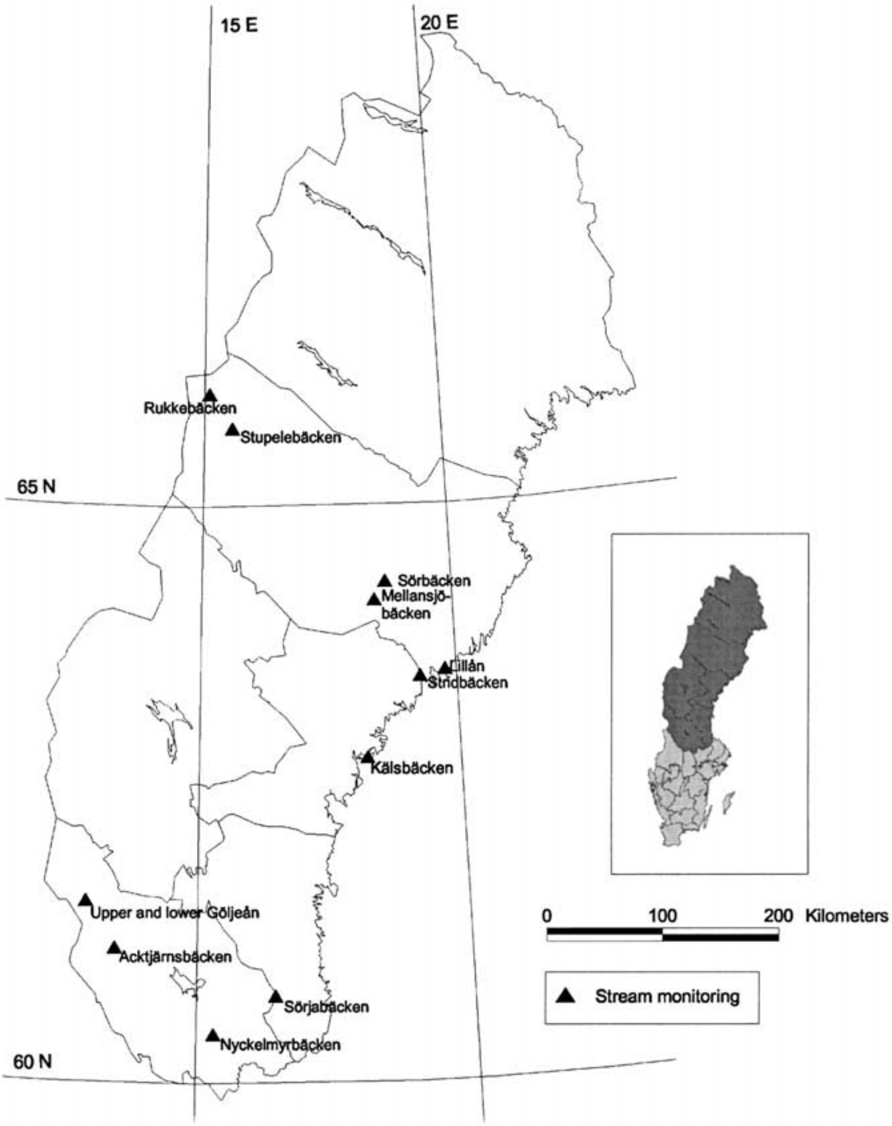

Figure 1. Sampling locations on a map of Sweden.

The *recovery phase* is defined as the period following peak flow. In most of the episodes this phase consists of two to five samples. In five of the spring flood events this period is missing since sampling was terminated before the recovery phase began.

Boreal Dilution Model (BDM)

The Boreal Dilution Model (BDM), Bishop et al. (2000), quantifies the natural pH (and ANC) in water in equilibrium with pCO_2 in air during hydrological events in catchments suffering from episodic acidification. The BDM is an extension of the ADM (ANC Dilution Model) which was developed to separate and quantify the driving mechanisms of ANC decline during hydrological events (Laudon & Bishop 1999; Laudon et al. 1999). Since aquatic organisms are primarily affected by changes in pH (and pH dependent changes in Al-speciation) the BDM was developed to provide a means of assessing the effect of anthropogenic deposition impact on the aquatic biodiversity from that of the natural pH decline during hydrological events.

Since pH is closely related to ANC, and because ANC is more robust from a modeling perspective than pH, the BDM is based on the charge balance definition of ANC (e.g. Munson & Gherini 1993). According to the electroneutrality principle, the equivalent sum of cations must equal the sum of anions (Stumm & Morgan 1981). ANC can therefore be calculated as the difference between the weak bases and weak acid anions (Eq. 1) or as the difference between strong bases and strong acid anions (Eq. 2).

$$\mathrm{ANC} = [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] + [\mathrm{RCOO^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}] - [\mathrm{Al^{n+}}] \quad (1)$$

$$\mathrm{ANC} = [\mathrm{BC}] - [\mathrm{Cl^-}] - [\mathrm{SO_4^{2-}}] - [\mathrm{NO_3^-}] = \mathrm{BC} - \mathrm{ANSA} - \mathrm{Cl^-} \quad (2)$$

where $RCOO^-$ stands for the dissociated organic acids, Al^{n+} is the equivalent sum of positively charged monomeric inorganic aluminum, BC is the sum of base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and ANSA is the anthropogenically significant anions (SO_4^{2-} and NO_3^-). All concentrations are in μeq L^{-1}.

One of the most important natural factors influencing the episodic decline in ANC is the dilution of baseflow ANC by dilute rain or snow melt water. Since the natural dilution of ANC is dependent on how much pristine, but weakly buffered, snowmelt water is contributed to the stream at different times, a method for quantifying the dilution using a dilution index (DI) has been used. In the calculation of DI and later in the modeling of natural levels of ANC and pH during episodes, the base flow chemistry is used as a 'benchmark' for natural conditions. The DI at different sampling occasions (t) is calculated using a tracer to quantify the natural dilution. In this work, base cations have been used for this quantification (Eq. 3).

$$\mathrm{DI_{(t)}} = [\mathrm{BC}]_{(t)}/[\mathrm{BC}]_{(\mathrm{base})} \quad (3)$$

Without anthropogenic deposition, and with natural levels of SO_4^{2-} and NO_3^-, the dilution of these solutes is assumed to behave similarly to the variation in the dilution tracer. By forcing the anthropogenic components of SO_4^{2-} and NO_3^-, together with BC, to dilute as DI, the natural preindustrial ANC (ANC_{preind}) of the stream at different times (t) during the high flow event is calculated (in μeq L^{-1}) (Eq. 4). Although Cl^- can contribute to the ANC decline during spring flood (Laudon & Bishop 1999), the source of Cl^- is assumed to be exclusively from natural origin which can cause extensive sea-salt induced episodes in coastal regions (Heath et al. 1992). Chloride, therefore, is not forced to dilute as the dilution index. Failure to exclude Cl^- from diluting as the DI would result in the natural Cl^- component of episodic ANC decline being incorrectly attributed to anthropogenic sources.

$$ANC_{(preind,t)} = (BC_{(base)} - ANSA_{(base)}) * DI_{(t)} - [Cl^-]_{(t)} \tag{4}$$

By combining equation 1 and 4, the preindustrial air-equilibrated pH (pH_{preind}) can be calculated from the ANC_{preind} in combination with an organic acid model.

$$\begin{aligned} pH_{(preind,t)} = {} & -\log([HCO_3^-]_{(t)} + [CO_3^{2-}]_{(t)} + [RCOO^-]_{(t)} + \\ & [OH^-]_{(t)} - [Al^{n+}]_{(t)} - ANC_{(preind,t)}) \end{aligned} \tag{5}$$

$RCOO^-$ is calculated with a calibrated pH dependent pKa model described in detail in Laudon et al. (2000). Since several of the components in Eq. 5 are pH dependent, the pH_{preind} in solution must be solved for iteratively.

The difference between the modeled observed ANC_{obs} (Eq. 2) and the predicted preindustrial ANC_{preind} (Eq. 4) is interpreted as the anthropogenic influence on buffering capacity (ΔANC_{poll}; Eq. 6). Similarly, the difference between the modeled aired pH_{obs} during the episode and the preindustrial pH_{preind} is the anthropogenic influence on pH (ΔpH_{poll}; Eq. 7).

$$\Delta ANC_{(poll,t)} = ANC_{(preind,t)} - ANC_{(obs,t)} \tag{6}$$

$$\Delta pH_{(poll,t)} = pH_{(preind,t)} - pH_{(obs,t)} \tag{7}$$

The BDM is based on three critical model assumptions that are important for the model result. These assumptions are;

1. a ‘dilution tracer’ can be used for modeling the natural dilution of ANC during hydrological events, in this case BC are used,
2. the ANC and pH of the baseflow have not been altered by anthropogenic acidification in the region, or can be adjusted to the natural level,
3. the amount and character of TOC or DOC has not changed due to anthropogenic acidification or forestry practice.

Results

The onset of spring flood during 1997 and 1998 came at the end of April for the coastal catchments and progressively later for the inland and mountains sites. In the southern transect, the spring flood started approximately half to one and a half months earlier. The spring flood marked the end of four to five months of full snow cover in the northern transect while the winter in the southern transect was shorter at most sites. All 22 spring flood episodes started from baseflow conditions.

During the observed spring floods, both pH and ANC declined as soon as the discharge began to increase. Except for the 1997 spring flood in Stridbäcken, the most acid condition occurred at maximum discharge (Laudon et al. 2000). At Stridbäcken, minimum pH occurred at a smaller flow peak at the end of the snow melt.

The pH decline in the 22 spring flood events ranged from 0.5 to close to 2.5 pH units. According to the BDM, 13 of the episodes had an average ΔpH_{poll} during the peakflow phase that was larger than 0.1 pH units (which is twice the measurement error of standard pH electrode measurements under perfect conditions; Davidsson & Woof 1985) (Figure 2; Table 1). In general the streams in the southern transect showed a larger anthropogenic contribution compared to the streams in the northern transect. The largest anthropogenic component during spring flood was most commonly found during peak flood, although a few sites experienced their largest anthropogenic influence during the recovery phase. In most streams there was typically a larger anthropogenic component during the 1998 spring flood compared to the previous year. This was especially noticeable in the coastal and inland areas of the northern transect and in the coastal area of the southern transect (Table 1).

Discussion

The pattern of anthropogenic ANC and pH decline followed the differences in the anthropogenic SO_4^{2-} deposition pattern over northern Sweden well. The highest ΔpH_{poll} and ΔANC_{poll} occurred along the east coast and in the southern part of the study region where deposition levels during the 1997–98 winter were approximately 50 to 75% higher than during the previous winter in the coastal areas (Hallgren-Larsson 1999). The major exceptions to this spatial pattern are the coastal Sörjabäcken site and the two alpine Göljeån sites. The lack of consistency in Sörjabäcken is probably due to the small amount of snow in the catchment prior to the spring flood which had a relatively small anthropogenic signal. The two Göljeån sites which

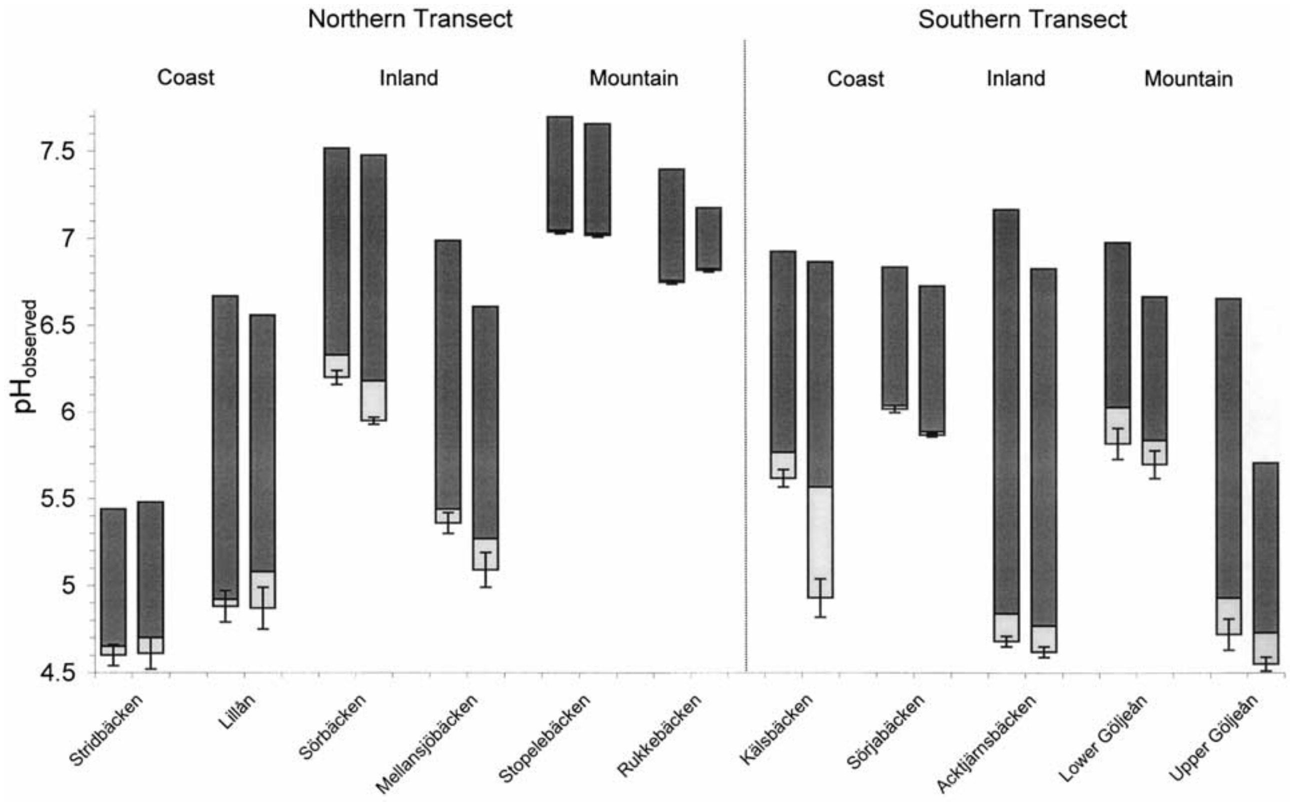

Figure 2. Variation in baseflow/peakflow pH. The first column for each stream is the 1997 spring flood, the second column is the 1998 flood. The dark grey area is the natural pH decline. The light grey area is the anthropogenic pH decline (ΔpH_{poll}). The error bars denote the standard deviation in the ΔpH_{poll} of the peak flow phase.

Table 1. Anthropogenically driven pH (ΔpH_{poll}) and ANC (ΔANC_{poll}) decline in the 11 sites during spring flood 1997 and 1998. The northern transect (NT) is located in the county of Västerbotten and the southern transect (ST) traverses the counties of Dalarna, Gävleborg and Västernorrland. The figure in parentheses is the standard deviation. The '†' indicates that no sampling of the recovery phase was carried out

Stream	Year	Location	Initiation phase		Peak flow phase		Recovery phase	
			ΔANC_{poll}	ΔpH_{poll}	ΔANC_{poll}	ΔpH_{poll}	ΔANC_{poll}	ΔpH_{poll}
Stridbäcken	1997	NT/coast	4.2 (4.1)	0.06 (0.06)	4.8 (1.6)	0.07 (0.02)	8.2 (2.3)	0.13 (0.05)
Stridbäcken	1998	NT/coast	3.7 (7.4)	0.05 (0.11)	10.9 (3.6)	0.16 (0.06)	4.3 (6.0)	0.06 (0.08)
Lillån	1997	NT/coast	0.1 (0.2)	0.00 (0.00)	1.5 (1.6)	0.02 (0.03)	4.2 (5.9)	0.06 (0.08)
Lillån	1998	NT/coast	19.7 (10.7)	0.22 (0.12)	12.8 (0.8)	0.16 (0.02)	8.6 (6.8)	0.11 (0.08)
Sörbäcken	1997	NT/inland	16.1 (1.5)	0.14 (0.03)	8.5 (2.4)	0.11 (0.02)	11.1 (1.0)	0.15 (0.04)
Sörbäcken	1998	NT/inland	18.7 (5.1)	0.17 (0.08)	21.1 (0.8)	0.28 (0.02)	17.5 (2.9)	0.22 (0.04)
Mellansjöbäcken	1997	NT/inland	2.6 (1.8)	0.03 (0.02)	2.8 (1.7)	0.04 (0.03)	9.1 (0.2)	0.16 (0.01)
Mellansjöbäcken	1998	NT/inland	5.8 (5.0)	0.09 (0.09)	15.2 (5.1)	0.27 (0.08)	12.5 (5.5)	0.22 (0.09)
Stopelebäcken	1997	NT/mountains	1.8 (1.5)	0.01 (0.01)	1.8 (1.6)	0.01 (0.01)	2.3 (1.9)	0.01 (0.01)
Stopelebäcken	1998	NT/mountains	0.0 (0.0)	0.00 (0.00)	2.1 (2.9)	0.01 (0.01)	†	†
Rukkebäcken	1997	NT/mountains	0.0 (0.0)	0.00 (0.00)	0.4 (0.7)	0.01 (0.01)	†	†
Rukkebäcken	1998	NT/mountains	2.7 (2.4)	0.01 (0.01)	3.2 (1.7)	0.02 (0.01)	†	†

Table 1. Continued

Stream	Year	Location	Initiation phase		Peak flow phase		Recovery phase	
			ΔANC_{poll}	ΔpH_{poll}	ΔANC_{poll}	ΔpH_{poll}	ΔANC_{poll}	ΔpH_{poll}
Kälsbäcken	1997	ST/coast	5.1 (0.5)	0.05 (0.01)	6.3 (2.0)	0.15 (0.06)	4.4 (3.6)	0.11 (0.10)
Kälsbäcken	1998	ST/coast	1.8 (2.5)	0.04 (0.06)	26.4 (3.5)	0.69 (0.13)	9.7 (8.7)	0.26 (0.24)
Sörjabäcken	1997	ST/coast	1.5 (2.9)	0.02 (0.04)	0.0 (0.0)	0.00 (0.00)	0.0 (0.0)	0.00 (0.00)
Sörjabäcken	1998	ST/coast	0.9 (0.4)	0.02 (0.01)	1.2 (1.0)	0.01 (0.01)	0.8 (1.1)	0.01 (0.01)
Acktjärnsbäcken	1997	ST/inland	6.4 (3.1)	0.09 (0.05)	10.5 (0.7)	0.15 (0.01)	9.9 (2.3)	0.18 (0.05)
Acktjärnsbäcken	1998	ST/inland	7.2 (4.9)	0.14 (0.08)	9.7 (1.7)	0.15 (0.03)	8.1 (1.1)	0.13 (0.01)
Lower Göljeån	1997	ST/mountains	6.5 (2.5)	0.17 (0.08)	8.9 (1.3)	0.27 (0.06)	5.0 (3.0)	0.14 (0.08)
Lower Göljeån	1998	ST/mountains	3.6 (3.5)	0.09 (0.09)	4.5 (0.5)	0.16 (0.03)	†	†
Upper Göljeån	1997	ST/mountains	0.9 (0.6)	0.01 (0.01)	12.4 (3.1)	0.28 (0.11)	†	†
Upper Göljeån	1998	ST/mountains	6.9 (7.0)	0.14 (0.14)	11.0 (2.9)	0.17 (0.05)	6.7 (0.2)	0.16 (0.03)

displayed relatively large anthropogenic components compared to the deposition load are the least buffered sites with extensive snow cover located partly or entirely above the timberline. These sites have also been shown to collect large amounts of anthropogenic deposition due to rime accumulation which is not accounted for in the standard bulk precipitation network (Westling & Ferm 1997).

Using the BDM, a strong correlation between the SO_4^{2-} deposition and the average ANC loss during 27 spring flood episodes in 18 acid sensitive catchments in northern Sweden (including the streams in this study) was found (Bishop et al. 2000). The strong correlation between SO_4^{2-} deposition and anthropogenic acidification during spring flood suggest that the anthropogenic component probably was significantly higher (ca. 100%) a decade ago when the deposition was more than twice the present level (O. Westling, unpublished data).

The BDM indicates that the anthropogenic contribution to pH declines in most streams in this study is currently limited, even though well-correlated to anthropogenic S deposition. Instead it was the natural sources of acidity that were responsible for most of the ANC and pH decline associated with the spring flood in the 22 episodes. However it should be recognized that since pH denotes a logarithmic concentration of the H^+, a 0.3 pH unit decrease denotes a doubling in its concentration. Even a small anthropogenic pH component in the most acid sensitive sites in this study has also been shown to cause detrimental effects on Brown Trout (Laudon 2000).

The most important factor influencing the pH decline in the studied streams is the fact that organic acids (TOC) do not dilute to anywhere the extent of the BC dilution. By diluting TOC to the same extent as BC, the pH decline is 75 to 85% less than the actual measured pH decline on average for all streams (Table 2). In Figure 3, the change in pH/ANC for all the 22 spring flood events can be observed on a nomograph showing the relationship between $pH_{aerated}$, ANC and TOC.

ANC dilution tracers

While the results of the BDM are consistent with the pattern of anthropogenic winter deposition of SO_4^{2-}, it is important to examine assumptions and sources of errors in the use of the model. One of the most important assumptions is that the dilution tracer provides an accurate quantification of the natural ANC dilution. An erroneous quantification of the dilution will not only provide an inaccurate buffering capacity dilution but also give an incorrect anthropogenic contribution during the episode.

When quantifying the natural dilution of ANC, the sum of base cations is used to quantify the difference between the contemporary dilution of ANC

Table 2. The role of TOC for the pH decline in the 22 spring flood events from northern Sweden. Comparison of the modeled observed pH decline ($pH_{observed}$) and pH assuming that TOC would dilute proportionally to the BC dilution (pH_{-TOC}) in the different event phases. The '†' indicates that no sampling of the recovery phase was carried out

Stream	Year	Baseflow	Initiation phase		Peak flow phase		Recovery phase	
		$pH_{observed}$	$pH_{observed}$	pH_{-TOC}	$pH_{observed}$	pH_{-TOC}	$pH_{observed}$	pH_{-TOC}
Stridbäcken	1997	5.44	4.61	5.30	4.60	5.27	4.68	5.23
Stridbäcken	1998	5.47	4.95	5.25	4.61	5.08	5.08	5.55
Lillån	1997	6.64	5.75	6.64	4.88	6.48	5.13	6.42
Lillån	1998	6.54	5.51	6.60	4.87	6.29	4.98	6.59
Sörbäcken	1997	7.52	6.71	7.23	6.20	7.14	6.43	7.11
Sörbäcken	1998	7.48	6.39	7.27	5.95	7.14	6.39	7.19
Mellansjöbäcken	1997	6.99	5.46	6.91	5.36	6.81	5.47	6.71
Mellansjöbäcken	1998	6.61	5.45	6.60	5.08	6.29	5.34	6.38
Stopelebäcken	1997	7.69	7.25	7.41	7.04	7.23	7.18	7.36
Stopelebäcken	1998	7.65	7.34	7.42	7.02	7.17	†	†
Rukkebäcken	1997	7.42	6.89	7.11	6.75	6.94	†	†
Rukkebäcken	1998	7.21	7.19	7.21	6.82	6.88	†	†

Table 2. Continued

Stream	Year	Baseflow	Initiation phase		Peak flow phase		Recovery phase	
		$pH_{observed}$	$pH_{observed}$	pH_{-TOC}	$pH_{observed}$	pH_{-TOC}	$pH_{observed}$	pH_{-TOC}
Kälsbäcken	1997	6.90	6.86	6.83	5.62	6.65	6.50	6.88
Kälsbäcken	1998	6.87	5.91	6.69	4.93	6.03	5.88	6.56
Sörjabäcken	1997	6.84	6.17	6.59	6.01	6.62	6.45	6.54
Sörjabäcken	1998	6.73	6.34	6.71	5.87	6.72	6.53	6.89
Acktjärnsbäcken	1997	7.18	5.86	6.95	4.68	6.59	5.14	6.68
Acktjärnsbäcken	1998	6.83	5.31	6.40	4.62	6.03	4.70	6.18
Lower Göljeån	1997	6.98	5.76	6.70	5.82	6.43	6.01	6.49
Lower Göljeån	1998	6.65	5.99	6.52	5.70	6.26	†	†
Upper Göljeån	1997	6.65	6.44	6.50	4.71	4.95	†	†
Upper Göljeån	1998	5.70	5.03	5.06	4.54	4.83	4.74	5.02

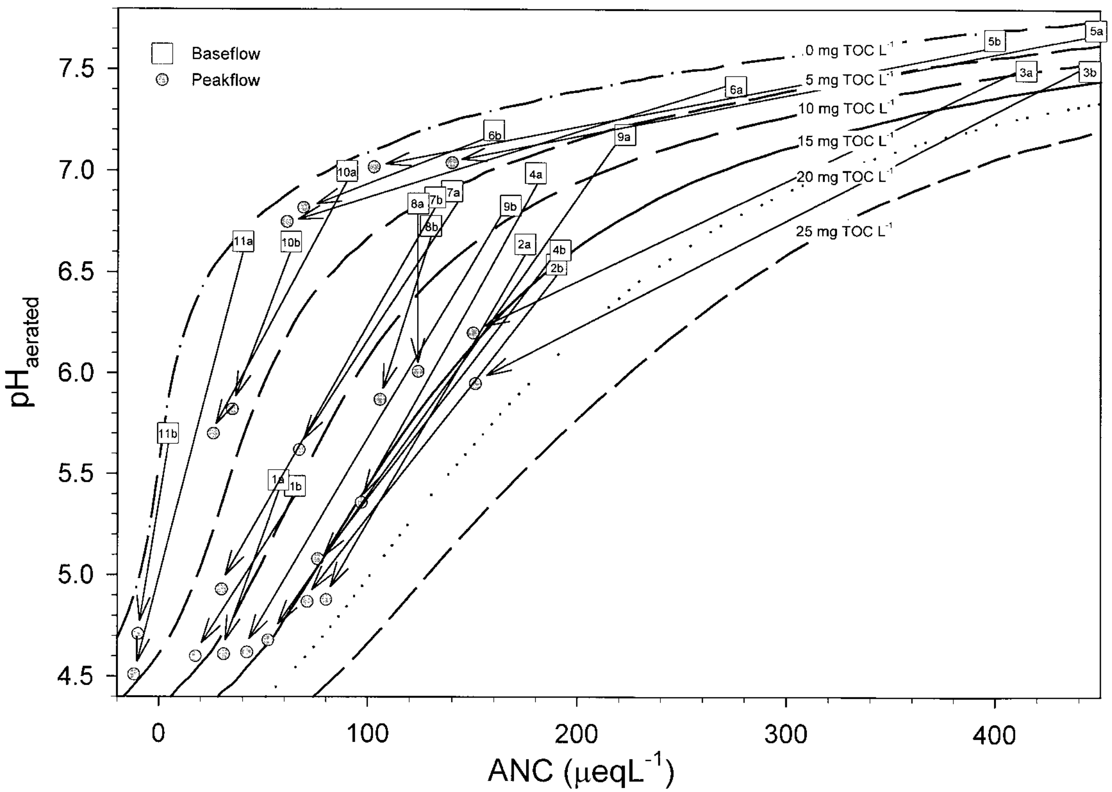

Figure 3. Changes in hydrochemistry from the baseflow phase to the peak flow phase for each episode. The change in pH/ANC overlays the nomograph showing the relationship between pH, ANC and TOC for northern Sweden (Laudon et al. 2000). Number “1” through “11” denotes Stridbäcken, Lillån, Sörbäcken, Mellansjöbäcken, Stopelebäcken, Rukkebäcken, Kälsbäcken, Sörjabäcken, Acktjärnsbäcken, Upper Göljeån and Lower Göljeån respectively while ‘a’ is the 1997 spring flood and ‘b’ is the 1998 spring flood.

and the preindustrial ANC dilution. The purpose of the dilution index is not to be analogous with a two-component mixing model where unpolluted snowmelt dilutes a pre-event component represented by the baseflow (Bishop et al. 2000). Instead the use of BC to define the contemporary dilution is taken as a surrogate for the natural preindustrial ANC dilution which is not conceptualized as two component mixing.

An important reason for using BC as DI in the BDM is the "self-compensating" response in BC to anthropogenic acidity which has been described and quantified by Bishop et al. (2000). Two "self-compensating" effects of BC are conceivable. The first being neutralization of precipitation acidity in the soil (or snow) which correctly will reduce the BDM prediction of anthropogenic influence on the episode although extra anthropogenic anions will reach the stream. The other "self-compensating" response is caused by a depletion of BC in the pre-event water leaving the catchment. This will be especially noticeable when superficial flow pathways rise into more BC-depleted soil horizons, from acidification or vegetation uptake, which will reduce the flux of BC relative to preindustrial levels. This decreased flux in BC will increase the BDM prediction of anthropogenic acidification during the episode.

The sum of base cations has also been used in other studies to separate sources of episodic acidification during high flow events (Kahl et al. 1992; Campbell et al. 1992). The ANC separation approach to episodic acidification that was first presented by Molot et al. (1989) and later used in numerous episode studies (DeWalle & Swistock 1994; Evans et al. 1995; Hyer et al. 1995) also indirectly used base cations as a separation tracer of dilution and acid contribution.

Bishop et al. (2000) quantified potential error sources using BC as a dilution index. They suggested that the most important potential error in forested streams of the Boreal region is the organic anion increase relative to the BC dilution during the spring flood. If a significant amount of BC are co-transported by organic anions to the stream, this would keep BC from diluting proportionally to the natural ANC dilution. Such an error would make the BC DI tend to underestimate the natural ANC dilution, and hence the anthropogenic component in the BDM calculation.

Despite the limitation in using two-component hydrological models for estimating ANC dilution, comparison of the dilution pattern of traditional hydrological tracers, such as silica, with that of BC can be used to estimate the potential error created by co-transport of BC with TOC. Possible explanations to a lack of consistency in the dilution pattern of silica and base cations could be that: (1) Base cations are co-transported with anthropogenic anions to the stream as a result of precipitation being neutralized in the soil (which

Table 3. Theoretical co-transport of BC with TOC in μeq (mg TOC)$^{-1}$ for streams with TOC exceeding 5 mg L^{-1}. The interaction is calculated by closing the gap between BC and Si dilution assuming that the difference between the dilution of BC and Si is due to BC-TOC co-transport

Stream	Year	γ-value
Stridbäcken	1997	2.01 ± 0.76
Stridbäcken	1998	2.08 ± 1.04
Lillån	1997	0.30 ± 0.70
Lillån	1998	1.99 ± 0.52
Sö|rbäcken	1997	0.09 ± 1.33
Sörbäcken	1998	1.40 ± 0.99
Mellansjöbäcken	1997	2.49 ± 0.83
Mellansjöbäcken	1998	2.20 ± 1.00
Kälsbäcken	1997	0.47 ± 1.23
Kälsbäcken	1998	0.40 ± 1.60

is a self compensating effect of BC), (2) base cations are co-transported with natural anions to the stream (i.e. organic anions) or (3) silica does not behave conservatively in catchments with large wetland areas and therefore does not function as a hydrological tracer.

Of the 22 spring flood episodes, silica was analyzed in 13 episodes. Of these, five episodes displayed a larger than 5% deviation, at peak flow, between the Si and BC dilution measures (Laudon et al. 2000). (The measurement error of BC is 4% while the error for Si is 7% [Wilander et al. 1998]). By closing the gap between the silica and base cation dilution, the highest theoretical co-transport of base cations with TOC was approximated for each stream. This factor, γ, is calibrated for each stream by subtracting BC (in μeq) per TOC (in mg) during the episode until the dilution of silica and the TOC corrected BC concentration ($BC_{TOCcorr}$) were equal. Between 0.1 and 2.5 μeq BC (mg TOC)$^{-1}$ could theoretically be co-transported to the stream assuming TOC is the single factor causing the dilution pattern discrepancy (Table 3). Neutralized anthropogenic sulfate would however, also lead to a discrepancy between the base cations and silica dilution pattern, which would reduce the apparent BC-TOC interaction.

To test the sensitivity of the BDM to BC-TOC co-transport, a TOC corrected BC ($BC_{TOCcorr}$) was used as an alternative DI. In order for the BDM to function with the alternative DI, the BC co-transported by TOC ($BC_{\gamma * TOC}$) needs to be added back to the calculation (Eq. 8). In Figure 4, the γ-value for each individual episode has been used for streams where silica has been measured. In the remaining streams the maximum average (observed (2.5 μeq BC (mg TOC)$^{-1}$ has been used. Of the 22 spring flood episodes, two showed a larger than 0.1 pH unit (but less than 0.12 pH unit) deviation between the BC DI and the $\mathrm{BC_{TOCcorr}}$ DI (Figure 4).

$$\mathrm{ANC}_{(\mathrm{preind},\mathrm{t},\gamma)} = (\mathrm{BC}_{\mathrm{base}} - \mathrm{ANSA}_{\mathrm{base}}) * \mathrm{DI}_{(\mathrm{t})} - [\mathrm{Cl}^-]_{(\mathrm{t})} + \mathrm{BC}_{(\gamma * \mathrm{TOC},\mathrm{t})} \quad (8)$$

A disadvantage with silica as a hydrological tracer is that it is not conservative in all environments. Wels et al. (1991) found that silica can not be used as a hydrological tracer in catchments draining peatland areas since wetlands act as a source of dissolved silica during baseflow and a sink during the spring flood. Similar results was found by Cory (1999) when comparing silica and BC with oxygen-18 as hydrological tracers in a catchment with extensive riparian wetlands. In Cory's study, BC and oxygen-18 gave almost identical separations, while silica overestimated the melt water component during the spring flood. The findings of Wels et al. (1991) and Cory (1999) suggest that a possible explanation to the discrepancy in the dilution pattern of silica and base cations is the large wetland percentage in the study catchments which prevents silica from behaving conservatively during hydrological events. In Figure 5 the percentage wetland area and the (factor are shown. The strong correlation between γ and wetland area ($r^2 = 0.59$) suggests that the discrepancy in the dilution pattern between silica and base cations probably is more dependent on the non-conservative nature of silica than on BC-TOC co-transport. The use of silica to quantify the BC-TOC interaction will hence overestimate that interaction. This will in turn over-predict the anthropogenic contribution of acidity during the spring flood.

The lack of a clear relationship between BC and TOC could possibly be explained by the spatial independence of the sources of BC and TOC (Bishop et al. 2000). BC originates mainly from weathering of mineral soils in the catchment, while the main source for TOC are organic soils in wetlands and in the riperian zone. On the catchment scale this source independence can be observed in Figure 6 where the wetland areas, which are the source of much TOC, have a negative correlation with the base cation concentration of the base flow. While there are theoretical arguments for TOC affecting the BC dilution, available evidence does not suggest that such an effect is significant for the application of the BDM with BC as the DI in the study streams.

Baseflow

An important assumption in the modeling of natural ANC and pH during spring flood events is that the baseflow has not been affected by anthropogenic

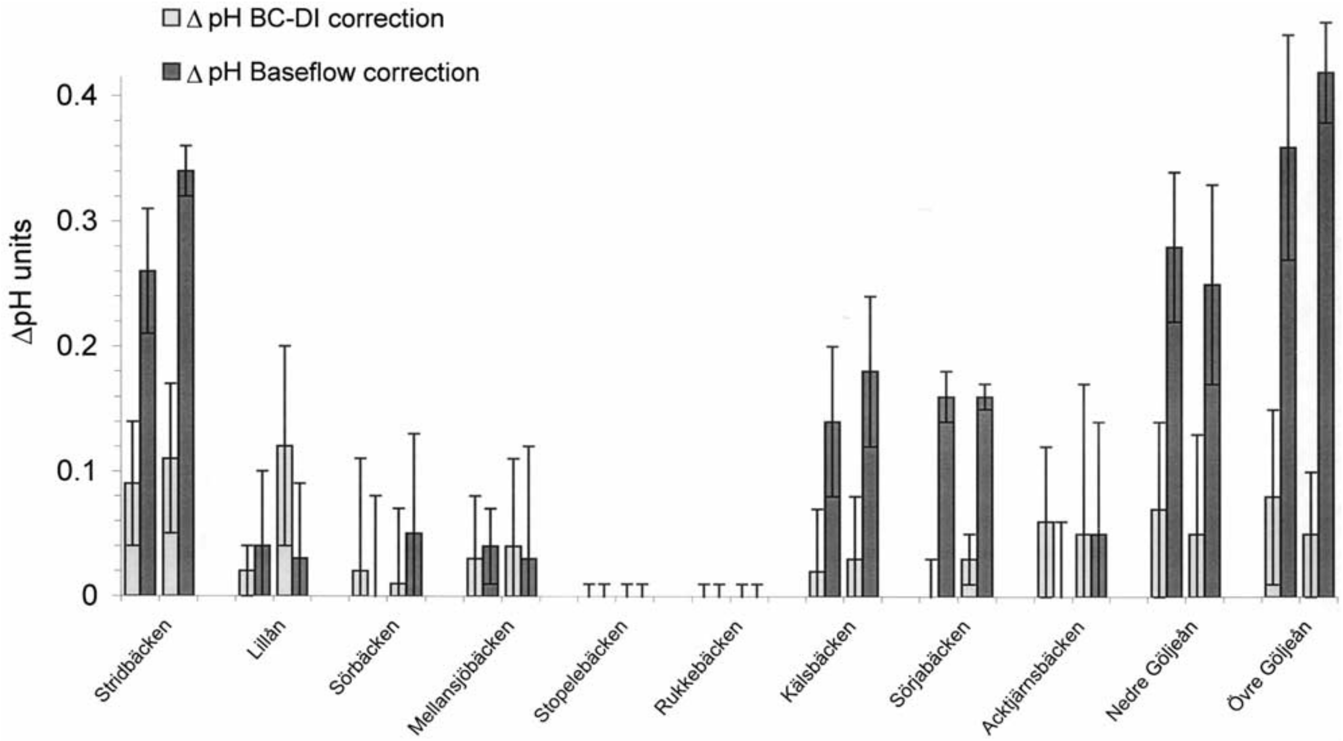

Figure 4. Possible errors associated with the use of BC as the DI and an assumption of unacidified baseflow. The light gray column is the sensitivity using a TOC corrected BC ($BC_{TOCcorr}$) as an alternative DI adding the maximum estimated BC-TOC co-transport from Table 3. The dark gray column is the effect using the F-factor corrected baseflow (Wilander et al. 1998) on the model outcome. The error bars denote the standard deviation of the peak flow phase samples. The first and second set of columns for each stream is the 1997 and 1998 spring flood respectively.

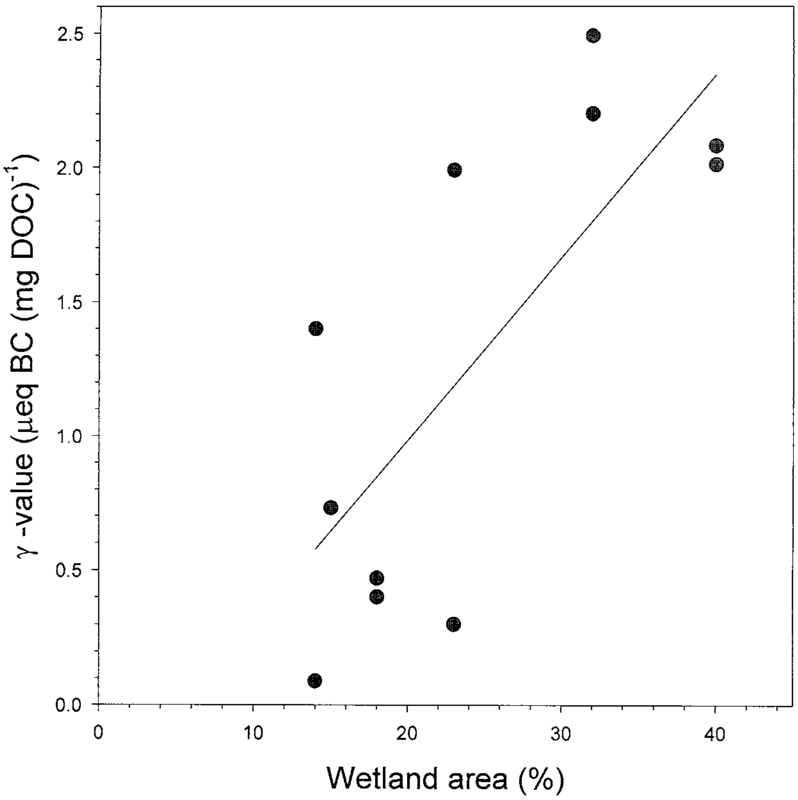

Figure 5. Correlation between wetland percentage and the γ-value (estimated BC transport by TOC) as presented in Table 3 ($r^2 = 0.59$).

deposition. This assumption has been confirmed by studies in the northern half of the northern Sweden region by paleolimnological work (Korsman 1993, 1999) of over 120 geographically representative lakes. In this region, the paleolimnological findings are confirmed by both MAGIC simulation of a acid sensitive headwater lake (Kram et al., in press) and by soil chemical studies comparing recent analyses with work carried out at the beginning of the century on the same locations (Jacks 1991; Tamm & Hallbäcken 1988). The base saturation of the soil in this region has also not been significantly altered (Eriksson et al. 1992). This suggests that the forest soils still have most of the acid buffer potential that they had a century ago.

In the southern part of the area included in this study, Renberg and Ek (1988) showed that pH has remained constant around 4.8 in three weakly buffered headwater lakes in the township of Borlänge despite a history of extreme SO_4^{2-} deposition from the 1000 years of mining activity in the area.

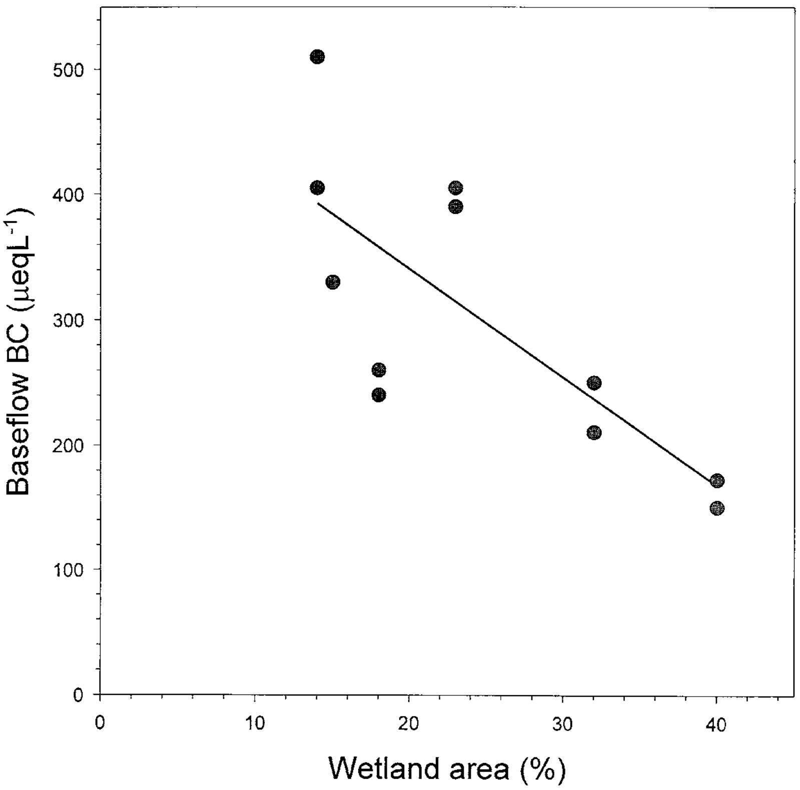

Figure 6. Correlation between wetland percentage and baseflow BC concentration ($r^2 = 0.57$).

In another study by Ek and Renberg (1998) in the same region, 14 lakes were studied. Of these, 5 lakes had been acidified 200 to 300 years ago, while two lakes increased in pH during this same period. One lake acidified after 1950. In the most south-eastern corner of the study region, one soil study has shown a significant decline in pH down to 0.6 meters soil depth during the last decades (Stegman 1990). The base saturation in this southern region has also decreased marginally (Eriksson et al. 1992). This suggests that the largest potential for chronic baseflow acidification in northern Sweden largely follows the past deposition pattern of SO_4^{2-} with the highest levels in the southern part of the region.

Even though evidence points against baseflow changes in most of the region, the Steady State Water Chemistry (SSWC) Model, as implemented by Wilander et al. (1998) can be used to test the sensitivity of a baseflow correction on the modeling of the ANC and pH of the 22 episodes (Bishop et al. 2000). In ten of the episodes the SSWC-adjusted baseflow pH was more then 0.1 pH units higher following the correction (Figure 4). In five of the episodes, the adjustment was more than 0.2 pH units. The five most affected episodes were from the two Göljeå sites (upper and lower) and Stridbäcken, which are the least buffered streams in this study. Both of these catchments have thin soils and much exposed bedrock.

Criticism concerning the validity of the SSWC Model, and the F-factor on which the model is based, for surface waters in northern Sweden has recently been put forward (e.g. Rapp 1998). Therefore, the F-factor correction of the baseflow is not to be seen as a recommendation but rather as one attempt to define the sensitivity of the baseflow chemistry in the studied streams.

Changes in TOC

Forestry practices in Sweden can lead to changes in both hydrology and hydrochemistry since both the runoff and the groundwater level can be affected (Grip 1982). The increase in runoff from clear-cut areas can be up to 100% (Grip 1982). The use of clear-cuts can also lead to increased degradation and mineralization of organic material, which potentially can enhance the leakage of TOC and solutes. Following a clear-cut of 2–6% of the catchment area, Juto and Temnerud (1999) demonstrated that no significant effects could be observed during the spring flood in any hydrochemical parameter. The result that TOC is not affected by upstream clear-cuts has been confirmed by the paleolimnological studies already cited showing that the color of surface waters in Norrbotten and Västerbotten has not changed significantly over the last 200 years (Korsman 1993).

Studies of TOC dynamics following ditching of wetlands have demonstrated that TOC often decreases in concentration following an initial TOC flush (Magnusson 1982). By channeling the water away from the wetland with deep ditches down to the underlying mineral soil, the contact zone between water and organic material is reduced. Thus changes in the hydrological pathways in wetlands in northern Sweden associated with forest drainage could potentially lead to decreased concentrations of TOC in surface waters in the region. Larger watercourses in Sweden do, however, not demonstrate any trends in the last 20 years (Löfgren & Fölster 1998), but rather a precipitation-related variation.

One important assumption for the pH modeling in the use of the BDM is that the character of TOC is constant over time and space. This has been confirmed by several studies in the region (Köhler 1999; Köhler et al. 1999; Hruška et al. in press). Köhler et al. (1999) showed that the spatial variation in the acid-base character in 74 lakes in northern Sweden does not lead to significant effects on the modeling of pH and anion charge contribution for surface waters in the region. A lack of significant temporal variation in the acid-base character of TOC has also been confirmed in conjunction with spring flood episodes in the region (Hruška et al. in press). The reasonable reproduction of measured air equilibrated pH from ANC, pCO_2 and TOC with a standard deviation of 0.21 pH units (Laudon et al. 2000) further confirms a relatively consistent TOC character in northern Sweden.

Conclusions

The BDM is a systematic approach that makes it possible to assess hydrochemical changes over time, and between regions in the response to hydrological episodes. The purpose of the BDM is to serve as a readily available tool for assessing the extent of the anthropogenic component in episodic acidification that can help in the planning of liming activities in areas that are not chronically acidified. The tool and the sampling strategy it is based upon could also be used in environmental monitoring programs where it has previously been difficult to justify special sampling programs to evaluate hydrochemical variation during hydrological episodes despite their influence on biodiversity.

The assessment of the anthropogenic contribution to spring flood pH decline using the Boreal Dilution Model on spring flood data during 22 episodes from 1997 and 1998 in northern Sweden found that the often substantial pH decline is largely caused by natural processes. The most important factors driving the natural pH decline were TOC increase in combination with ANC dilution. The results to date suggest that the current geographic extent of major anthropogenic impacts on episodic acidification in northern Sweden is limited. However, even marginal anthropogenic sources of acidity superimposed on the natural pH dynamic could, of course, lead to more toxic levels of acidity in sensitive systems and hence to negative consequences for the natural biodiversity.

The largest anthropogenic acid component during spring flood was generally found in the weakly buffered, acid sensitive catchments. These streams are also the sites where the sensitivity of the BDM to changes in the baseflow chemistry are the largest.

The BDM also demonstrates that the anthropogenic component of ANC/pH decline appears sensitive to the S-load in snow. The strong correlation between winter deposition and the anthropogenic episodic acidification suggests that the anthropogenic component was more important a decade ago when the deposition load was substantially higher. By the same token, though, decreases in S deposition also appear to have brought an almost simultaneous reduction in the anthropogenic contribution to spring flood pH decline.

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