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Long-term response in episodic acidification to declining SO_4^{2-} deposition in two streams in Nova Scotia

Hjalmar Laudon[1,2], Thomas A. Clair[3] and Harry F. Hemond[1]

[1]Ralph M. Parsons Laboratory, Department of Civil and Environmental Engineering, MIT, Cambridge, MA, 02139, USA
[2]Present address: Department of Forest Ecology, Swedish University of Agricultural Sciences, 901 83 Umeå, Sweden
[3]Environment Canada, Atlantic Region, PO Box 6227, Sackville, N. B. E4L 1G6, Canada

E-mail for corresponding author: Hjalmar.Laudon@sek.slu.se

Abstract

Trends in anthropogenically driven episodic acidification associated with extended winter snow melt/rain episodes between 1983 and 1998 were investigated for two streams in Nova Scotia, Canada. The anthropogenic contribution to Acid Neutralization Capacity (ANC) was analysed using the Boreal Dilution Model (Bishop *et al*., 2000) modified by applying a sea-salt correction to all input hydrochemistry. The anthropogenic contribution to episodic ANC decline was statistically significant and strongly correlated with the decline in acid deposition, which decreased by approximately 50% during the period of record. Sensitivity analysis demonstrated that the BDM can be applied to surface waters with sea-salt contributions although the correction increases model uncertainty. Results of this study demonstrate the effectiveness of reduced emissions in North America in the last decades in decreasing the severity of episodic acidification in the Atlantic region of Canada.

Keywords: episodic acidification, acidification recovery, Nova Scotia, snowmelt, winter

Introduction

Recent studies of surface waters in northeastern United States and Western Europe have demonstrated Acid Neutralization Capacity (ANC) recovery toward pre-industrial values in response to declining acid deposition, but the rate is slow (Stoddard *et al*., 1999; Evans *et al*., 2001; Skjelkvåle *et al.,* 2001) and does not always correlate with the change in deposition (Newell and Skjelkvåle, 1997). Most previous studies of acidification recovery, including those undertaken within the framework of the International Co-operative Programme on Assessment of Rivers and Lakes (ICP-waters (Stoddard *et al*., 1999)) and the European Commission's Environment and Sustainable Development Programme (RECOVER: 2010 (Ferrier *et al.*, 2001)), have been based on monthly to yearly sampling frequency. However, the ecological significance of acidification recovery may lie primarily in explaining the episodic intensity of reductions in ANC associated with snow melt and rain storm, rather than in the increase of annual ANC values.

The timing, duration and extent of decline in ANC and pH is of particular importance during snow melt because spring is a period when many aquatic species are at sensitive stages of their life cycle (Vanoffelen *et al*., 1994). Thus, snowmelt-induced episodic acidification has been studied in regions associated with intensive spring flood (Molot *et al*., 1989; Campbell *et al*., 1992; Eshleman *et al*., 1995; Laudon *et al*., 2000, 2001).

However, many high- and mid-latitude regions with strong marine influence do not undergo discrete snow-melt episodes in spring. Instead, these regions often experience extensive runoff episodes lasting several months, caused by intermittent snow melt and rainfall periods. Although less studied, anthropogenic acidification associated with such extended runoff events can constitute an environmental threat in regions such as coastal areas of northwestern Europe and northeastern North America.

Southwestern Nova Scotia (SWNS) is a region known to suffer from acidification-related decline in Atlantic Salmon populations (Watt, 1987). From mid-autumn to late spring

this region experiences frequent acid pulses (Clair *et al*., 2001), causing episodes of water chemistry that can be toxic for Atlantic Salmon (Lacroix and Townsend, 1987; Lacroix and Korman, 1996).

Several physical characteristics make the surface waters of SWNS susceptible to acidification. Firstly, the waters have low natural levels of base cations and buffering capacity due to regional geology. Secondly, the region is surrounded by the Atlantic Ocean and the Bay of Fundy, which give rise to high concentrations of sea-salt in precipitation. Although these neutral salts do not alter the acid-base chemistry of the surface waters directly, they are involved in ion exchange processes which tend to deplete soils of base cations through exchange reaction of sea-salt sodium (Thompson, 1982). Finally, because of the low topographic relief, the area contains wetlands (Clair *et al*., 1994), which can result in locally high natural dissolved organic carbon concentration (DOC) and thus high levels of natural organic acids, which further depress stream water pH.

Because multiple factors influence the acid-base chemistry of Nova Scotian waters, it is difficult to separate the role of acid deposition from that of natural variability in surface water chemistry. To separate the response in surface water chemistry to acid deposition from natural variability during the extended winter episodes, the Boreal Dilution Model (BDM) (Bishop *et al*., 2000; Laudon, 2000) was used. The objective was to determine if the two- decade- long decline in acid deposition measured in Nova Scotia (Clair *et al*., 2002) has resulted in measurable surface water chemistry improvements during winter episodes in the region. To do this, the BDM was modified to account for marine proximity and the sensitivity of this modified model was tested.

Field sites and sampling

Precipitation in SWNS is quite variable, being derived both from storms originating in areas that are major sources of acidic contaminants, such as the East coast of the United States and central North America, and from storms arriving from the open ocean, which contribute minimal acid loads (Shaw, 1979). Kejimkujik National Park currently receives between 10 and 14 kg ha^{-1} of sea-salt-corrected SO_4^{2-} and approximately 10 kg ha^{-1} of NO_3^- per annum (Beattie *et al*., 2000).

The region is influenced by a cool, temperate climate with a mean annual precipitation of 1352 mm, of which 56% occurs between November and April. Total snow amounts average 169 mm in water equivalents, somewhat more than 10% of total precipitation. Because of its proximity to the Atlantic Ocean (approximately 60 km), rain often occurs during the winter months when soils are frozen and snow-covered. This generates a high number of runoff events superimposed on a generally high winter discharge. Total runoff averages approximately 1000 mm per year.

Two streams in the Kejimkujik National Park in SWNS (Fig. 1), were studied, using weekly stream water chemistry data collected from 1983 to 1998. The Mersey River is a

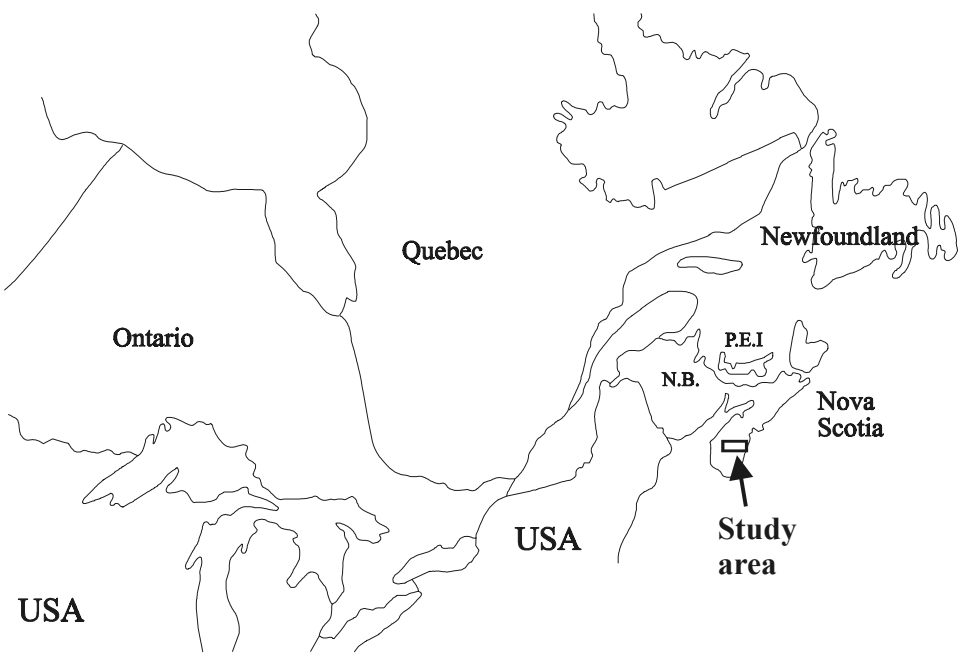

Fig. 1. *The location of the field sites*

4th order stream, draining a 297 km^2 area of conifer and mixed hardwood forests. Moose Pit Brook is a 17 km^2 basin similar to the Mersey River catchment. The basins are influenced minimally by human activity, though some logging is done in both. The bedrock is either granite or slate, both of which are resistant to weathering, resulting in low buffer capacity of soils and surface waters. Although wetlands occupy less than 1% of the surface area in both basins (Yanni, 1996), both the Mersey River and Moose Pit Brook have abundant wetlands along the stream edges. This causes stream DOC concentrations greater than 10 mg L^{-1} in Moose Pit through most of the year, and averaging 7 mg L^{-1} for the Mersey. Mean annual pH values are around 5.0 for both streams, with extensive seasonal and daily fluctuations (Freedman and Clair, 1987).

Both study streams were sampled on a weekly or more frequent basis from 1982 to 1999, except for a two-month sampling break in the winter of 1993 in the Mersey River. Water samples were analysed for major ions, dissolved organic carbon (DOC), and nitrate at an Environment Canada's laboratory in Moncton, New Brunswick (Table 1). Sea-salt-correction was made for all major ions, using ion to chloride ratios (SO_4^{2-}/Cl^-, Mg^{2+}/Cl^-, Ca^{2+}/Cl^-, Na^+/Cl^-, K^+/Cl^-) of sea water (Watt *et al*., 1979) and assuming that all chloride is of marine origin.

Table 1. Average peak flow–base flow concentrations for the study streams. All concentrations are sea-salt-corrected.

	Base flow – peak flow
MOOSE PIT	
ANC µeq L^{-1}	109 – 8
DOC mg L^{-1}	26 – 8
SO_4^{2-} µeq L^{-1}	34 – 44
Mg^{2+} µeq L^{-1}	40 – 12
Ca^{2+} µeq L^{-1}	59 – 26
Na^+ µeq L^{-1}	35 – 5
K^+ µeq L^{-1}	9 – 8
MERSEY RIVER	
ANC µeq L^{-1}	35 – 2
DOC mg L^{-1}	10 – 6
SO_4^{2-} µeq L^{-1}	34 – 35
Mg^{2+} µeq L^{-1}	11 – 4
Ca^{2+} µeq L^{-1}	39 – 29
Na^+ µeq L^{-1}	14 – 4
K^+ µmeq L^{-1}	5 – 4

Evaluation of long-term and episodic response

To evaluate the hydrochemical response to the decline in acid deposition, the winter runoff was separated into four phases:

- The *baseflow phase,* defined here as the period with the lowest runoff during the summer/autumn. This phase occurred between August and October and generally consisted of a flow of less than 10% of peak flow. In most of the episodes studied the baseflow phase was the average chemistry of 8 to 15 samples (the average number of samples was 12 per episode).
- The *initiation phase* was defined as the period between baseflow and peak flow. The number of samples in this phase averaged 40 samples per episode.
- The *peak flow phase* was defined as the average of the 10 most acid consecutive samples. This period generally occurred in March or early April.
- The *recovery phase* was defined as the period following peak flow phase until ANC returned close to baseflow levels, generally in the beginning of June. This phase included, on average, 18 samples per episode.

The significance of average trends in the stream water chemistry during the four phases was analysed using a modified Seasonal Kendall analysis (Loftis *et al*., 1991). For the magnitude of the trend, the slope was calculated based on the average chemistry of each phase (Helsel and Hirsch, 1992). The test is non-parametric and is used to identify monotonic long-term trends. The slope and significance of average trends were calculated for ANC, discharge, pH, DOC, anions (NO_3^-, SO_4^{2-}), individual base cations (Mg^{2+}, Ca^{2+}, Na^+, K^+) and for the sum of base cations (BC). ANC is calculated as the difference between the sum of base cations and strong mineral acid anions. All tests were carried out on sea-salt-corrected stream water chemistry

The driving mechanisms of episodic ANC decline were separated into natural and anthropogenic components using a modified version of the Boreal Dilution Model (BDM) (Bishop *et al*., 2000; Laudon, 2000). Because of the large marine influence, the BDM was modified by applying a sea-salt-correction to all of the input hydrochemistry. The model with this correction applied was designated BDM_s. The BDM_s was used on the initiation, peak flow, and recovery phases separately to evaluate differences in driving forces of the ANC decline during different stages of the episodes.

The BDM_s is based on the observed ANC ($ANC_{(obs, t)}$ (Eqn. 1) and a dilution index ($DI_{(t)}$; Eqn. 2) at any time "t" during

the flow event.

$$ANC_{(obs,\ t)} = 2*[Ca^{2+}]_{(t)}+2*[Mg^{2+}]_{(t)}+[Na^{+}]_{(t)}+[K^{+}]_{(t)}- 2*[SO_4^{2-}]_{(t)} - [NO_3^{-}]_{(t)} = BC_{(t)} - ANSA_{(t)} \quad (1)$$

$$\Delta I_{(t)} = BC_{(t)} / BC_{(base)} \quad (2)$$

The ΔI is calculated using the sum of base cations (BC = $2*[Ca^{2+}] + 2*[Mg^{2+}] + [Na^{+}] + [K^{+}]$), which simulates the natural dilution of both BC and the anthropogenically significant anions of strong mineral acids (ANSA = $2*[SO_4^{2}] + [NO_3^{-}]$) during runoff episodes. The natural, pre-industrial ANC ($ANC_{(preind,\ t)}$) is predicted using Eqn. 3. The difference between the predicted pre-industrial $ANC_{(preind,\ t)}$ (Eqn. 3) and the observed $ANC_{(obs,\ t)}$ (Eqn. 1) is interpreted as the human influence on the ANC ($\Delta ANC_{(poll,\ t)}$, Eqn. 4) during the episode.

$$ANC_{(preind,\ t)} = DI_{(t)} * (BC_{(base)} - ANSA_{(base)}) \quad (3)$$

$$\Delta ANC_{(poll,\ t)} = ANC_{(preind,\ t)} - ANC_{(obs,\ t)} \quad (4)$$

Because the purpose of modelling was limited to determining the changes in $\Delta ANC_{(poll,\ t)}$ of runoff episodes, it was not necessary to satisfy all of the assumptions that must be invoked in modelling natural pH decline in the original BDM (Bishop *et al.*, 2000). However, one assumption that must be fulfilled in this use of BDM_s is that the sum of base cations can be used as a surrogate for the natural dilution of ANC. Therefore, the potential effects of marine proximity on the dilution index are tested and discussed.

Results and discussion

The total winter deposition of SO_4^{2-} (October-April) declined by approximately 50% in the region during the last two decades (r^2=0.61; p<0.001; Fig. 2). Winter precipitation, deposition of NO_3^{-}, Cl^{-}, sea-salt-corrected Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in precipitation demonstrated no significant change during the same time period (p>0.1).

The marine proximity of the study catchments leads to high concentrations of Cl^{-} and Na^{+} in runoff. Cl^{-} is the dominant anion in the two streams, with concentrations two to three times greater than SO_4^{2-}, while Na^{+} is the dominant cation, with levels substantially exceeding the sum of the remaining cations. According to the sea-salt-correction, 50% of BC and 24% of the SO_4^{2-} in Moose Pit Brook was of marine origin. In the Mersey River 72% of the BC and 32% of the SO_4^{2-} originated from the sea.

During the baseflow phase, few statistically significant

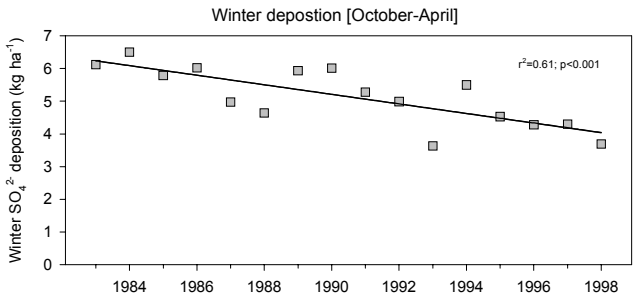

Fig. 2. *Winter bulk SO_4^{2-} deposition at the field sites during the study period*

trends were observed over the study period (Table 2). Statistically significant trends were found, however, during the peak flow phase, with decreasing SO_4^{2-} in both streams. In Mersey River, the decline in SO_4^{2-} was accompanied by a decrease in base cations (mainly Mg^{2+} and Ca^{2+}), preventing a change in ANC. In Moose Pit Brook, the decline in SO_4^{2-} generated a weakly significant increasing trend in ANC, as the decreasing trends of Mg^{2+} and Ca^{2+} were counteracted by an increase in Na^{+}.

The anthropogenic contribution to the ANC decline, $\Delta ANC_{(poll)}$, was in general largest during the peak flow phase (Fig. 3). $\Delta ANC_{(poll)}$ during peak flow declined substantially since the initiation of the monitoring programme in the early 1980s. The magnitude of this anthropogenic contribution during the episodes, for both streams, was well correlated with both total deposition of SO_4^{2-} and concentration of SO_4^{2-} in precipitation (Fig. 4). The anthropogenic contribution to seasonal ANC decline was significantly larger at Moose Pit Brook than at the Mersey River. The strong correlation between $\Delta ANC_{(poll)}$ and winter deposition of SO_4^{2-} suggests that the winter hydrochemistry responds directly and rapidly to changes in the deposition of SO_4^{2-}. Despite relatively high deposition of NO_3^{-}, nitrogen appears to have limited effect on the hydrochemistry of the two streams, as the terrestrial ecosystems currently prevent NO_3^{-} leakage from the catchments (e.g. Hemond and Eshleman, 1984).

A similarly strong correlation between $\Delta ANC_{(poll)}$ and the deposition of SO_4^{2-} has been recorded for spring snow melt episodes in northern Sweden (Laudon and Hemond, 2002); although different in magnitude, the general trend between winter S concentration and $\Delta ANC_{(poll)}$ was similar to that found in the present study (Fig. 4). Average winter concentration in deposition was similar in magnitude between the two regions, but an approximately two to three times higher winter precipitation led to deposition loads being two to three times higher in Nova Scotia. The difference in response between the Mersey River and Moose Pit Brook could be caused by catchment size. Because

Table 2. Average annual trends in baseflow, initiation, peak flow and recovery phases during the period 1983–1998

	Base flow phase	*Initiation phase*	*Peak flow phase*	*Recovery phase*
MOOSE PIT				
Number of samples	184	371	150	298
ANC meq L^{-1} yr^{-1}	0.99	-0.40	0.87*	0.49
Discharge L s^{-1} yr^{-1}	0.00	0.01	0.03	0.00
pH yr^{-1}	0.00	0.00	0.01	0.01**
DOC mg L^{-1} yr^{-1}	-0.29*	-0.08	-0.06	-0.06
NO_3^- meq L^{-1} yr^{-1}	0.00	0.00	0.00	0.00
SO_4^{2-} meq L^{-1} yr^{-1}	2.91	0.33*	-1.04**	-0.05
Mg^{2+} meq L^{-1} yr^{-1}	1.85	-0.39	-0.50*	-0.18**
Ca^{2+} meq L^{-1} yr^{-1}	0.62	-0.47	-0.65*	-0.29**
Na^+ meq L^{-1} yr^{-1}	1.66*	1.22**	1.41*	0.88*
K^+ meq L^{-1} yr^{-1}	-0.17	-0.15	-0.05	0.00
BC meq L^{-1} yr^{-1}	4.04	0.25	-0.01	0.43*
MERSEY RIVER				
Number of samples	174	837	150	230
ANC meq L^{-1} yr^{-1}	-0.61	0.37	0.03	0.30
Discharge L s^{-1} yr^{-1}	-0.04	0.19	-0.72*	-0.34
pH yr^{-1}	0.00	0.00	0.00	0.01
DOC mg L^{-1} yr^{-1}	-0.05	-0.02	-0.02	-0.01
NO_3^- meq L^{-1} yr^{-1}	0.00	-0.01	0.00	0.00
SO_4^{2-} meq L^{-1} yr^{-1}	0.44	0.18	-0.59**	-0.45*
Mg^{2+} meq L^{-1} yr^{-1}	-0.18	-0.39***	-0.71***	-0.67*
Ca^{2+} meq L^{-1} yr^{-1}	-0.23*	-0.31	-0.40**	-0.26
Na^+ meq L^{-1} yr^{-1}	0.19	1.02	0.34	0.59
K^+ meq L^{-1} yr^{-1}	0.03	0.08	0.02	-0.01
BC meq L^{-1} yr^{-1}	0.46	0.12	-0.63**	0.01

Significance level *<0.1; **<0.05; ***<0.01

smaller streams have a shorter transit time of water, they may experience more rapid response to changes in deposition. This, however, was not seen in studies in northern Sweden (Laudon, 2000; Laudon *et al.*, 2001; Laudon and Hemond, 2002), where catchments ranging in size over several orders of magnitude responded similarly to changes in SO_4^{2-} deposition.

One important difference between the northern Sweden sites and the two catchments reported here lies in the nature of antecedent conditions. Winter high-flow episodes in the Nova Scotia streams were generally preceded by rainfall, whereas the springtime high flow episodes in northern Sweden were preceded by four to six months of winter conditions with thick snow packs and at least partly frozen soils. Laudon and Hemond (2002) suggested that the strong correlation between $\Delta ANC_{(poll)}$ and winter SO_4^{2-} deposition in northern Sweden implies that previously deposited sources of SO_4^{2-} are relatively unimportant during spring flood episodes, possibly due to cold soil temperatures resulting in slow reaction kinetics in the soil. Because the preceding conditions in Nova Scotia are warmer and wetter than in northern Sweden the soil influence during the winter episode could be more important.

Despite a significant declining trend in $\Delta ANC_{(poll)}$ during winter episodes, only limited changes in the average peak flow chemistry were observed over the study period (Table 2). This difference between the statistical approach to study average peak flow chemistry trends and the BDM_s is due to the natural inter-annual variability in the stream water chemistry caused by differences in base flow chemistry and variability in precipitation and runoff patterns. The strength of the BDM_s is that it reduces the natural variability in the

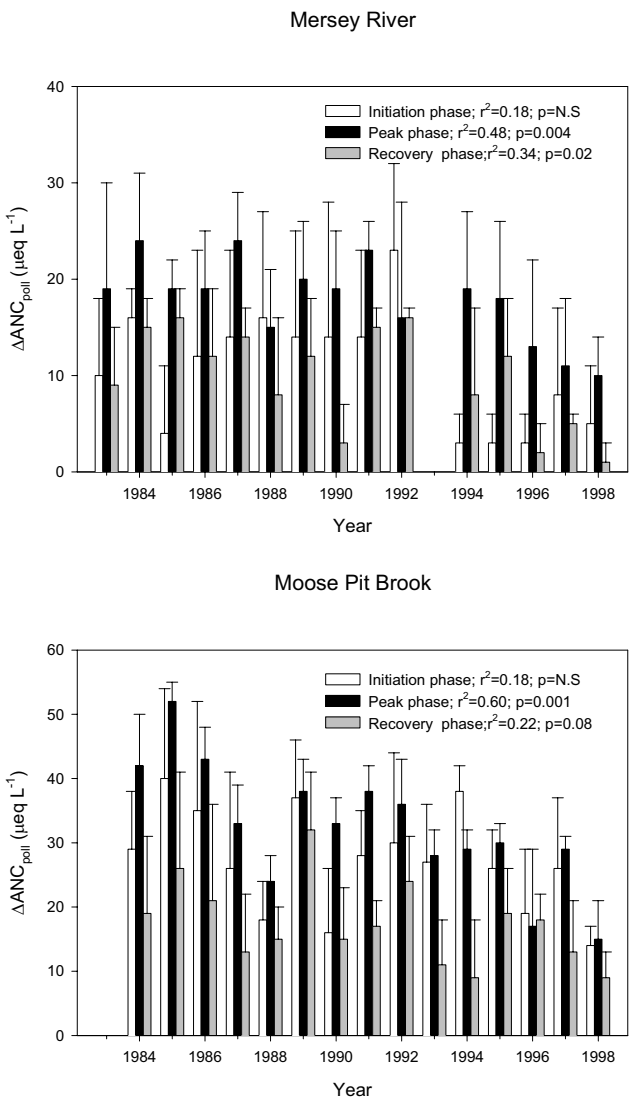

Fig. 3. The $\Delta ANC_{(poll)}$ of initiation, peak flow, and recovery phases, calculated using BDM_s. The whiskers denote one standard deviation.

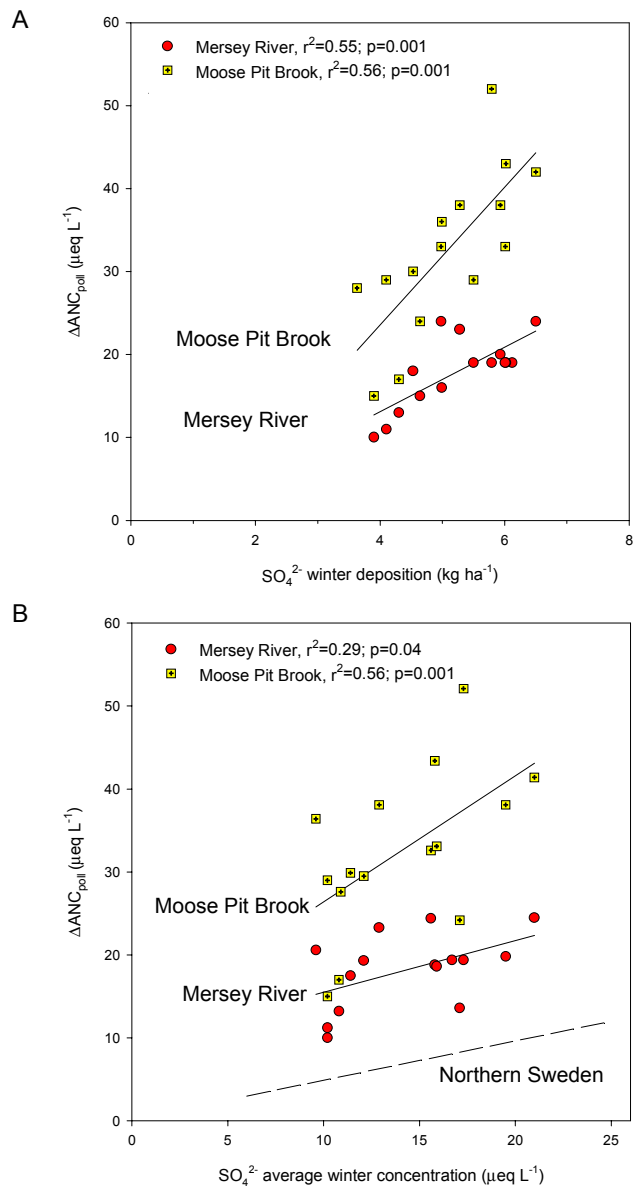

Fig. 4. *A). Correlation between SO_4^{2-} winter deposition (kg-S ha^{-1}) and $\Delta ANC_{(poll)}$. B). Correlation between SO_4^{2-} average winter concentration in precipitation (meq L^{-1}) and $\Delta ANC_{(poll)}$. The range and correlation in Northern Sweden is also shown (Laudon and Hemond, 2002).*

decline in ANC into "natural" and "anthropogenic" sources, which is not possible using the statistical approach (Laudon and Hemond, 2002).

MODEL UNCERTAINTY

The most prominent difference between northern Sweden, where the BDM has previously been used and tested, and the two streams in Nova Scotia is the marine influence. Despite the fact that the sea-salt-correction of the hydrochemistry does not alter the calculated ANC, a significant difference in $\Delta ANC_{(poll)}$ (at 95% confidence interval) is generated, depending on the model used (Fig. 5 A and B). The significant difference between the BDM_s and the original BDM (Bishop *et al*., 2000) is due to a change in dilution pattern caused by the sea-salt-correction. The larger decrease in BC generates a larger change in the dilution from base flow to peak flow compared to the change in the SO_4^{2-} dilution, which increases the calculated $\Delta ANC_{(poll)}$. A complication in assessing $\Delta ANC_{(poll)}$ in the two streams is that the sea-salt-correction occasionally produces negative values of Na^+ during winter episodes. Assuming that the sea-salt-correction of major chemical constituents should be in equal proportions to sea water (Watt *et al*., 1979;

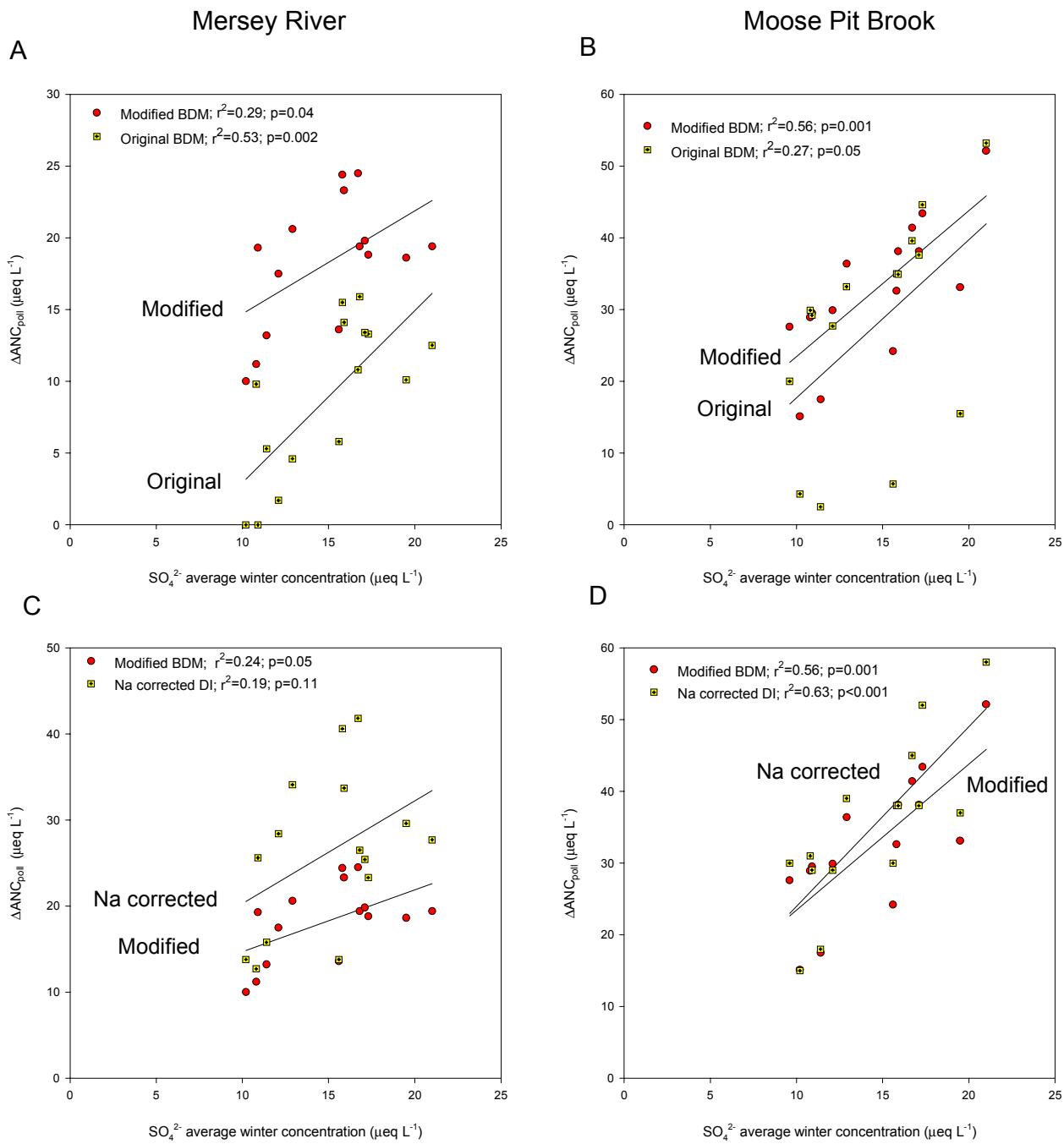

Fig. 5. *Sensitivity analyses comparing the output of BDM and BDM_s (panels A and B). Panels C and D are outputs of BDM_s using the further assumption that Cl^- behaves as strong anthropogenic acid anion. Note the difference in scale*

Thompson, 1982), a likely reason for corrected Na^+ becoming negative is a difference in residence time of Na^+ and Cl^-. This could arise from ion exchange buffering of sodium in the catchment soils (Neal and Kirchner, 2000), and is also consistent with the observation of more strongly dampened Na^+ signals during the peak flow phase. The exchange buffering of Na^+ suggests that some excess Cl^- reaching the stream is co-transported with other base cations or with alternative cations such as protons, which would generate sea-salt induced acid surges (Wright *et al.,* 1988; Heath *et al.,* 1992).

If the excess Cl^-, not balanced by Na^+, is instead associated with other base cations, such as Ca^{2+}, then Cl^- behaves as the natural non-acidifying constituent it commonly is

assumed to be. On the other hand, if the excess Cl^- is associated with protons, originating from anthropogenic deposition, as a result of exchange reactions in the soil, then the excess Cl^- behaves as an anthropogenically derived strong acid anion. To test the sensitivity of the BDM_s, the maximum Cl^- excess co-transport of anthropogenic protons was added to the model, assuming that the natural non-marine Na^+ concentration is zero (Fig. 5 C and D). Computationally this is done by extracting the effect of Na^+ on the dilution pattern of DI, which eliminates the effect caused by the difference in residence time between Cl^- and Na^+ on the calculated $\Delta ANC_{(poll)}$. In the Mersey River, $\Delta ANC_{(poll)}$ increases on average by 36% as a result, while the increase in Moose Pit Brook is 8%. This difference, as well as the one in Fig. 5 C and D, shows the maximum potential effect of Cl^- excess co-transport of anthropogenic protons; part of the difference between the Na^+ corrected and the BDM_s probably is made up by other base cations (see above) or naturally derived protons in the catchment. Despite the uncertainty associated with asynchrony of Cl^- and Na^+ on the modelled $\Delta ANC_{(poll)}$, the trend in recovery due to a decline in SO_4^{2-} deposition remains essentially unaffected.

Compared to spring flood episodes in northern Sweden, where the BDM has previously been used, the winter episodes of Nova Scotia last for several months. Because the definition of peak flow was set arbitrarily to the ten most acid consecutive samples, a test of sensitivity to the length of this phase was carried out. In varying the number of samples in the peak flow phase from 3 to 20, results did not differ significantly (at the 95% confidence interval) until the number of samples exceeded 15 (or duration exceeded four weeks, on average). For individual years, the difference was in a few instances significant statistically when a sample size of three was chosen, although the general trend remained the same.

Because the BDM_s has been applied uniformly to all episodes, uncertainty associated with model output would likely affect each episode similarly, with the observed recovery trend remaining even if the absolute levels were somewhat affected. Thus, although some uncertainty remains, it will not likely alter the conclusion that the decline in SO_4^{2-} deposition has decreased the anthropogenically driven ANC drop during spring flood episodes in these catchments. In summary, this study concludes that reduced emissions in North America have led to a rapid improvement in the anthropogenic component of acidity associated with spring floods. This study also indicates that the BDM can be usefully applied to surface waters of marine proximity, with caution about the sensitivity to sea-salt-corrections.

Acknowledgement

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