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Climate-Induced Episodic Acidification of Streams in Central Ontario

H. LAUDON,*,† P. J. DILLON,‡ M. C. EIMERS,‡ R. G. SEMKIN,§ AND D. S. JEFFRIES§

Department of Forest Ecology, Swedish University of Agricultural Sciences, 901 83 Umeå, Sweden, Environmental and Resources Studies, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada, and Environment Canada, National Water Research Institute, Burlington, Ontario L7R 4A6, Canada

In this study we have analyzed the hydrochemical effect of drought conditions during 311 hydrological episodes in nine headwater streams in central Ontario over the past 20 years. Acid Neutralization Capacity (ANC) was logarithmically correlated ($p < 0.05$) to antecedent discharge in eight of the nine streams, with the largest decline in ANC occurring after low antecedent flow. In eight of the nine streams SO_4^{2-} was the most important driving mechanism of ANC decline, but dilution as well as organic acidity was important in several streams. No decrease in the SO_4^{2-} driven ANC decline was observed over the 20 year study period despite a ~40% reduction in SO_4^{2-} deposition. The strong correlation between ANC decline and low antecedent discharge demonstrates that episodic acidification during rain events is strongly associated with preceding drought conditions, especially in wetland-dominated catchments. The results have important implications for recovery from acidification, especially in northern ecosystems where climate scenarios forecast that warmer and drier conditions will be more common.

Introduction

A significant reduction in anthropogenic acidic deposition in North America and western Europe has led to a progressive recovery from acidification in some surface waters (*1*−*4*). However, many other sites show limited or no recovery (*5, 6*), while others perform a recovery that is reversed frequently by climate-related events (*7, 8*). Most assessments of acidification recovery, undertaken for example within the framework of the International Cooperative Program on Assessment of Rivers and Lakes (ICP-waters (*1*)) and the European Commission's Environment and Sustainable Development Program (RECOVER: 2010 (*9*)), have used a monthly to yearly sampling frequency to follow changes in annual estimates of pH and Acid Neutralization Capacity (ANC). However, such assessments do not adequately address the biological significance of chemical recovery because aquatic biota are strongly affected by transient pH and ANC declines associated with snowmelt and rain episodes.

Most previous work on episodic acidification has been short term because long-term, intensive sampling programs are costly and labor intensive (*10*). Except for a few studies of snowmelt induced acidification (*11, 12*) analysis of trends in episodic acidification over the longer term has been constrained by a lack of data with a sampling resolution adequate for detecting episodic events. It has therefore been difficult to discern if temporal changes in the intensity of episodic pH and ANC declines are an expression of their inherent variability, or changes in acid deposition, and/or climatic variability.

Climatic change toward warmer conditions is expected for most of the terrestrial world (*13*). Although it is difficult to predict hydrological feedback effects using physical climate models (*14*), an outcome expected from greenhouse gas-induced global warming is an intensification of weather extremes, including droughts and floods (*13*). Summer droughts have been shown to cause extensive biogeochemical perturbations in soils and surface waters (*15*−*17*). One of the more pronounced biogeochemical effects of a summer drought in humid glaciated regions is the draw down of the water table of wetlands which results in reoxidation of previously reduced compounds. Reports from acidified regions in Europe and North America have shown that this reoxidation of previously water-logged organic soil leads to pulses of acidic, SO_4^{2-} rich water (*18*−*20*). Transient changes in ANC associated with acidic episodes pose a potentially large threat to many aquatic communities (*21*). It is unknown, however, whether these drought-induced episodes will be affected by climate change and if a decline in acidic precipitation will reduce their future intensity.

In this paper we evaluate the importance of summer and fall drought on episodic acidification in nine headwater streams in central Ontario that have been intensively monitored for nearly two decades. Using an ANC dilution model (*22*), 311 hydrological episodes have been analyzed in order to separate and quantify the driving mechanisms of ANC decline during summer and fall episodes. The objective was to determine if the two-decade-long decline in acid deposition observed over much of northeastern North America (*5, 6, 23*) has resulted in measurable water chemistry improvements with regard to episodic acidification of streams in central Ontario.

Study Region and Data

Of the nine long-term monitored streams considered in this study, three (S1, S47, and S50) are located in the Turkey Lakes Watershed (TLW, 47° N, 84° W) approximately 50 km north of Sault Ste Marie in the Algoma region of central Ontario (Figure 1). The remaining six streams drain into Plastic Lake (PC1) and Harp Lake (HP3, HP3A, HP4, HP5, and HP6A) which are within 50 km of Dorset in the Muskoka-Haliburton region of south-central Ontario (45° N, 78° W). Detailed information on the TLW is presented by Jeffries et al. (*24*), and Devito and Dillon (*25*) and Dillon and Molot (*26*) provide further detail on the Harp and Plastic catchments.

The study catchments range in size from 4 to 185 ha. Wetlands, which typically occupy bedrock depressions and valley bottoms in this region (*20*), cover 0% to 13% of the catchment areas. All streams were sampled on a weekly or more frequent basis for most of the period between 1983 and 1999. During this monitoring period, 311 hydrological episodes were identified in the nine streams.

At the TLW SO_4^{2-} deposition declined by 43% between 1982 and 1999, and NO_3^- deposition exhibited no trend (*27*). Similarly, at the Plastic and Harp Lake sites, deposition of

* Corresponding author phone: +46-90-786 8509; e-mail: Hjalmar.Laudon@sek.slu.se.
† Swedish University of Agricultural Sciences.
‡ Trent University.
§ National Water Research Institute.

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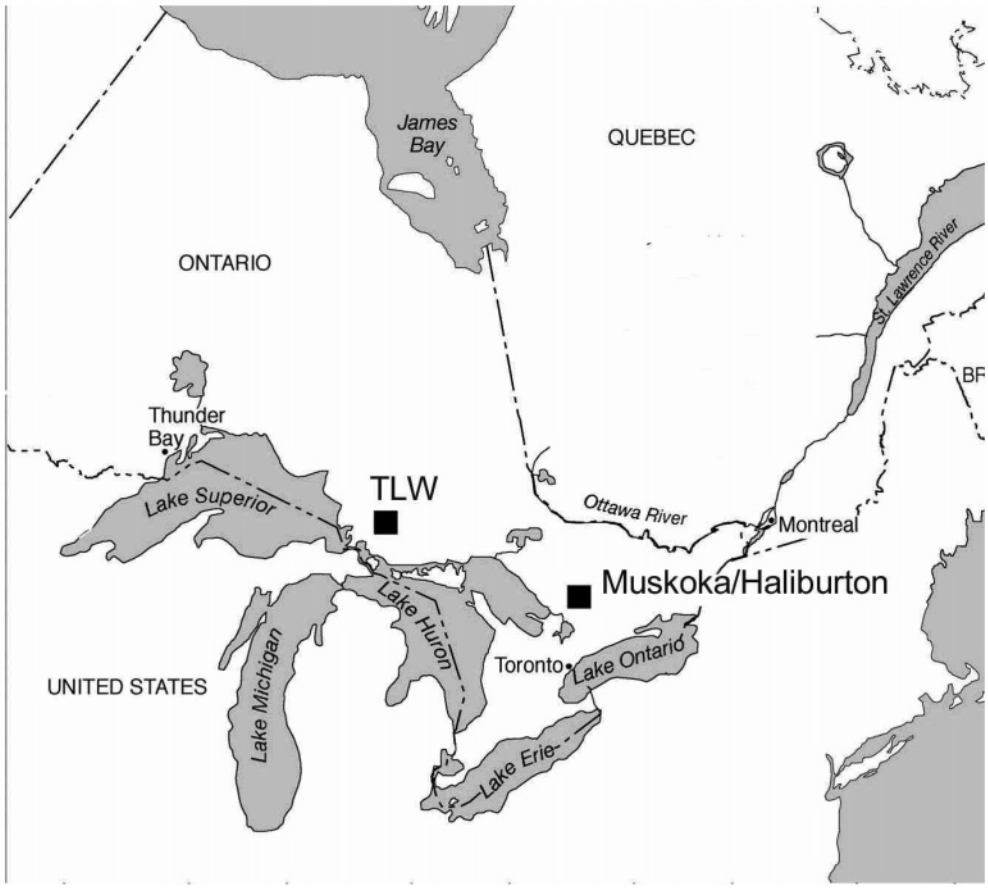

FIGURE 1. Study locations.

SO_4^{2-} has declined by 40−45% since 1980, with most of the decline occurring in the first 7 or 8 years (*7*, *23*). At the same time, N deposition has remained approximately constant.

At the TLW, stream samples were taken at least weekly at the weir where continuous records of stream stage were recorded. Immediately after collection, water samples were analyzed for pH and specific conductance and then processed for further chemical analysis. Gran alkalinity, NO_3^-, NH_4^+, and DOC were generally determined within 24 h; samples for other major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}) were stored at 4 °C until analysis. The accuracy of ion data for individual samples was evaluated by calculating electrochemical charge balances, and any outlying sample (beyond ±10% of the charge balance) was reanalyzed and the data were accepted or rejected.

Water samples from the Muskoka-Haliburton streams were collected approximately weekly over the period of study. Samples were coarse filtered (80 μm Nitex) in the field and transported to the laboratory in insulated containers for chemical analysis. Samples were analyzed for major ions and DOC following standard methods and quality control procedures (*27*). Stream discharge is monitored continuously at a V-notched (PC1, HP3, HP3A, HP6A) or H-flume (HP4, HP5) weir at the base of each catchment.

Data Analysis

The 311 rain-driven summer and fall episodes considered in this study were analyzed using the ANC dilution model (ADM (*22*)) see Appendix A. A similar model has been used to distinguish quantitatively the driving mechanisms of transient episodic decline of ANC in northern Sweden during snowmelt-driven hydrological episodes (*12*, *28*), rain-driven episodes (*29*), and during rain-on-snow events in Nova Scotia, Canada (*11*). The ADM separates and quantifies the relative contribution of sulfate, nitrate, chloride, organic-acidity, and dilution, respectively, to episodic declines in ANC.

Episodes in the data record were identified based on hydrological changes. An episode was defined as a 10-fold (or more) increase in discharge from one sample occasion to the next e.g. 0.001 to 0.01 L s^{-1} or 10 to 100 L s^{-1}. Antecedent discharge was calculated as the average discharge during the 10 days preceding the episode. In the case where the streams became completely dry prior to an event, antecedent discharge was calculated as an average of the dry period and the 10 preceding days thereby allowing the antecedent discharge to become infinitely small (but never zero) depending on how long the stream had been dry.

Results

The total ANC decline ($\Delta ANC_{(tot)}$) was logarithmically correlated ($p<0.05$) to antecedent discharge in eight of the nine streams (Figure 2), catchment S47 in the TLW being the exception. The lower the runoff preceding each episode (which is used as a surrogate for antecedent moisture conditions in the catchments) the larger the ΔANC_{tot} became. Although most streams follow the same general pattern, there were distinct differences between sites. In eight of the nine streams SO_4^{2-} was the most important driving mechanism of the decline in ANC. Again, catchment S47 was the exception, where NO_3^- was the most important driving mechanism. The second most important factor influencing ANC varied among sites, but dilution as well as organic acidity affected ANC in several streams (Table 1).

Because of the hydrology-based definition of episodes, the hydrochemical response did not always result in a decline in ANC; in approximately 5% of the analyzed episodes, ANC

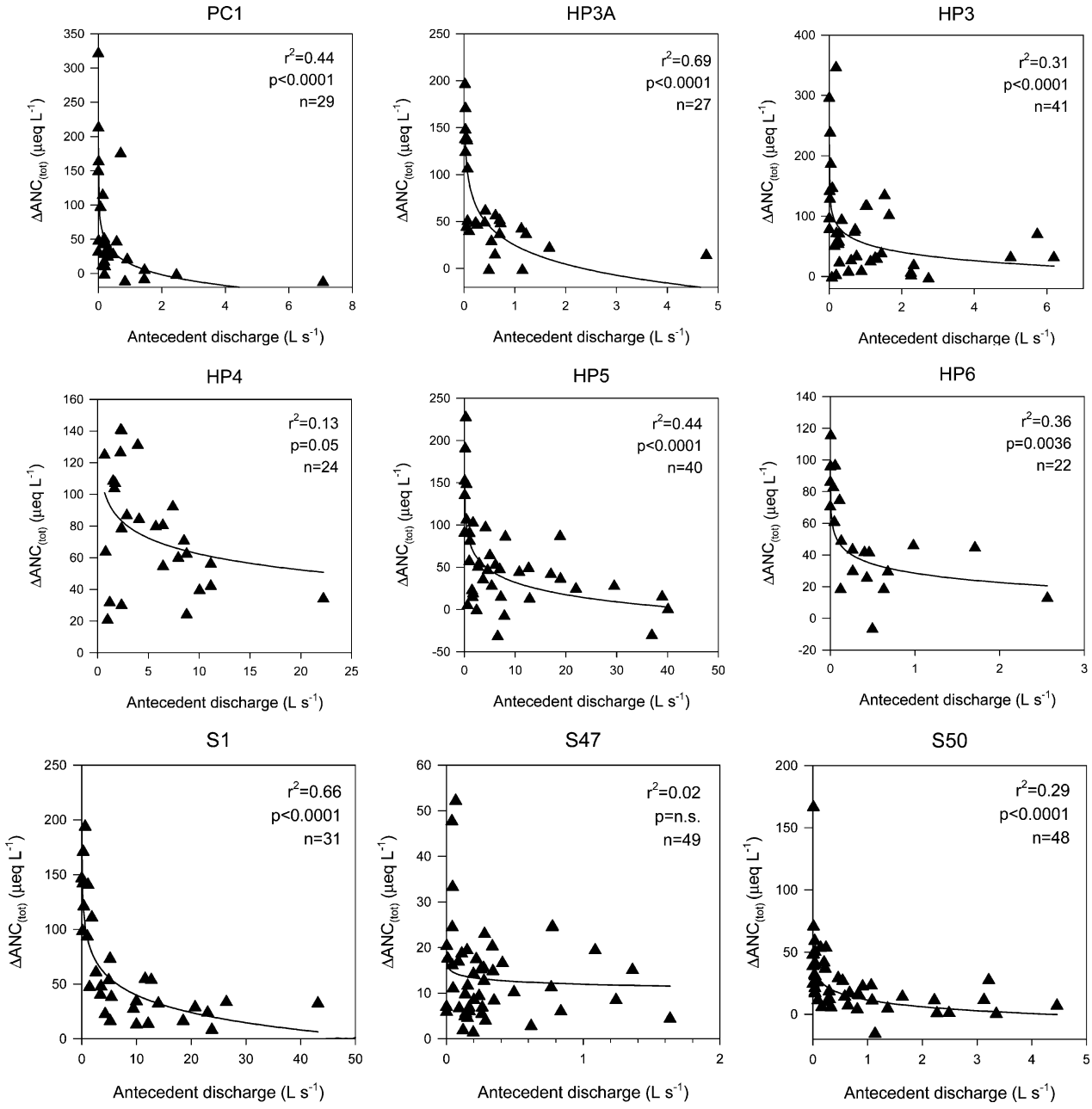

FIGURE 2. Relationship between antecedent discharge and $\Delta ANC_{(tot)}$ during episodes in the nine streams.

increased as a result of increasing runoff. Both base cations and most of the strong acid anions counteracted the ANC decline during certain episodes. The increased ANC caused by dilution was an effect of an increased BC concentration during the episode. The increased ANC from acid anions was due to a larger relative decrease in the anion concentration compared to the change in the dilution index.

There was a strong correlation between calculated ANC and titrated Gran alkalinity (r^2=0.94; $p<0.0001$; n=7597; Figure 3). This suggests that the assumed 5 μeq mg^{-1} of TOC (*30*, *31*) is an appropriate estimate of strong organic acidity in the study sites.

To analyze if the intensity of the driving mechanisms of ΔANC changed over the 20-year study period due to the decline in SO_4^{2-} deposition, the episodes at each site were separated into antecedent discharge-based quartiles. In none of the antecedent discharge-based quartiles was a statistically significant ($p>0.1$) change in $\Delta ANC_{(poll)}$ observed. However, the average $\Delta ANC_{(poll)}$ for the lowest antecedent discharge-based quartile was significantly correlated with the areal extent of wetlands (r^2=0.60; p=0.01; Figure 4).

Discussion

The strong correlation between $\Delta ANC_{(tot)}$ and antecedent discharge at individual streams demonstrates that episodic acidification during rain events is strongly associated with preceding drought conditions. The results also indicate that drought-induced episodic acidification is further enhanced in wetland-dominated catchments caused by reoxidation of sulfur. Several reports of the effect of reoxidation of sulfur sources in organic soils have been presented previously (*18*−*20*), and the linkage of hydrological data and geochemical influence on runoff chemistry has successfully been used to predict acid deposition effect on water quality (*21*, *32*−*34*). However, this is one of the first reports that quantifies the relationship between the anthropogenic contribution to the ANC decline during hydrological episodes and its correlation to drought conditions. The results from this study have

TABLE 1. Contribution from the Different Driving Mechanisms in μeq L^{-1} to the $\Delta ANC_{(tot)}$ at Different Runoff Quartiles[a]

S1	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	86	−9	3	16	43
2nd quartile	33	−9	4	12	17
3rd quartile	16	−5	2	7	8
4th quartile	15	5	1	0	7
S50	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	45	1	0	4	−1
2nd quartile	27	0	1	1	−1
3rd quartile	23	0	0	−4	−4
4th quartile	8	1	1	0	0
S47	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	6	10	2	5	5
2nd quartile	1	10	2	5	3
3rd quartile	4	6	1	5	2
4th quartile	4	6	1	5	2
PC1	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	271	−50	−14	−47	1
2nd quartile	69	4	−2	−33	1
3rd quartile	49	−3	2	−18	2
4th quartile	16	0	5	10	−5
HP3A	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	124	12	5	−2	−4
2nd quartile	54	−1	5	5	−5
3rd quartile	18	0	0	5	−11
4th quartile	11	2	1	4	−10
HP3	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	189	−10	40	−48	−35
2nd quartile	46	0	35	4	−7
3rd quartile	37	0	−9	10	14
4th quartile	38	2	−8	1	11
HP4	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	43	0	5	7	19
2nd quartile	38	−1	5	16	55
3rd quartile	32	−1	2	15	38
4th quartile	24	1	5	9	15
HP5	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	139	1	1	2	−27
2nd quartile	40	1	−2	−7	2
3rd quartile	39	0	−4	−4	6
4th quartile	29	0	−3	−9	8
HP6A	ΔSO_4^{2-}	ΔNO_3^-	ΔCl^-	ΔA^*	ΔDil
1st quartile	244	−1	−20	−45	47
2nd quartile	86	−1	0	−41	15
3rd quartile	72	0	−11	−31	2
4th quartile	41	−1	−3	−18	1

[a] The 1:st quartile is the 25% of episodes with the lowest antecedent runoff in each stream. The 4:th quartile is the episodes with the highest antecedent runoff.

important implications for the prediction of acidification recovery in the future especially in northern ecosystems where climate scenarios forecast that warmer and drier conditions will be especially prominent (*13*).

The rapid release of SO_4^{2-} causing the large $\Delta ANC_{(poll)}$ associated with drought conditions is clearly not primarily caused by the most recent deposition of atmospheric sulfur. Instead, previous work in the Plastic Lake and Harp Lake watersheds has shown that transformation and mobilization

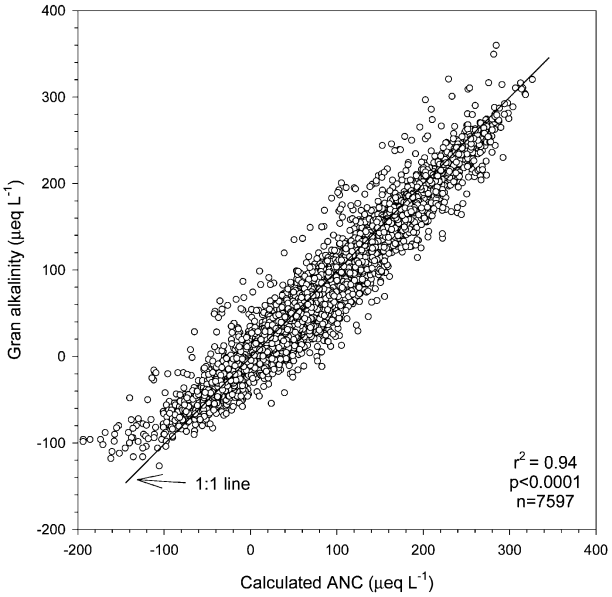

FIGURE 3. Correlation between titrated Gran alkalinity and calculated ANC using eq 1.

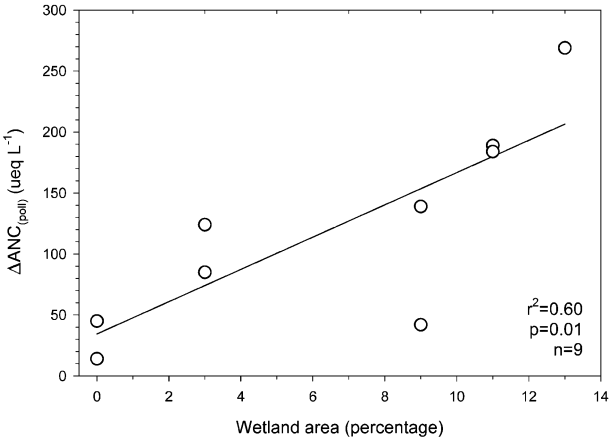

FIGURE 4. Relationship between average $\Delta ANC_{(poll)}$ of the lowest antecedent discharge quartile and percentage wetland in the nine catchments.

of stored reduced SO_4^{2-} is strongly related to the hydrogeology of wetlands (*19, 20*). Recent trend analyses at the Turkey Lakes Watershed also demonstrate that long-term or multiseason drought-induced SO_4^{2-} mobilization retards a general acidification recovery (*27*). Alewell et al. (*35*) hypothesized that mineralization of organic S compounds in organic soils could be an important mechanism in generating SO_4^{2-} rich pulses, which at least temporarily transform some catchments from SO_4^{2-} sinks to sources. A plausible explanation for the strong correlation between low antecedent discharge, $\Delta ANC_{(poll)}$, and the areal extent of wetlands in this study is that the lowering of the groundwater level in organic rich soils leads to oxidation of previously reduced S compounds which transforms immobile sulfides to readily mobile sulfates that are washed out during hydrological episodes (*8, 20*). Sulfur isotope analyses at the Plastic and TLW catchments have indicated that SO_4^{2-} export in wetland outflows is largely a function of S redox reactions in peat (*36*).

In contrast to drought-induced acid episodes, where SO_4^{2-} is the most important driving mechanism, episodes associated with snowmelt are often more affected by dilution (*28, 37*). In a snowmelt study in Dorset by Molot et al. (*38*) it was demonstrated that SO_4^{2-} was important mainly in the streams that were most acidic. In a long-term analysis of the response

of spring flood episodes to declining SO_4^{2-} deposition in northern Sweden (*12*), $\Delta ANC_{(poll)}$ was found to be strongly correlated with the amount of SO_4^{2-} in the snowpack. This suggests that previously deposited SO_4^{2-} is relatively unimportant during spring flood episodes at these northern study sites, although large $\Delta ANC_{(poll)}$ episodes could be observed during rain fall events following periods of drought (*29*).

In general both the Turkey Lakes and Dorset regions have experienced a decline in streamwater SO_4^{2-} concentration (without an equivalent increase in alkalinity and/or pH) over the last two decades that has been driven by a decline in acid deposition (*1*, *27*, *39*). Despite the general decline in streamwater SO_4^{2-}, no improvement in drought-induced SO_4^{2-} acid pulses was found in the study streams. The magnitude of these SO_4^{2-} pulses is primarily dependent on the size and particularly the lability of sulfur pools in catchment soil and wetlands. The future magnitude of SO_4^{2-} pulses will likely be determined by the frequency and magnitude of drought conditions, which strongly influence the conversion of reduced S in wetland soil to the more mobile SO_4^{2-} form. Drying and rewetting of forest floor material has also been shown to release SO_4^{2-} although at a lower magnitude than observed in wetland peat (*40*). The rather stabile $\Delta ANC_{(poll)}$ for the lowest antecedent discharge-based quartile over the almost 20 year study period, despite a ~40% decline in sulfur deposition in eastern Canada, suggests that the source pool of SO_4^{2-} in soils is significantly larger than the export associated with drought induced episodes. In catchment PC1, Eimers et al. (*41*) calculated that current net annual stream export of SO_4^{2-} constitutes only a few percent of the S pool in the catchment. Therefore, despite a likely continuation of emission reductions over most of North America, drought-induced SO_4^{2-} episodes will probably continue to cause large episodic ANC declines in the foreseeable future.

Only a few degrees change in average annual temperature has increased evaporation rates and caused many permanent first-order streams in northwestern Ontario to become ephemeral, without a change in precipitation pattern (*42*). In the TLW, the annual average temperature increased by 0.11 °C yr^{-1} during the study period, with the majority of change occurring in the spring and fall months resulting in a longer warm season (*27*). A declining water yield at catchments in the TLW was attributed to increased evapotranspiration because there was no trend in precipitation (*42*).

Global climate models predict a further increased temperature in central Canada during the coming decades without major changes in precipitation patterns (*13*). As evaporation increases with rising temperature the future is likely to bring more frequent and pronounced drought conditions in the study region. If this prediction is correct, toxic summer episodes at Dorset and Turkey Lakes could possibly become more frequent and even more acidic especially in catchments containing wetlands.

The results from this study could have important ecological implications for many streams and lakes. It is not large hydrological episodes during summer and fall periods that create the most critical hydrochemical conditions. Instead, the most toxic situations causing the largest episodic decreases in ANC are associated with precipitation events following drought conditions, with associated runoff that is often below the summer average.

In summary, severe drought conditions are found to cause the highest anthropogenic contribution to the ANC decline during rain-induced episodes in central Ontario, particularly in basins containing wetlands. This study demonstrates that long-term streamwater data can be used to estimate the episodic response of streamwater chemistry to climate variability and also shows that failure to account for hydrological episodes may overemphasize the role of declining acid deposition in many surface waters. It is likely that other regions in northern climates with wetland areas may be similarly sensitive to drought conditions.

Appendix A

The ANC dilution model (ADM) is based on the observed ANC ($ANC_{(obs,t)}$) at any time "t" during the flow event (eq 1) and a dilution index ($DI_{(t)}$; eq 2). DI is used to estimate the dilution of ANC as well as the changes in ANC that can be attributed to the strong mineral and organic acid anions: sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and organic acids (A*). The sum of base cations (BC = $[Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]$) is used in the determination of the DI (eq 2). Base flow ANC ($ANC_{(base)}$) is used as a benchmark in the model against which transient changes in ANC (ΔANC) are calculated

$$ANC_{(obs,t)} = \sum \text{base cations}_{(t)} - \sum \text{strong acid anions}_{(t)}$$

$$= [BC]_{(t)} - [SO_4^{2-}]_{(t)} - [NO_3^-]_{(t)} - [Cl^-]_{(t)} - [A^*]_{(t)} \quad (1)$$

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

where concentrations of BC, SO_4^{2-}, NO_3^-, Cl^-, and A* are expressed as μequiv L^{-1}. The contribution of strong organic acidity to the ANC is estimated from eq 3 (*30, 31*).

$$[A^*] = [TOC] \times 5\ \mu\text{equiv mg}^{-1}\ [TOC] \quad (3)$$

The decline in ANC resulting from dilution alone (ΔANC_{dil}) is calculated as if the five components in the ANC expression dilute in the same proportions as DI (eq 4)

$$\Delta ANC_{(dil,t)} = ANC_{(base)} \times DI_{(t)}$$

$$= (BC_{(base)} - SO_4^{2-}{}_{(base)} - NO_3^-{}_{(base)} - Cl^-{}_{(base)} - A^*{}_{(base)}) \times DI_{(t)} \quad (4)$$

where the subscript "base" denotes a water sample that is collected during the low flow or baseflow period prior to the hydrological event and "t" denotes water that is collected at any point in time during the episode.

The combined effect of dilution and the individual strong acid anions, for example SO_4^{2-} ($\Delta ANC_{(dil+SO4,t)}$), excluding the contribution from the remaining three acids (NO_3^-, Cl^-, and A*) to the ANC decline, are calculated as if BC, NO_3^-, Cl^-, and A* are diluted in the same proportion as DI, while the measured concentration of SO_4^{2-} was used for each sample (eq 5a). Similarly, the combined effect of dilution and NO_3^- ($\Delta ANC_{(dil+NO3,t)}$), dilution and Cl^- ($\Delta ANC_{(dil+Cl,t)}$), and dilution and organic acidity ($\Delta ANC_{(dil+A^*,t)}$), on the ANC decline during the episode were calculated using eqs 5b, 5c, and 5d, respectively.

$$\Delta ANC_{(dil+SO4,t)} = (BC_{(base)} - NO_3^-{}_{(base)} - Cl^-{}_{(base)} - A^*{}_{(base)}) \times DI_{(t)} - SO_4^{2-}{}_{(t)} \quad (5a)$$

$$\Delta ANC_{(dil+NO3,t)} = (BC_{(base)} - SO_4^{2-}{}_{(base)} - Cl^-{}_{(base)} - A^*{}_{(base)}) \times DI_{(t)} - NO_3^-{}_{(t)} \quad (5b)$$

$$\Delta ANC_{(dil+Cl,t)} = (BC_{(base)} - SO_4^{2-}{}_{(base)} - NO_3^-{}_{(base)} - A^*{}_{(base)}) \times DI_{(t)} - Cl^-{}_{(t)} \quad (5c)$$

$$\Delta ANC_{(dil+A^*,t)} = (BC_{(base)} - SO_4^{2-}{}_{(base)} - NO_3^-{}_{(base)} - Cl^-{}_{(base)}) \times DI_{(t)} - A^*{}_{(t)} \quad (5d)$$

The discrete effect of SO_4^{2-}, NO_3^-, Cl^-, and A* on the ANC decline during the episode was calculated using eqs 6a, 6b,

6c, and 6d, respectively.

$$\Delta ANC_{(SO4,t)} = ANC_{(dil+SO4,t)} - ANC_{(dil,t)} \quad (6a)$$

$$\Delta ANC_{(NO3,t)} = ANC_{(dil+NO3,t)} - ANC_{(dil,t)} \quad (6b)$$

$$\Delta ANC_{(Cl,t)} = ANC_{(dil+Cl,t)} - ANC_{(dil,t)} \quad (6c)$$

$$\Delta ANC_{(A^*,t)} = ANC_{(dil+A^*,t)} - ANC_{(dil,t)} \quad (6d)$$

The combined effect of all driving mechanisms on the transient ANC decline ($\Delta ANC_{(tot)}$) was calculated using eq 7, whereas the anthropogenic ($\Delta ANC_{(poll)}$) and natural ($\Delta ANC_{(nat)}$) driving mechanisms were estimated using eqs 8 and 9, respectively.

$$\Delta ANC_{(tot,t)} = \Delta ANC_{(dil,t)} + \Delta ANC_{(SO4,t)} + \Delta ANC_{(NO3,t)} + \Delta ANC_{(Cl,t)} + \Delta ANC_{(A^*,t)} \quad (7)$$

$$\Delta ANC_{(poll,t)} = \Delta ANC_{(SO4,t)} + \Delta ANC_{(NO3,t)} \quad (8)$$

$$\Delta ANC_{(nat,t)} = \Delta ANC_{(dil,t)} + \Delta ANC_{(Cl,t)} + \Delta ANC_{(A^*,t)} \quad (9)$$

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