

Predicted response of stream chemistry to acid loading tested in Canadian catchments

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SHORT-TERM acidification of lakes and streams can cause biological damage by lowering pH and increasing concentrations of inorganic aluminium¹⁻⁴. Storms laden with acids and sea salts, rapid melting of acidic snow and remobilization of acids stored in catchment soils can cause episodes of acidification lasting from hours to months. These episodes can help to reveal the mechanisms that regulate catchment runoff chemistry⁵⁻⁷. Here we use extreme, climatically triggered acidification episodes in 18 intensively monitored streams in Canada to test a geochemical theory⁸ that predicts the chemical response of catchments to changes in acid loading. At all 18 catchments, changes in base cation (Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺) concentrations offset about 75–95% of the observed changes in acid anion (SO₄²⁻, NO₃⁻, Cl⁻, OA⁻) levels; increases in hydrogen and aluminium ions and decreases in bicarbonate accounted for the remaining 5–25%. In response to equal acid anion increases, however, some catchments released over 35 times more H⁺ or 50 times more inorganic aluminium than others. The observed chemical responses to shifts in acid anion loading agreed with *a priori* geochemical predictions derived⁸ from the chemical composition of runoff, indicating that catchment vulnerability to acidification can be assessed, in advance, directly from surveys of lake and stream chemistry.

The theory tested here is a simple mechanistic method for predicting catchment response to changing acid anion concentrations directly from runoff chemistry⁸. The governing equations resemble those underlying many acidification computer models⁹⁻¹², but they are solved analytically, yielding catchment acidification response as a function of concentrations in catchment runoff. In a charge balance for typical acid-sensitive waters

$$2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + \text{OA}^- \\ = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+] \\ + 3[\text{Al}^{3+}] + 2[\text{Al}(\text{OH})^{2+}] + [\text{Al}(\text{OH})_2^+] + 2[\text{AlF}_2^+] \\ + [\text{AlF}_2^+] - [\text{HCO}_3^-] - [\text{OH}^-] - [\text{F}^-] + \dots \quad (1)$$

the left side expresses the total acid burden, and we hypothesize that the principal species of the right side are regulated, in the short term, by equilibria with solid, adsorbed and gas phases (for example by ion exchange, mineral dissolution or carbonate equilibria). In such heterogeneous equilibria, the concentrations C of any two ions i and j are related by the expression

$$(\gamma_i C_i)^{z_i} = K_{i,j} (\gamma_j C_j)^{z_j} \quad (2)$$

where γ_i and γ_j are single-ion activity coefficients, z_i and z_j are ionic valences, and the reaction constant $K_{i,j}$ subsumes the thermodynamic equilibrium constant, the activity of the non-aqueous phase and any intermediate reactions. If the solution composition shifts incrementally (and therefore activity coefficients and non-aqueous activities are constant), the relative shifts in the two concentrations will be

$$\frac{\partial C_i}{\partial C_j} = \frac{z_i}{z_j} \frac{C_i}{C_j} \quad (3)$$

We hypothesize that heterogeneous equilibria regulate the main species on the right-hand side of equation (1). We therefore rewrite (1) as

$$\Sigma \text{acids} = \sum_{i=1}^n z_i C_i \quad (4)$$

where Σacids is the sum of strong acid and organic anions. Differentiating equation (4), applying equation (3) throughout and rearranging terms yields

$$\frac{dC_j}{d\Sigma \text{acids}} = \frac{z_j C_j}{\sum_{i=1}^n z_i^2 C_i} \quad (5)$$

Given only the equilibrium concentrations of the n species on the right-hand side of equation (1), equation (5) predicts each ion's response to changes in Σacids . Equation (5) implies that shifts in Σacids will primarily be accommodated within the heterogeneous system by ions with high concentrations and large valences, not large shifts in minor ions.

Predicted responses for individual ions can be added⁸, yielding acidification responses for important water quality indicators, such as the sum of base cations (SBC)

$$\frac{d\text{SBC}}{d\Sigma \text{acids}} = \frac{4[\text{Ca}^{2+}] + 4[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+]}{\sum_{i=1}^n z_i^2 C_i} \quad (6)$$

the titratable acid neutralizing capacity¹³ (ANC)

$$\frac{d\text{ANC}}{d\Sigma \text{acids}} = \frac{d\text{SBC}}{d\Sigma \text{acids}} \\ + \frac{9[\text{Al}^{3+}] + 6[\text{Al}(\text{OH})^{2+}] + 3[\text{Al}(\text{OH})_2^+]}{\sum_{i=1}^n z_i^2 C_i} - 1 \quad (7)$$

and the molar sum of inorganic aluminium (Al_i)

$$\frac{d\text{Al}_i}{d\Sigma \text{acids}} \\ = \frac{3[\text{Al}^{3+}] + 2[\text{Al}(\text{OH})^{2+}] + [\text{Al}(\text{OH})_2^+] + 2[\text{AlF}_2^+] + [\text{AlF}_2^+]}{\sum_{i=1}^n z_i^2 C_i} \quad (8)$$

We used acid episodes observed during long-term monitoring studies¹⁴⁻¹⁶ in central Ontario to test whether equations (5)–(8) accurately predict catchment response to changes in acid loading. Acute droughts in the summers of 1987–90 permitted oxidation and mobilization of sulphur stored in catchment soils and wetlands¹⁷. In many catchments, autumn storms following summer droughts yielded streamflow with very high sulphate concentrations (Fig. 1). Acid anion levels remained high for months, falling throughout the year until the next summer's drought. Pronounced changes in base cation, hydrogen ion and aluminium concentrations, as well as titratable alkalinity, accompanied the acid anion variations (Figs 1 and 2).

At 18 intensively monitored catchments spanning a range of run-off chemistries (Table 1), we averaged solute concentrations from stream samples taken before the 1987 drought, inserted the averaged values into equations (5)–(8), and compared the calculated estimates of catchment response with stream chemistry observed in the following four drought years (Fig. 2). This is a severe test for four reasons. First, unlike typical catchment acidification models, the theory contains no *ad hoc* empiricisms, arbitrary constants or adjustable parameters. Second, the chemical behaviour of catchment runoff before the first drought is very different from the behaviour against which the theory is tested (Fig. 1). Third, the type of input information

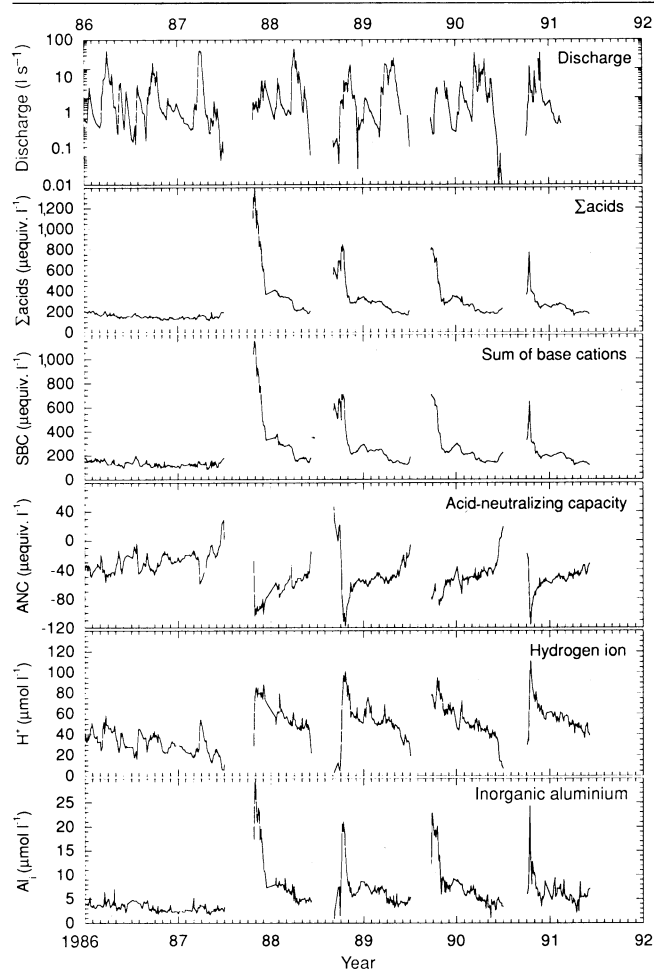


FIG. 1 Effects of summer droughts on stream discharge and chemistry at catchment 1, Plastic Lake, Ontario. Large data gaps indicate droughts (periods of no streamflow). Sampling interval for chemical data averaged 3 days, excluding drought gaps. Before the mid-1987 drought, runoff chemistry fluctuated within relatively narrow bounds. Droughts in four successive summers were followed by runoff with elevated concentrations of acid anions, base cations, hydrogen ions and inorganic aluminium, and sharply reduced acid neutralizing capacity. Each of these concentrations remained outside its pre-drought range for several months after each drought ended. Acid anion variations were dominated by sulphate; the sum of nitrate, chloride and organic acids averaged $70 \mu\text{equiv. l}^{-1}$, and never exceeded $250 \mu\text{equiv. l}^{-1}$, over the period shown. Runoff chemistry is not strongly correlated with streamflow over the period analysed here. Acid episodes are often driven by dilution effects or changes in flowpaths resulting from extreme hydrological events such as intense rainstorms or sudden snowmelt²⁸. Snowmelt episodes have been observed at some of our catchments during non-drought years²⁹, but during 1987–90 flow effects were dwarfed by the large changes in acid anion concentrations. In typical catchment data, where acid loading varies over a much narrower range, flow effects may obscure catchment response to acid anion variations.

(average concentrations) is distinct from the type of prediction (slopes of relative changes in concentrations). Fourth, the large changes in acid levels dwarf other sources of variation, so the data reflect catchment response to acid anions rather than to other factors (such as streamflow fluctuations).

Figure 2 compares acidification responses at two sites with the geochemical predictions derived from average pre-drought run-off chemistry. The lines shown are *a priori* predictions, not fitted relationships, so there are naturally some discrepancies with the data. Nonetheless, concentrations of base cations, hydrogen ions and aluminium generally respond to acid anion variations as predicted, and the theory predicts the observed differences in response between the catchments.

We constructed plots similar to Fig. 2 for all 18 study sites. We then compressed the results (Fig. 3), by comparing predicted slopes derived from pre-drought mean streamwater concentra-

tions (the solid lines in Fig. 2) with the least-squares regression slopes of all the data for each catchment. Equations (5)–(8) correctly predict both the magnitude of the average response across the 18 sites, and the differences in response between different sites (Fig. 3). When the 18 sites are ranked by the responsiveness of a given ion to acid anion concentrations, the rankings generally correspond to those predicted from pre-drought mean chemistry (Spearman $r_s > 0.65$, $p < 0.01$, for all ions in Fig. 3).

The large acid anion variations analysed here resulted from internal loading (changes in catchment sulphate storage) rather than external loading (changes in acid deposition rates). The prediction method tested here also explains catchment response to external loading⁸ at Birkenes¹⁸ (Norway) and Hubbard Brook¹⁹ (USA), where acid deposition has varied historically, and at Sogndal and Risdalsheia (Norway), where acid deposi-

TABLE 1 Mean pre-episode runoff concentrations

	Plastic Lake catchment 4	Harp Lake catchment 6A	Range for all sites
Measured concentrations			
pH	4.38	5.17	4.20–5.48
ANC	–46	20	–71–80
SO ₄	73	101	25–147
NO ₃	0.5	6.4	0.1–8.0
Cl	14	12	8–30
Ca	47	106	42–132
Mg	28	48	23–69
Na	24	28	16–43
K	6.4	5.1	2.2–14.9
NH ₄	0.3	0.6	0.2–11.0
Al _{org} ($\mu\text{mol l}^{-1}$)	10.3	3.5	2.4–10.3
Al _i ($\mu\text{mol l}^{-1}$)	6.5	0.5	0.2–6.8
F _T ($\mu\text{mol l}^{-1}$)	3.7	2.1	2.1–4.0
Si ($\mu\text{mol l}^{-1}$)	129	96	47–129
DIC (mg l^{-1})	2.0	3.0	0.8–6.0
DOC (mg l^{-1})	15	9	3–21
Calculated speciation			
Al ³⁺	9.1	0.1	0.0–9.1
Al(OH) ²⁺	0.3	0.0	0.0–1.3
Al(OH) ₂ ⁺	0.0	0.0	0.0–0.2
AlF ²⁺	6.3	0.6	0.2–6.3
AlF ₂ ⁺	0.2	0.2	0.1–0.6
HCO ₃ [–]	1.3	14	0.7–51
OA [–]	63	53	7–130

Concentrations (in $\mu\text{equivalents l}^{-1}$ except as noted) are simple means of analytical values for samples collected before 1987 drought. Analytical methods and quality control data are described in detail elsewhere^{21–23}. Acid neutralizing capacity was measured by Gran titration, total fluoride (F_T) by ion-selective electrode with TISAB buffer, and organic and inorganic aluminium (Al_{org} and Al_i, respectively) by catechol violet colorimetry before and after ion exchange²⁴. Speciation of aluminium followed the procedure of Schecher and Driscoll²⁵. Organic anions (OA[–]) were calculated from pH and dissolved organic carbon (DOC) by a slight modification¹⁴ of the method of Oliver *et al.*²⁶. Bicarbonate was calculated²⁷ from measured dissolved inorganic carbon (DIC) and pH.

tion was experimentally altered²⁰. Those sites pose a less exacting test, however, because acid loading changed less.

Long-term catchment response to acid loading will be affected by disequilibrium processes, such as base cation leaching, in addition to the equilibrium mechanisms analysed here. Extensions to the theory outlined above yield quantitatively reasonable predictions of the long-term effects of progressive base cation depletion from catchment soils, as may be occurring at Hubbard Brook⁸. Unfortunately, data for a precise test do not exist.

The spatial variability of catchment geochemical properties has little effect on predicted acidification response⁸, because equation (5) is not strongly nonlinear and catchment runoff

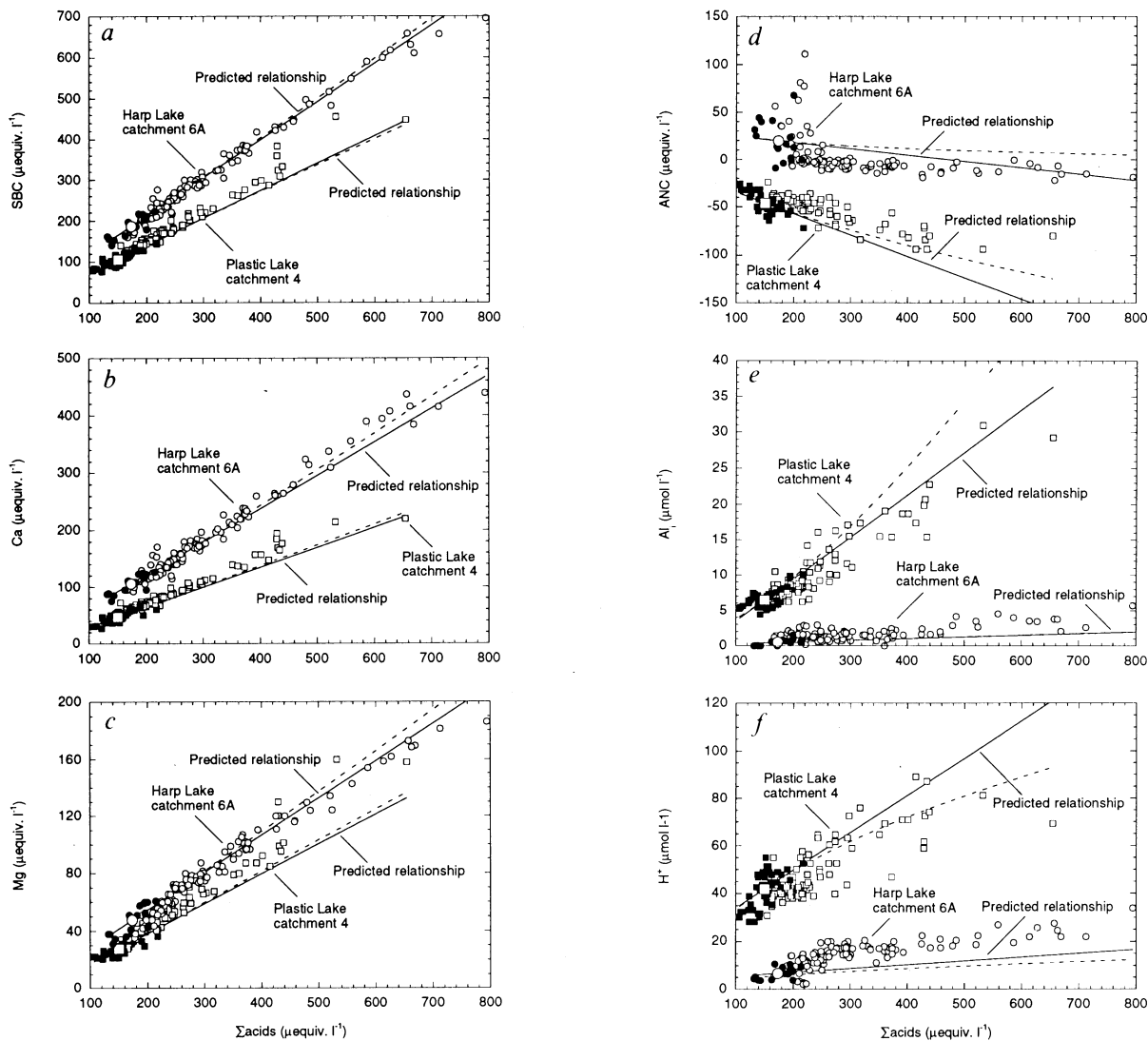


FIG. 2 Response of two monitored catchments to variation in acid anion concentrations (Σacids) resulting from summer droughts, compared to relationships predicted from equations (5)–(8) (solid lines) from averages (large open symbols) of samples taken before onset of 1987 drought (solid symbols). Panels show the effect of acid anion loading on (a) sum of base cations (SBC); (b) calcium concentrations; (c) magnesium concentrations; (d) acid neutralizing capacity; (e) inorganic aluminium concentrations; (f) hydrogen ion concentrations. All samples taken after the onset of the first drought (used to test, but not derive, predicted response) shown by small open symbols. Circumneutral Harp Lake tributary 6A and acidic Plastic Lake tributary 4 (see Table 1) drain forested catchments of 15 and 5 hectares, respectively. Linear extrapolations of slopes predicted from pre-drought

averages both the solute concentrations and acidification responses of its geochemically diverse contributing regions in similar ways. Consequently, equation (5) is as good a predictor of whole-catchment acidification response at our largest catchment (456 ha) as at our smallest (1 ha). It cannot, however, address the effects of flowpath changes altering the relative flows from geochemically distinct sources, although it will predict acidification response for individual hydrological regimes, from samples taken under those flow conditions (J.W.K., manuscript in preparation).

Equations (5)–(8) are relatively insensitive to the variability of runoff chemistry with time⁸, because they use ratios of concentrations that generally covary in compensating ways. Reliable acidification predictions can usually be obtained from individual runoff samples. Predictions derived from individual streamwater samples differed from the mean predictions at each site by, on average, 0.028 (or 3%) for $d\text{SBC}/d\Sigma\text{acids}$, 0.015 (6%) for

average concentrations (solid lines) are approximations to the nonlinear relationships (dashed lines) observed when equation (5) is integrated over large ranges of Σacids . Similarly, linear regression slopes plotted in Fig. 3 are approximations to the test data, which show some curvature, particularly for monovalent cations. The direction and approximate magnitude of the nonlinearities in the data can be predicted (J.W.K., manuscript in preparation) by differentiating equation (5). Data for extremely high acid anion concentrations ($\Sigma\text{acids} > 800 \mu\text{equiv. l}^{-1}$) have been omitted here, and omitted from regression relationships in Fig. 3; the response of some ions is markedly nonlinear above this range. Similar plots have been used to test computer simulation models of catchment acidification^{30,31}.

$d\text{Ca}/d\Sigma\text{acids}$, 0.008 (8%) for $d\text{Mg}/d\Sigma\text{acids}$, 0.026 (18%) for $d\text{ANC}/d\Sigma\text{acids}$, 0.018 (29%) for $d\text{H}^+/d\Sigma\text{acids}$ and 0.005 (64%) for $d\text{Al}_i/d\Sigma\text{acids}$. Expected errors in acidification predictions from single samples are therefore much smaller than uncertainties in catchment acidification response before prediction, which for H^+ and Al_i may exceed an order of magnitude. Therefore, although this critical test uses large data sets from intensively monitored catchments, useful acidification predictions could be derived where only a few samples are available.

Because acid anion changes were largely offset by shifts in base cation concentrations, these acid episodes decreased acid neutralizing capacity only 5–25% as much as they raised acid anion concentrations (Figs 1–3). Catchment base cation and ANC responses to acidification were confined to relatively narrow ranges, as predicted (Figs 2–3). By contrast, acidification affected hydrogen ion and aluminium concentrations at different catchments in markedly different ways, but again, these

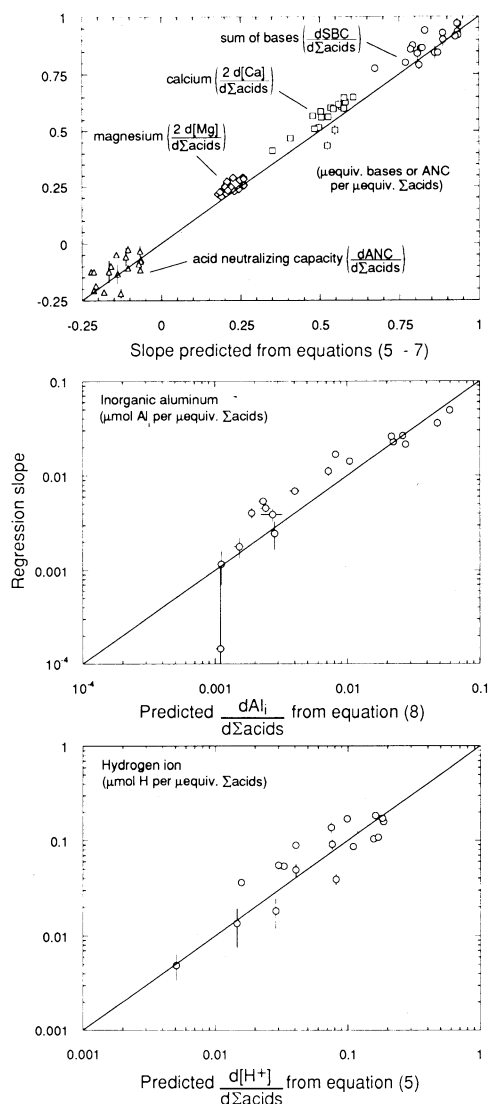


FIG. 3 Comparison of predicted and observed response to shifts in acid anion concentrations in runoff from 18 monitored catchments. Diagonal line indicates perfect agreement. Predicted slopes, like slopes of solid lines in Fig. 2, derived by inserting pre-drought average streamwater concentrations into equations (5)–(8). Observed slopes are least-squares regression slopes of measured concentrations as a function of Σ acids, similar to data plotted in Fig. 2. Thus, for each catchment, the experimental data plus predicted line shown in Fig. 2 become a single point here. All samples, both pre-drought and post-drought, are used in calculating observed regression slopes. Error bars show standard errors of prediction and standard errors of regression, where larger than plot symbols.

responses agreed with the theoretical predictions (Figs 2, 3). These results show that runoff chemistry and acidification response are related by simple mechanistic formulas, and that catchment acid sensitivity can be evaluated directly from runoff chemistry data. □

Received 14 February; accepted 22 June 1992.

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ACKNOWLEDGEMENTS. We thank R. Reid, R. Girard and L. Scott for sample collection, A. Neary for supervision of the chemical analyses, M. Futter for database management, and G. Mierle, J. Harte, B. A. Roy, A. H. Jahren and N. Christophersen for their comments. Our collaboration was sponsored by a NATO grant to J.W.K. Sample collection and analysis were done as part of the Acid Precipitation in Ontario Study.