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Acid Rain Effects on Aluminum Mobilization Clarified by Inclusion of Strong Organic Acids

G. B. LAWRENCE,*,† J. W. SUTHERLAND,‡
C. W. BOYLEN,§
S. W. NIERZWICKI-BAUER,§ B. MOMEN,∥
B. P. BALDIGO,† AND H. A. SIMONIN⊥

*U.S. Geological Survey, 425 Jordan Road, Troy, New York
12180, P.O. Box 2641, Nantucket, Massachusetts 02584,
Darrin Fresh Water Institute, Rensselaer Polytechnic Institute,
5060 Lakeshore Drive Bolton, Landing, New York 12810,
Department of Natural Resource Sciences and Landscape
Architecture, University of Maryland, College Park, Maryland
20742, and New York State Department of Environmental
Conservation, 8314 Fish Hatchery Road, Rome, New York
13440*

Assessments of acidic deposition effects on aquatic ecosystems have often been hindered by complications from naturally occurring organic acidity. Measurements of pH and ANC_G, the most commonly used indicators of chemical effects, can be substantially influenced by the presence of organic acids. Relationships between pH and inorganic Al, which is toxic to many forms of aquatic biota, are also altered by organic acids. However, when inorganic Al concentrations are plotted against ANC (the sum of Ca^{2+}, Mg^{2+}, Na^+, and K^+, minus SO_4^{2-}, NO_3^-, and Cl^-), a distinct threshold for Al mobilization becomes apparent. If the concentration of strong organic anions is included as a negative component of ANC, the threshold occurs at an ANC value of approximately zero, the value expected from theoretical charge balance constraints. This adjusted ANC is termed the base-cation surplus. The threshold relationship between the base-cation surplus and Al was shown with data from approximately 200 streams in the Adirondack region of New York, during periods with low and high dissolved organic carbon concentrations, and for an additional stream from the Catskill region of New York. These results indicate that (1) strong organic anions can contribute to the mobilization of inorganic Al in combination with SO_4^{2-} and NO_3^-, and (2) the presence of inorganic Al in surface waters is an unambiguous indication of acidic deposition effects.

Introduction

Assessments of the effects of acidic deposition on terrestrial and aquatic ecosystems have long been complicated by natural acidity derived from acidic functional groups of dissolved organic carbon (DOC) (*1*). Derived from the decay of plant matter, DOC can influence pH, ANC_G (ANC deter-

* Corresponding author phone: (518) 285-5601; fax: (518)285-5601; e-mail: glawrenc@usgs.gov.
† U.S. Geological Survey.
‡ P.O. Box 2641, Nantucket, Massachusetts 02584.
§ Rensselaer Polytechnic Institute.
∥ University of Maryland.
⊥ New York State Department of Environmental Conservation.

mined by Gran titration), and Al mobilization and speciation (*2*). In lakes in the Adirondack region of New York, where effects of acidic deposition may be more severe than in any region in the United States, DOC concentrations have been shown to vary by more than a factor of 10 (*1*). Application of a triprotic model of organic acidity showed that an increase in DOC concentration of 183 μmol L^{-1} would decrease ANC_G by 10 μeq L^{-1} in Adirondack lakes (*3*). Similar efforts to account for natural acidity during high flows in European surface waters have been made (*4*). The influence of organic acidity also complicates assessments of recovery from acidification because concentrations of DOC have increased over the past 10−15 years in the Adirondack region, as well as in other regions in the eastern United States (*5*), at the same time that S deposition has been decreasing (*6*).

Despite the well-known effects of natural organic acids on ANC_G, this measurement continues to serve as the primary chemical indicator in the United States for assessing past effects of acidic deposition, and the recovery expected from decreasing atmospheric deposition (*5*, *7*). European assessments use a different approach, in which acidification is measured by the sum of base cation concentrations (Ca^{2+}, Mg^{2+}, Na^+, K^+) minus the sum of inorganic strong-acid anion concentrations (SO_4^{2-}, NO_3^-, Cl^-), which has been termed both ANC (*8*), and calculated ANC (*9*). The sum of base-cation concentrations reflects the ability of a watershed to neutralize acid inputs through the release of base cations, and the sum of inorganic strong-acid anions largely reflects the input of acidic deposition. The difference in these two quantities (hereafter referred to as ANC) provides a relative measure of acidic deposition effects, whereas ANC_G reflects the acid neutralizing capacity of the complete chemical system, including weak acids associated with DOC and inorganic Al (*1*).

The most common indicators used to infer biological effects of acidic deposition are pH and Al concentrations because they can be directly toxic to biota. The health of biota does not relate directly to ANC_G or ANC, but fish status has been shown to be empirically related to ANC (*7*). In high-DOC waters, the strength of this relationship was increased when the concentration of strong organic anions was included as a component of ANC (*10*). Although most species of plants and animals are sensitive to certain ranges of pH, naturally acidic environments with indigenous species are common in areas affected by acidic deposition (*11*).

Inorganic Al, the form of Al toxic to many forms of aquatic biota, can be dissolved within the soil by acidic deposition, then hydrologically transported into surface waters (*12*). Organically complexed Al is mobilized in the soil by organic acids as part of the natural process of podzolization, but has been shown to have little or no toxic effects in aquatic environments (*13*).

To assess recovery from acidification, chemical measurements are needed to distinguish acid rain effects from natural acidity more clearly than those in current use. More information is needed on how pH, ANC_G, ANC, and Al relate to each other in reflecting natural vs human-induced acidification processes to accurately quantify recovery. Therefore, the objective of this paper is to investigate relationships among these measurements in an effort to develop an assessment approach that can identify chemical changes resulting exclusively from acidic deposition.

Materials and Methods

Streamwater data from three programs are presented in this paper. Through the Adirondack Effects Assessment Program

(AEAP), samples from the North and South Tributaries of Buck Creek, in the western Adirondack region of New York, were collected approximately biweekly for water years 1999–2004. During this period, samples were also collected during high-flow events with automated samplers, April through November. Data for approximately 250 samples from each tributary are presented here. Further details of the Buck Creek tributary watersheds are available elsewhere (14).

Through the Western Adirondack Stream Survey (WASS), stream samples were collected in two surveys conducted in the western Adirondack region October 28–30, 2003, and March 29–31, 2004. Approximately 200 streams were selected randomly from a population of 565 streams that were (1) identified as accessible, and (2) had less than 25% of their drainage area affected by upstream ponds and lakes. Most selected streams were sampled in each survey so that approximately 195 samples were collected in both October 2003 and March 2004.

Through the U.S.EPA Long-Term Monitoring (LTM) Program, samples were collected for water years 2001–2004 in Winnisook reach, the uppermost headwaters of the West Branch of the Neversink River, in the Catskill Mountain region of New York. Samples were collected approximately biweekly throughout the year and during high-flow events with automated samplers from April through November. Data for 238 samples are presented here. Further information on Winnisook Reach and its watershed are available elsewhere (15).

Water temperature was recorded at all sites and all samples were analyzed for pH, ANC_G, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-, total F, DOC, Si, NH_4^+, total monomeric Al, and organic monomeric Al (hereafter organic Al). Inorganic monomeric Al (hereafter inorganic Al) was determined by subtracting organic Al from total monomeric Al. Samples from Buck Creek and Winnisook Reach were analyzed at the U.S. Geological Survey Laboratory, Troy, New York, according to published methods (16). Samples collected in the extensive stream surveys were analyzed in the Adirondack Lakes Survey Corporation Laboratory according to U.S.EPA methods (5). The chemical equilibrium model, ALCHEMI (17), was used to estimate the charge of inorganic Al species for the purpose of developing charge balances. Because a reliable method has not been developed to estimate the charge of organically complexed Al species we assumed a charge of 2+ to calculate the charge balances. Had a charge of 1+ been assumed, the estimate of strongly acidic organic anion concentrations would have been lowered by only 4.6 and 3.2 μeq L^{-1}, for the October 2003 and March 2004 stream survey data, respectively,

Concentrations of strongly acidic organic anions (hereafter strong organic anions) were estimated by first determining the charge balances in samples from the October 2003 and March 2004 stream surveys that had pH values from 4.0 to 4.5. These datasets were used because they had a significant number of samples in this pH range. The only charged species in solution that was not measured in these low-pH samples was assumed to be deprotonated (strongly acidic) organic functional groups. Organic functional groups that generally would be considered weakly acidic would be protonated (uncharged) in this pH range. Anion deficits of these low-pH samples were therefore assumed to represent the concentration of strongly acidic organic functional groups. To verify our assumption, anion deficits for these samples were related to DOC concentrations (Figure 1). The strength and linearity of this relationship over a large range in DOC concentrations indicates that the concentration of titratable organic anions in the pH range of 4.0 to 4.5 was low relative to the concentration of organic anions that would remain unprotonated in this range (1). On this basis, the anion deficit was considered to be a valid approximation of strongly acidic
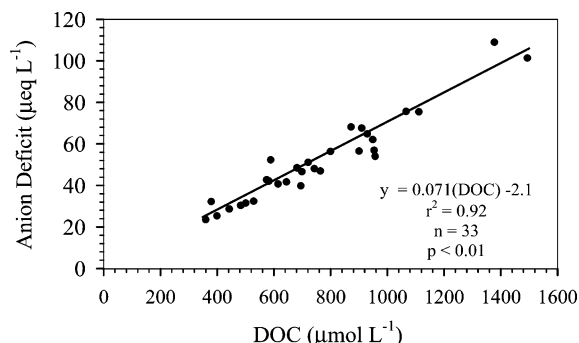

FIGURE 1. Anion deficits of charge balances, as a function of dissolved organic carbon (DOC) concentrations, in western Adirondack stream samples with pH values 4.0–4.5. The best-fit line determined by linear regression is also shown.
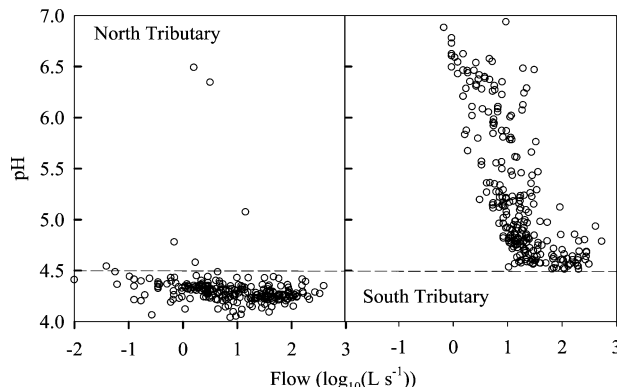

FIGURE 2. pH as a function of flow in the North and South Tributaries of Buck Creek.

organic anion concentrations for samples with pH values from 4.0 to 4.5.

Most of the samples from the two stream surveys had pH values above 4.5. In these samples the anion deficit could not be used to estimate strongly acidic organic anion concentrations because some of the weakly acidic functional groups would also be unprotonated (charged) and contribute to the anion deficit. However, the acid–base properties of DOC have been shown to be similar across regions of similar vegetation and environmental conditions (18). Therefore, the concentrations of strong organic anions for samples with a pH value above 4.5 were calculated from DOC concentrations and the equation developed in Figure 1, and shown below.

$$RCOO^-_s = 0.071(DOC) - 2.1 \qquad (1)$$

Results and Discussion

Contrasting Stream Chemistry in Neighboring Watersheds. Water chemistry in the Buck Creek tributaries is characteristic of the two general types of acidic regimes found in the Adirondack region. The North Tributary can be considered chronically acidic, with pH values that remain mostly below 4.5 and do not vary with changes in flow. The South Tributary can be considered episodically acidic, with pH values that vary over 2 units and are lowest during periods of high flow (Figure 2). These streams drain nearby watersheds with similar geology and levels of acidic deposition.

The difference in pH between these two streams is largely the result of differences in organic acidity associated with DOC. Concentrations of DOC in the South Tributary seldom exceed 500 μmol L^{-1}, whereas concentrations of DOC in the North Tributary are seldom less than 1000 μmol L^{-1}. The headwater wetland and thick forest floor (average thickness
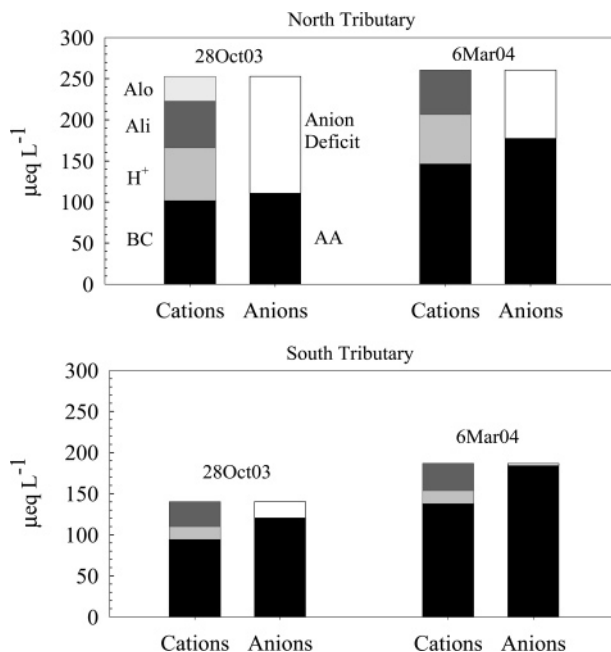
FIGURE 3. Charge balances in stream samples collected on October 28, 2003, and March 6, 2004, in the North and South Tributaries of Buck Creek. BC represents base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+); Ali represents inorganic Al; Alo represents organic Al, AA represents inorganic strongly acidic anions (SO_4^{2-}, NO_3^-, and Cl^-).

FIGURE 4. Inorganic Al as a function of pH and ANC determined by Gran titration (ANC_G) in the North (a) and South (b) Tributaries of Buck Creek.

20.7 cm) throughout the North Tributary watershed provide abundant opportunity for the dissolution of soluble organic matter, whereas the relatively thin forest floor (average thickness 7.9 cm) of the South Tributary watershed produces relatively low concentrations of DOC throughout the year. Differences in the mobility of soluble organic matter derived from the abundant coniferous vegetation in the North Tributary vs that derived from the dominant beech vegetation in the South Tributary may also contribute to the difference in DOC concentrations between the streams (19). Previous work in the Adirondack region has shown that watersheds with abundant coniferous vegetation tend to have low pH and high DOC concentrations (20).

The chemical influence of organic acidity can be shown by comparing the charge balances of the predominant inorganic ions (those with concentrations >3 μeq L^{-1}). The unmeasured organic anion concentrations, estimated by the total difference between cation and anion bars, are considerably higher in the North Tributary than in the South Tributary (Figure 3) and higher during a high-flow event in the fall than during a snowmelt event in early March, when DOC concentrations were near their annual minimum.

Organic acidity also plays a role in the relationship between pH and inorganic Al in the North and South Tributaries. The general shape of the pH–Al relationship is similar between the streams, as is the range in concentrations of inorganic Al, despite a pH range of 4.0–4.5 for most samples in the North Tributary, and a pH range of 4.5–6.5 for samples in the South Tributary (Figure 4a). Higher concentrations of DOC in the North Tributary than in the South Tributary result in greater complexation of Al by organic functional groups, which lowers the concentration of inorganic Al at a given pH. The large anion deficit at low pH observed in the North Tributary, however, supports the existence of organic functional groups that are both unprotonated and uncomplexed with Al.

Inorganic Al concentrations in the North tributary showed little or no relationship to ANC_G as a result of the confounding influences of organic acidity and complexation (Figure 4b). In the South Tributary, however concentrations of inorganic
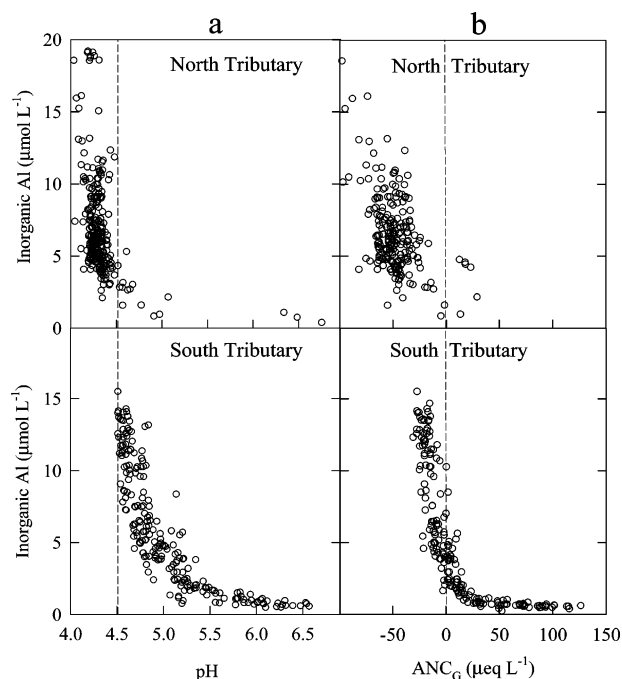
Al related to ANC_G in a manner similar to the relationship observed between inorganic Al concentrations and pH (Figure 4b). This similarity can be attributed to limited effects from weakly acidic organic acids in the South Tributary, which resulted in ANC_G being largely a function of pH (21). The Al concentration threshold at about pH 5.3 (Figure 4a) in the South Tributary can be attributed to pH-dependent solubility (21). Below pH 4.6, concentrations no longer appeared to be dependent on pH. Conservative behavior of inorganic Al concentrations with regard to pH, below a pH value of 4.6, has been shown previously in natural waters (22). Organic complexation (23) and uncertain controls of mineral solubility (24) at low pH complicate efforts to model dissolved Al concentrations in waters affected by acidic deposition.

The Al Mobilization Threshold. The relationships among pH, ANC_G, and inorganic Al in the two Buck Creek tributaries demonstrate the difficulty of discerning acidic deposition effects from natural processes of acidification. However, in each stream a distinct threshold is observed, below which inorganic Al concentrations increase linearly as the ANC decreases (Figure 5a and b). The threshold occurs at a higher ANC value in the North Tributary than in the South Tributary. In contrast, ANC is unrelated to organic Al concentrations in either stream, and the distribution of the values differs markedly between these streams (Figure 5c and d).

To test the generality of this relationship, data from the extensive stream surveys were plotted for October 2003 (Figure 6a) and March 2004 (Figure 6b). Based on Buck Creek data, DOC concentrations in streams of this region were near the annual maximum during the October 2003 sampling and near the annual minimum during the March 2004 sampling. A threshold relationship, similar to that seen in the Buck Creek tributaries, was observed for both sampling periods, and the value of the x-intercept was highest for the October 2003 survey, when DOC concentrations were also highest (Figure 6a).

These results suggest a role for organic acidity in the mobilization of inorganic Al. Mobilization of organically complexed Al by organic acids has long been recognized (25), but mobilization of inorganic forms of Al have tradi-
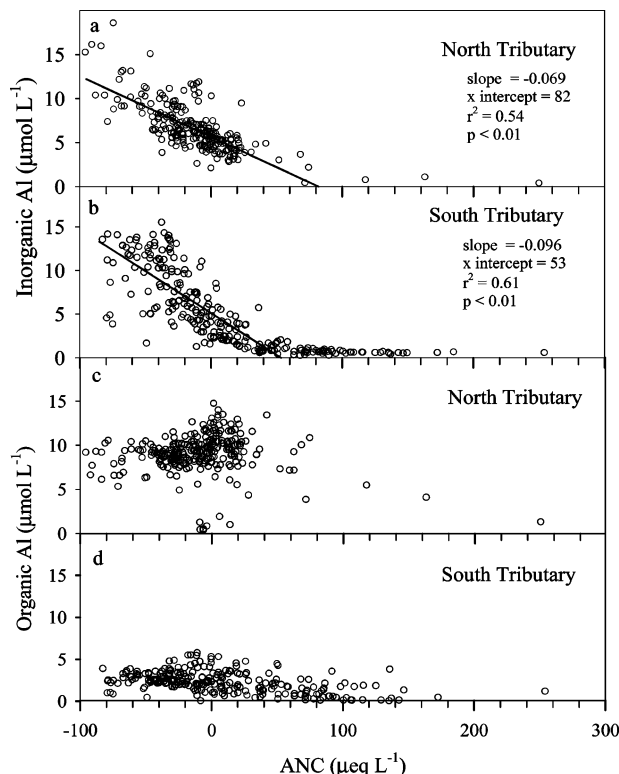
FIGURE 5. Inorganic Al as a function of ANC in the North (a) and South (b) Tributaries of Buck Creek, and organic Al as a function of ANC in the North (c) and South (d) Tributaries of Buck Creek. The best-fit lines in (a) and (b) are based only on data with an *x* value to the left of the *x*-intercept. The *x*-intercept was determined by iterative comparison between an estimate and the value determined by linear regression, after data to the right of the intercept were removed. Several points with base cation values greater than 300 μeq L^{-1} were omitted to facilitate graphing. All of these points had Al concentrations less than 1.0 μmol L^{-1}.
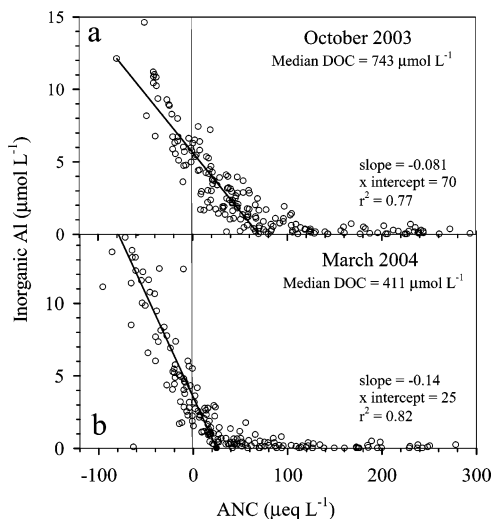

FIGURE 6. Inorganic Al as a function of ANC in stream surveys conducted in October 2003 (a), and March 2004 (b). The best-fit lines in (a) and (b) are based only on data with an *x* value to the left of the *x*-intercept. The *x*-intercept was determined by iterative comparison between an estimate and the value determined by linear regression, after data to the right of the intercept were removed. Several points with base cation values greater than 300 μeq L^{-1} were omitted to facilitate graphing. All of these points had Al concentrations less than 1.0 μmol L^{-1}.

tionally been attributed to strong inorganic acids from acidic deposition (*26*) or acid mine drainage (*22*). Nevertheless,
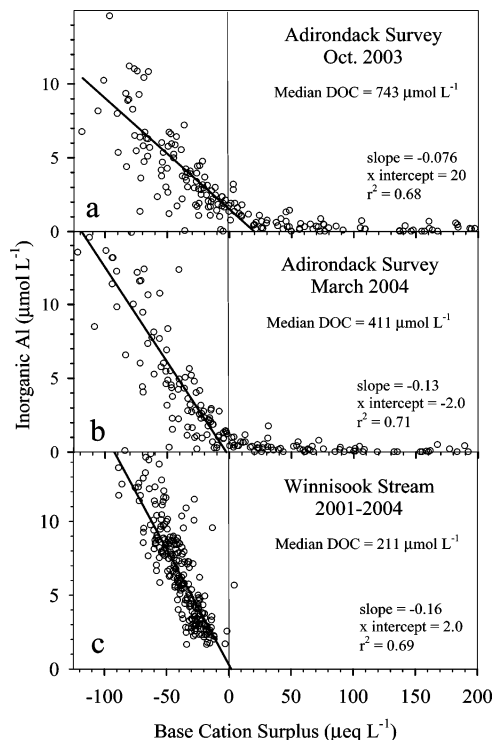

FIGURE 7. Inorganic Al as a function of base-cation surplus in stream surveys conducted in October 2003 (a), March 2004 (b), and in Winnisook Reach from 2001 to 2004 (c). The best-fit lines in (a), (b), and (c) are based only on data with an *x* value to the left of the *x*-intercept. The *x*-intercept was determined by iterative comparison between an estimate and the value determined by linear regression, after data to the right of the intercept were removed. Several points with base cation values greater than 200 μeq L^{-1} were omitted to facilitate graphing. All of these points had Al concentrations less than 1.0 μmol L^{-1}.

strongly acidic organic acids should be expected to behave similarly to strongly acidic inorganic acids with regard to mobilizing inorganic Al. If so, the ANC value would need to include strong organic anions. This adjusted ANC, termed the base-cation surplus, is defined by the following equation in which concentrations are expressed in μeq L^{-1}:

$$\text{base-cation surplus} = (Ca^{2+} + Mg^{2+} + Na^+ + K^+) - (SO_4^{2-} + NO_3^- + Cl^- + RCOO_s^-) \quad (2)$$

where $RCOO_s^-$ equals the concentration of strong organic anions.

Adjustment of ANC to include $RCOO_s^-$ (eq 2) lowered the threshold value for both October and March stream samples, and also reduced the difference between the threshold values for these data sets (Figure 7a and b). The October 2003 adjusted threshold value of +20 may reflect an overestimation of inorganic Al concentrations in samples with high DOC concentrations. The cation-exchange resin used to separate organically complexed Al from inorganically complexed Al disrupts some weak organic complexes in samples with high DOC concentrations (*27*), although this widely used Al-speciation method has been shown to be generally reliable (*28*). Nevertheless, disruption of weak organic-Al complexes in high DOC samples would cause some overestimation of inorganic Al concentrations and shift the position of the threshold to the right (higher base-cation surplus).

The increased similarity of the threshold values after inclusion of strongly acidic organic anion concentrations supports the assertion that strongly acidic organic acids contribute to the mobilization of inorganic Al. It is also

noteworthy that the threshold values approached zero—the value below which mobilization of inorganic Al would be expected on the basis of the solution charge balance.

The theoretical basis for inorganic Al mobilization can be conceptualized with the following equations (all concentrations expressed in μeq L^{-1}).

$$H^+ + C_b = A_s^- + A_w^- + HCO_3^- + CO_3^{2-} + OH^- \quad (3)$$

$$C_b - A_s^- = A_w^- + HCO_3^- + CO_3^{2-} + OH^- - H^+ \quad (4)$$

where C_b represents the sum of Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$; A$_s^-$ represents strongly acidic anions (both inorganic and organic); and A$_w^-$ represents weakly acidic organic anions.

Equation 3 gives the charge balance for solutions to the right of the Al mobilization threshold in Figure 7. Inorganic Al is essentially absent under this condition and therefore does not appear in the equation. Rearranging eq 3 yields eq 4, the right side of which represents the balance between all relevant weakly acidic anions (potential proton acceptors) and H$^+$. If the solution acidifies to the point at which each side of eq 4 becomes negative, H$^+$ is in excess of that which could be associated with weakly acidic anions. This excess H$^+$ (H^{+*}) is available to mobilize inorganic Al, but is neutralized in the process. Dropping out the weak acid components and associated H$^+$, and adding Al$_i$ (the sum of positively charged inorganic Al species), results in eq 5, which shows a direct relationship between the adjusted base-cation surplus (expressed as a positive term) and the H^{+*} plus inorganic Al.

$$A_s^- - C_b = H^{+*} + Al_i \quad (5)$$

The degree to which inorganic Al is mobilized by H^{+*} (the slope of the relationship to the left of the threshold) is likely to be dependent on soil characteristics such as organic matter content, mineralogy, and soil water flux.

The threshold relationship was also investigated in streamwater samples from Winnisook Reach in the Catskill region of New York. Median concentrations of DOC in this highly acidic stream were 211 μmol C L^{-1} for the 4 years of data used in the analysis, and the mean and median anion deficit equaled 1.8 and 1.1 μeq L^{-1}, respectively. Under these conditions the base-cation surplus was approximately equivalent to ANC for most samples. As for the Adirondack streams, the threshold for inorganic Al mobilization in Winnisook Reach occurred at a base-cation surplus value near zero (Figure 7c).

Inorganic Al Mobilization and the Base-Cation Surplus as Assessment Tools. The inclusion of strong organic anions as a negative component in the base-cation surplus does not necessarily imply that mobilization of inorganic Al can occur in the absence of acidic deposition. If the sum of base-cation concentrations exceeds the concentration of strong organic anions, excess H$^+$ will not be available for mobilization of inorganic Al without contributions of SO$_4^{2-}$ and NO$_3^-$ from acidic deposition. We found this to be the case for 388 out of the 389 stream samples collected in the two stream surveys. The sum of base-cation concentrations exceeded the estimate of strong organic anions by an average of 178 μeq L^{-1} for all samples collected in the October 2003 and March 2004 surveys. In combination with inorganic strong acids from acidic deposition, however, strongly acidic organic acids further decrease the value of the base-cation surplus. Production of strongly acidic organic acids therefore increases the sensitivity of a watershed to acidic deposition in a manner analogous to base-poor bedrock and till.

The role of strong organic anions in Al mobilization is particularly significant in regard to the trend of increasing DOC concentrations that has recently been identified in Adirondack lakes, and other surface waters in North America and northern Europe (*5, 29, 30*). Increasing DOC concentrations could possibly retard decreases in inorganic Al concentrations that would be expected from declines in SO$_4^{2-}$ and NO$_3^-$ concentrations. Decreasing trends in inorganic Al concentrations have been documented in Adirondack lakes from 1992 to 2004 (*31*), but the mean rate of decrease was small (<0.3 μeq L^{-1} y^{-1}). A similar decrease (0.2 μeq L^{-1} y^{-1}) was observed in a stream at the Hubbard Brook Experimental Forest, NH (*32*).

Because measurements of inorganic Al concentrations do not predate acidic deposition (the necessary analytical methods did not exist at that time), it is not possible to directly determine if inorganic Al occurred in surface waters in the absence of acidic deposition. However, the generality of the threshold relationship, its consistency with the theoretical basis for inorganic Al mobilization, and a lack of other known natural mechanisms to explain regional mobilization of inorganic Al, suggest that measurable concentrations of inorganic Al in surface waters provide an unambiguous indication of acidic deposition effects. An exception could occur in watersheds where large sources of sulfidic minerals lead to SO$_4^{2-}$ concentrations that exceed the base-cation surplus in soil waters, but we are not aware of any of these types of watersheds in regions affected by acidic deposition.

On the basis of its relationship to inorganic Al concentrations, the base-cation surplus seems more effective as a chemical indicator of human-induced acidification than pH, ANC$_G$, or ANC, which are often unsuccessful in distinguishing between natural acidity and acid rain. The base-cation surplus has also been shown to be more strongly related to fish status than ANC measurements in high-DOC waters (*10*).

Supporting Information Available

Summary data for water chemistry measurements from the three sampling programs used in this study (Tables S1 and S2), and the cumulative proportion of DOC concentrations, ANC, and inorganic Al concentrations in stream surveys conducted in October 2003 and March 2004 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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