

# Base Cation Depletion and Potential Long-Term Acidification of Norwegian Catchments

JAMES W. KIRCHNER\*

*Department of Geology and Geophysics, University of California, Berkeley, California 94720*

ESPEN LYDERSEN

*Norwegian Institute for Water Research, Box 173 Kjelsås, N-0411 Oslo, Norway*

Long-term monitoring data from Norwegian catchments show that since the late 1970's, sulfate deposition and runoff sulfate concentrations have declined significantly. However, water quality has not significantly improved, because reductions in runoff sulfate have been matched by equal declines in calcium and magnesium concentrations. Long-term declines in runoff Ca and Mg are most pronounced at catchments subject to highly acidic deposition; the observed rates of decline are quantitatively consistent with depletion of exchangeable bases by accelerated leaching under high acid loading. Even though water quality has not recovered, reductions in acid deposition have been valuable because they have prevented significant acidification that would otherwise have occurred under constant acid deposition. Ongoing depletion of exchangeable bases from these catchments implies that continued deposition reductions will be needed to avoid further acidification and that recovery from acidification will be slow.

## Introduction

Acid deposition is now decreasing in many regions (1–3) due to reductions in acid precursor emissions. These emission reductions have been costly and controversial, so it is worthwhile to assess whether they have resulted in measurable benefits to natural ecosystems. To this end, we have analyzed long-term runoff chemistry records from intensively monitored Norwegian catchments that span a strong gradient in acid loading. Given that acid deposition has been declining, how much improvement in catchment runoff chemistry should we expect to see? This question is complex, as the following two scenarios illustrate.

First, all else equal, reductions in acid loading should reduce runoff concentrations of sulfate and/or nitrate, raising runoff alkalinity. Although reductions in strong acid anion concentrations should also produce roughly proportional decreases in base cation concentrations (4–6),

the base cation reductions should be smaller, so the net effect on runoff alkalinity should be positive.

Secondly, however, high levels of acid loading should cause a steady decline in runoff alkalinity if bases are leached from catchment soils faster than they are resupplied by mineral weathering (7–11). As base cations become depleted from the catchment's ion-exchange sites, they become less available to runoff, leading to lower runoff alkalinity. The rate of this "progressive acidification" will be affected by the rate of base cation leaching by runoff, the rate of base cation release by mineral weathering, and the size of the exchangeable cation pool in the catchment.

In many regions, the current situation combines both of these scenarios; acid loading is now declining (so runoff water quality should improve), but it still remains far above natural levels (leading to base cation depletion and deteriorating water quality in catchments where weathering rates are low). Thus, water quality may either improve or deteriorate, depending on whether reductions in acid loading are rapid enough to offset the effects of ongoing depletion of base cations from catchment soils. In particular, runoff water quality may fail to improve, even though deposition is declining and even though emission reductions are having a beneficial effect (i.e., even though water quality is better than it would have been under constant acid deposition).

## Trends in Streamwater Chemistry

To assess the response of runoff chemistry to recent reductions in acid loading and continued high levels of acid deposition, we examined long-term trends in weekly streamwater samples from four Norwegian catchments. These catchments receive widely differing levels of acid and seasalt loading (Table 1), allowing us to observe the evolution of water quality under several different deposition regimes. As our primary indicator of runoff water quality, we used the balance between calcium and magnesium ( $\text{Ca} + \text{Mg}$ ) and sulfate and nitrate ( $\text{SO}_4 + \text{NO}_3$ ).  $(\text{Ca} + \text{Mg}) - (\text{SO}_4 + \text{NO}_3)$  approximates runoff alkalinity (the acid–base balance of runoff) while minimizing the effects of seasalt inputs and is correlated with other water quality variables, such as the concentrations of hydrogen ions ( $\text{H}^+$ ) and inorganic aluminum ( $\text{Al}_i$ ).

At Birkenes, Storgama, and Langtjern, reductions in acid deposition have resulted in comparable reductions in runoff sulfate concentrations (Table 2). However, although runoff concentrations of  $\text{SO}_4 + \text{NO}_3$  have declined by roughly 20–25% over the period of record, runoff  $\text{Ca} + \text{Mg}$  have also declined by roughly the same amounts, so alkalinity,  $\text{H}^+$ , and  $\text{Al}_i$  have not improved (Table 2, Figure 1). Kårvatn, which receives relatively little acid deposition, shows small and statistically insignificant trends in all chemical variables.

The observed loss of base cations from runoff might result from base cation depletion from catchment soils or might have several other causes. First, as acid anion loading to a catchment declines, base cation concentrations should also fall as equilibria between catchment soils and porewaters shift (4, 5, 10). Second, higher streamflows are associated with lower concentrations of base cations and higher concentrations of  $\text{H}^+$  at these sites, particularly at Birkenes (12). Third, variations in seasalt inputs can affect

\* Corresponding author telephone: (510) 643-8559; fax: (510) 643-9980; e-mail address: kirchner@moray.berkeley.edu.

TABLE 1

Acid Deposition and Runoff Chemistry at Four Norwegian Catchments<sup>a</sup>

	Birkenes	Storgama	Langtjern	Kårvatn
	Acid and Seasalt Deposition (mequiv m <sup>-2</sup> yr <sup>-1</sup> ) <sup>b</sup>			
NSS SO <sub>4</sub>	153 ± 14	73 ± 7	52 ± 5	24 ± 1
NO <sub>3</sub>	102 ± 9	48 ± 5	31 ± 3	7 ± 1
Cl	160 ± 18	32 ± 4	11 ± 1	112 ± 11
	Flow-Weighted Mean Runoff Concentrations (μequiv/L Except As Noted)			
pH	4.53 ± 0.01	4.49 ± 0.01	4.70 ± 0.01	6.03 ± 0.02
SO <sub>4</sub>	131.6 ± 3.8	70.6 ± 2.3	67.7 ± 2.1	16.0 ± 0.7
NO <sub>3</sub>	9.7 ± 0.9	11.0 ± 0.8	2.1 ± 0.2	0.8 ± 0.1
Cl	124.9 ± 5.9	32.7 ± 1.7	17.7 ± 0.8	54.4 ± 4.3
Ca	54.4 ± 1.9	33.6 ± 1.4	55.4 ± 2.1	20.8 ± 0.4
Mg	33.3 ± 1.1	12.5 ± 0.6	17.2 ± 0.7	13.6 ± 0.6
Na	117.7 ± 3.1	31.8 ± 1.7	24.6 ± 0.8	49.9 ± 2.9
Al <sub>i</sub> (μmol/L) <sup>c</sup>	13.8 ± 0.9	3.7 ± 0.2	2.5 ± 0.1	0.3 ± 0.0
Al <sub>o</sub> (μmol/L) <sup>d</sup>	4.1 ± 0.4	2.1 ± 0.2	3.8 ± 0.2	0.4 ± 0.1
TOC (mg/L)	5.1 ± 0.3	4.3 ± 0.1	8.9 ± 0.5	1.0 ± 0.1
OA <sup>-e</sup>	15.0 ± 0.9	16.8 ± 1.0	51.6 ± 4.6	0.6 ± 0.2
runoff (mm/yr)	1165 ± 78	956 ± 85	640 ± 58	1961 ± 106
catchment area (km <sup>2</sup> )	0.4	0.6	4.8	25

<sup>a</sup> All quantities reported as mean ± standard error. <sup>b</sup> Deposition of non-seasalt sulfate (NSS-SO<sub>4</sub>) and nitrate calculated assuming that ratios of NSS-SO<sub>4</sub> and NO<sub>3</sub> to Cl are the same in dry and wet deposition and assuming that chloride is conservative. <sup>c</sup> Al<sub>i</sub>, inorganic aluminum. <sup>d</sup> Al<sub>o</sub>, organic aluminum. <sup>e</sup> Organic anions (OA<sup>-</sup>) calculated from pH and total organic carbon (TOC) by the Oliver et al. method (30).

TABLE 2

## Trends in Runoff and Deposition Chemistry at Norwegian Catchments

	Birkenes	Storgama	Langtjern	Kårvatn
	Acid Deposition (mequiv m <sup>-2</sup> yr <sup>-1</sup> )			
NSS SO <sub>4</sub> + NO <sub>3</sub>	255 ± 17	121 ± 9	83 ± 6	31 ± 1
	Trends in Runoff Concentrations (μequiv L <sup>-1</sup> yr <sup>-1</sup> ) <sup>a</sup>			
(Ca + Mg) - (SO <sub>4</sub> + NO <sub>3</sub> )	0.10 ± 0.31	-0.02 ± 0.28	-0.65 ± 0.21**	-0.04 ± 0.30
SO <sub>4</sub>	-2.70 ± 0.37***	-1.13 ± 0.40*	-1.02 ± 0.30**	-0.14 ± 0.21
NO <sub>3</sub>	0.54 ± 0.11***	-0.01 ± 0.18	-0.02 ± 0.02	0.04 ± 0.02
Cl	1.46 ± 1.09	0.42 ± 0.32	-0.30 ± 0.13*	-0.22 ± 1.30
Ca	-1.38 ± 0.21***	-0.86 ± 0.20***	-1.27 ± 0.28***	-0.10 ± 0.12
Mg	-0.68 ± 0.15***	-0.30 ± 0.10*	-0.41 ± 0.09***	-0.04 ± 0.20
Na	0.09 ± 0.64	0.04 ± 0.35	-0.22 ± 0.15	-0.38 ± 0.86
H <sup>+</sup>	0.04 ± 0.17	-0.07 ± 0.15	0.10 ± 0.09	-0.02 ± 0.01
Al <sub>i</sub> (μmol L <sup>-1</sup> yr <sup>-1</sup> )	0.75 ± 0.44	0.06 ± 0.10	0.06 ± 0.09	0.01 ± 0.03
	Trends in Deposition (Runoff Equivalent μequiv L <sup>-1</sup> yr <sup>-1</sup> ) Adjusted for Evapoconcentration and Dry Deposition <sup>b</sup>			
(Ca + Mg) - (SO <sub>4</sub> + NO <sub>3</sub> )	1.31 ± 1.28	0.38 ± 0.98	1.52 ± 1.11	0.35 ± 0.40
SO <sub>4</sub>	-1.83 ± 0.66*	-0.94 ± 0.64	-2.04 ± 0.97	-0.48 ± 0.23
NO <sub>3</sub>	0.32 ± 0.70	0.48 ± 0.47	0.03 ± 0.56	-0.12 ± 0.09
Cl	1.63 ± 3.31	1.20 ± 0.58	-0.13 ± 0.24	0.31 ± 1.62
Ca	-0.21 ± 0.15	-0.19 ± 0.13	-0.43 ± 0.30	-0.23 ± 0.15
Mg	0.00 ± 0.35	0.11 ± 0.08	-0.05 ± 0.11	-0.01 ± 0.30
Na	1.28 ± 2.28	1.02 ± 0.44*	0.21 ± 0.22	0.18 ± 1.53
H <sup>+</sup>	-1.30 ± 0.67	-0.98 ± 0.62	-2.24 ± 0.83*	-0.23 ± 0.18

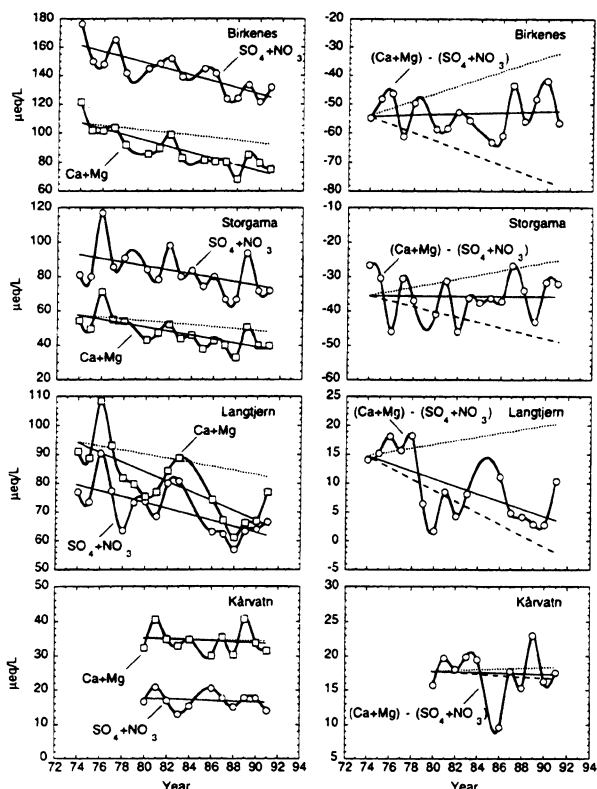
<sup>a</sup> Runoff trends (mean ± standard error) calculated by linear regression of annual flow-weighted mean concentrations. (\*), (\*\*), and (\*\*\*) indicate confidence levels of 95%, 99%, and 99.9%, respectively. Any weekly measurement representing more than 20% of total annual discharge was omitted from annual averages to prevent undue influence from a few high flows. Data for Kårvatn from 1980 through 1991 and for all other sites from 1974 through 1991, with several gaps due to interruptions in funding (1979 and 1984 missing at Birkenes, 1979 missing at Storgama; 1984 and 1985 missing at Langtjern; and 1985 missing at Kårvatn). Inorganic aluminum (Al<sub>i</sub>) data available only for 1986–1991; Al<sub>i</sub> trends may not be applicable to longer periods for which the other data are available. <sup>b</sup> Deposition trends calculated by linear regression of annual volume-weighted mean precipitation concentrations multiplied by ratio of mean Cl in runoff to Cl in precipitation to account for dry deposition and evapoconcentration, yielding trends that would result in runoff without the influence of catchment processes.

Ca and Mg concentrations, both because Na can exchange for Ca and Mg in catchment soils and because Mg is itself a significant seasalt component. To account for these factors and to clarify the long-term trends that they might obscure, we fitted the weekly runoff chemistry data for each site using multiple regression:

$$y = \beta t + \eta \log(q) + \gamma \text{Cl} + \phi(\text{SO}_4 + \text{NO}_3) \quad (1)$$

where  $y$  is the concentration of an ion of interest,  $t$  is time,

$\log(q)$  is the logarithm of streamflow, runoff Cl concentrations reflect seasalt loading, and runoff SO<sub>4</sub> + NO<sub>3</sub> concentrations reflect atmospheric acid deposition and catchment retention or release of sulfate and nitrate. At these sites, as elsewhere (6, 13), runoff cation concentrations are roughly linear functions of  $\log(q)$ , SO<sub>4</sub> + NO<sub>3</sub>, and Cl. The four coefficients— $\beta$ ,  $\eta$ ,  $\gamma$ , and  $\phi$ —express the linear effect of each variable (time, discharge, seasalt loading, and acid loading) on the ion of interest if the other three variables are held constant. We used different coefficients for Cl



**FIGURE 1.** Annual flow-weighted mean concentrations of calcium and magnesium (Ca + Mg) and sulfate and nitrate (SO<sub>4</sub> + NO<sub>3</sub>) at four Norwegian catchments (note 2-fold exaggeration of scale in right-hand plots). Solid straight lines show linear regression trends (Table 1). Dotted lines show trends that would occur from declining SO<sub>4</sub> + NO<sub>3</sub> alone, without depletion of exchangeable bases from catchments; slope of dotted lines calculated as trend in SO<sub>4</sub> + NO<sub>3</sub> times  $F_{Ca} + F_{Mg}$  (left-hand plots) or  $F_{Ca} + F_{Mg} - 1$  (right-hand plots). Comparing dotted lines and regression trends indicates that Ca and Mg declined more rapidly than expected from changes in SO<sub>4</sub> + NO<sub>3</sub> alone (left-hand plots) and that catchment base cation depletion offset significant alkalinity improvement that should have accompanied reductions in SO<sub>4</sub> + NO<sub>3</sub> (right-hand plots). Dashed lines show trends expected to result from base cation depletion under constant SO<sub>4</sub> + NO<sub>3</sub>; slopes of dashed lines calculated as  $\beta_{Ca} + \beta_{Mg}$ . Comparing dashed lines and regression trends suggests that reductions in SO<sub>4</sub> + NO<sub>3</sub> have offset significant alkalinity losses that would have occurred under constant SO<sub>4</sub> + NO<sub>3</sub>.

and SO<sub>4</sub> + NO<sub>3</sub> because, to the extent that Cl is accompanied by Na from seasalt, we expect Cl fluctuations to have a larger effect on Na and a correspondingly smaller effect on Ca or Mg.

If changes in SO<sub>4</sub> + NO<sub>3</sub> shift the chemical equilibrium between catchment soils and porewaters (thus altering runoff concentrations of Ca, Mg, H<sup>+</sup>, etc.), then the relationship between these ions and SO<sub>4</sub> + NO<sub>3</sub> should be geochemically predictable from first principles. It has been shown (6, 11) that under heterogeneous equilibrium, the theoretical effect of changes in SO<sub>4</sub> + NO<sub>3</sub> on Ca, Mg, H<sup>+</sup>, and Al<sub>i</sub> can be estimated directly from the chemical composition of runoff as follows:

$$F_y = \frac{\partial y}{\partial(\text{SO}_4 + \text{NO}_3)} = \frac{z_y[y]}{\sum_{i=1}^n |z_i| C_i} \quad (2)$$

where [y] and z<sub>y</sub> are the concentration and valence of the ion of interest y, and C<sub>i</sub> and z<sub>i</sub> are the concentrations and

valences of all ions that directly or indirectly participate in heterogeneous equilibrium reactions within the catchment. F<sub>y</sub> expresses the expected effect of a 1 µequiv/L change in SO<sub>4</sub> + NO<sub>3</sub> on the concentration of y (also in µequiv/L), resulting from shifts in catchment chemical equilibria. In other words, F<sub>y</sub> is the slope of the theoretical buffer curve relating y to SO<sub>4</sub> + NO<sub>3</sub>. (Equation 2 is comparable to eq 8 of ref 11, except that all concentrations are in microequivalents per liter, and the buffer slope F<sub>y</sub> is in microequivalents of y per microequivalent of SO<sub>4</sub> + NO<sub>3</sub>.)

At our sites, the direct effects of changes in SO<sub>4</sub> + NO<sub>3</sub> on major cations (ϕ, Table 3) are generally consistent with those expected for geochemical equilibria (F, Table 3). This suggests that ϕ measures the shift in catchment geochemical equilibria as SO<sub>4</sub> + NO<sub>3</sub> changes, as we hypothesized. The direct effect of declining SO<sub>4</sub> + NO<sub>3</sub> on Ca and Mg can be estimated from observed runoff SO<sub>4</sub> + NO<sub>3</sub> trends, by multiplying by either the theoretically expected equilibrium buffer slope (F) or the buffer slope that was actually observed (ϕ). Either approach yields the result that reductions in SO<sub>4</sub> + NO<sub>3</sub> have caused less than half (0.4–0.9 µequiv L<sup>-1</sup> yr<sup>-1</sup>) of the observed declines in Ca + Mg (1.2–2.1 µequiv L<sup>-1</sup> yr<sup>-1</sup>) at Birkesnes, Storgama, and Langtjern (dotted lines, Figure 1). Declining acid loading and shifting catchment equilibria can only account for part of the observed base cation losses.

Base cation losses could be higher than expected if, in addition to the shift in equilibrium modeled by F or ϕ, exchangeable bases are also being depleted from catchment soils. Long-term depletion of exchangeable bases should have a distinctive chemical signature; it should cause base cation concentrations to decline persistently through time when all other chemical and hydrologic variables are held constant. To look for this signature of base cation depletion, we can use the fitted regression coefficients from eq 1 to correct for the confounding effects of changes in SO<sub>4</sub> + NO<sub>3</sub>, Cl, and discharge. This dramatically clarifies the underlying time trends in the time series data (Figure 2). Correcting for these exogenous factors provides greater power to detect underlying trends in the data (14). It also reveals the underlying trends more exactly since the trend that would be observed under constant acid anion concentrations (β, Table 3) will differ from the base cation trend observed in the actual time series under declining acid anion loading (Table 2).

When the confounding effects of changes in SO<sub>4</sub> + NO<sub>3</sub>, Cl, and discharge are removed, the three catchments receiving highly acidic precipitation all show large and statistically significant losses of runoff Ca and Mg over time and show increases in H<sup>+</sup> and Al<sub>i</sub> (β, Table 3). The β values indicate that if acid loading were constant, runoff water quality at these sites would be systematically deteriorating over the long term. At Kårvatn, by contrast, acid loading is relatively low, and there are no substantial underlying trends (β) in any chemical variables. This suggests that the persistent base cation losses at Birkesnes, Storgama, and Langtjern are related to the high acid loading there. The negative result at Kårvatn also suggests that the observed trends at the other three sites are unlikely to be artifacts.

The three acid-impacted sites have a longer time series (1974–1991) than Kårvatn (1980–1991). Could this explain why we found long-term Ca and Mg trends at the three acid-impacted sites but not at Kårvatn? If we use only data from the shorter period (1980–1991) to fit eq 1, we obtain the same results at Birkesnes and Storgama, within error,

TABLE 3

Multiple Regression Trends in Runoff Chemistry<sup>a</sup>

	Birkenes	Storgama	Langtjern	Kårvatn
NSS SO <sub>4</sub> + NO <sub>3</sub>	255 ± 17	121 ± 9	83 ± 6	31 ± 1
Acid Deposition (mequiv m <sup>-2</sup> yr <sup>-1</sup> )				
Trends under Constant SO <sub>4</sub> + NO <sub>3</sub> , Cl, and Discharge ( $\beta_y = \partial y / \partial t$ , $\mu\text{equiv L}^{-1} \text{yr}^{-1}$ ) <sup>b</sup>				
$\beta_{\text{Ca}}$	-0.91 ± 0.16***	-0.69 ± 0.10***	-0.83 ± 0.14***	-0.13 ± 0.17
$\beta_{\text{Mg}}$	-0.52 ± 0.05***	-0.22 ± 0.03***	-0.24 ± 0.03***	0.04 ± 0.04
$\beta_{\text{Na}}$	-0.14 ± 0.18	0.12 ± 0.15	-0.01 ± 0.06	-0.12 ± 0.10
$\beta_{\text{H}^-}$	0.06 ± 0.07	0.22 ± 0.15	0.25 ± 0.08**	-0.01 ± 0.00*
$\beta_{\text{Al}_i}$ ( $\mu\text{mol L}^{-1} \text{yr}^{-1}$ )	0.44 ± 0.15**	0.08 ± 0.04	0.05 ± 0.06	-0.01 ± 0.01
Buffer Slope Estimated by Multiple Regression ( $\phi_y = \partial y / \partial (\text{SO}_4 + \text{NO}_3)$ , $\mu\text{equiv}/\mu\text{equiv}$ ) <sup>b</sup>				
$\phi_{\text{Ca}}$	0.22 ± 0.02***	0.25 ± 0.01***	0.32 ± 0.02***	0.33 ± 0.04***
$\phi_{\text{Mg}}$	0.14 ± 0.01***	0.11 ± 0.01***	0.12 ± 0.01***	0.11 ± 0.02***
$\phi_{\text{Na}}$	0.15 ± 0.02***	0.14 ± 0.01***	0.11 ± 0.01***	0.14 ± 0.04***
$\phi_{\text{H}^-}$	0.08 ± 0.01***	0.20 ± 0.01***	0.13 ± 0.02***	-0.01 ± 0.00**
$\phi_{\text{Al}_i}$ ( $\mu\text{mol}/\mu\text{equiv}$ )	0.05 ± 0.01***	0.04 ± 0.01***	0.01 ± 0.00*	0.00 ± 0.00
Buffer Slope Expected for Heterogeneous Geochemical Equilibria ( $F_y = \partial y / \partial (\text{SO}_4 + \text{NO}_3)$ , $\mu\text{equiv}/\mu\text{equiv}$ ) <sup>c</sup>				
$F_{\text{Ca}}$	0.25 ± 0.02	0.36 ± 0.02	0.53 ± 0.02	0.31 ± 0.01
$F_{\text{Mg}}$	0.16 ± 0.01	0.13 ± 0.01	0.16 ± 0.01	0.20 ± 0.01
$F_{\text{Na}}$	0.27 ± 0.01	0.17 ± 0.01	0.12 ± 0.01	0.37 ± 0.02
$F_{\text{H}^-}$	0.07 ± 0.01	0.17 ± 0.01	0.10 ± 0.01	0.01 ± 0.00
$F_{\text{Al}_i}$ ( $\mu\text{mol}/\mu\text{equiv}$ )	0.08 ± 0.01	0.05 ± 0.01	0.03 ± 0.01	0.00 ± 0.00

<sup>a</sup> All quantities reported as mean ± standard error. (\*), (\*\*), and (\*\*\*) indicate confidence levels of 95%, 99%, and 99.9%, respectively. <sup>b</sup> Time trends  $\beta_y = \partial y / \partial t$  and buffer slopes  $\phi_y = \partial y / \partial (\text{SO}_4 + \text{NO}_3)$  estimated by multiple regression (eq 1) of weekly runoff concentration data. Inspection of partial residual plots indicated that relationships were approximately linear and residuals were approximately normal. VIF was <3, indicating that multicollinearity was not severe (74). Residuals were, however, serially correlated; the Hildreth-Lu procedure (37) was used to correct for serial correlation. <sup>c</sup> Equilibrium buffer slopes were calculated from average runoff concentrations (Table 1) using eq 2.

that we do with the longer time series (at Birkenes,  $\beta_{\text{Ca}+\text{Mg}} = -1.43 \pm 0.17 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1974–1991 and  $-1.16 \pm 0.29 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1980–1991; at Storgama,  $\beta_{\text{Ca}+\text{Mg}} = -0.91 \pm 0.10 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1974–1991 and  $-0.91 \pm 0.17 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1980–1991). At Langtjern, the shorter time period substantially alters the fitted trend ( $\beta_{\text{Ca}+\text{Mg}} = -1.07 \pm 0.14 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1974–1991 but  $-0.37 \pm 0.24 \mu\text{equiv L}^{-1} \text{yr}^{-1}$  for 1980–1991). This statistically confirms what Figure 2 visually suggests: the underlying trends are steady and persistent at Birkenes and Storgama, but quite uneven at Langtjern. We are not sure why Langtjern's time series is so uneven, although we note that organic carbon concentrations are significantly higher there and that TOC is somewhat correlated with Ca and Mg; abrupt changes in TOC production could thus create subtle distortions in the Ca + Mg record. More data will be needed to clarify Langtjern's long-term trend. Assuming that Langtjern's actual long-term trend is somewhat less than  $-1.07 \mu\text{equiv L}^{-1} \text{yr}^{-1}$ , we can conclude that the rates of base cation loss from streamwater correspond closely to levels of acid loading at our four sites.

### Evidence for Base Cation Depletion from Catchments

The pattern revealed here—persistent losses of Ca and Mg, beyond what is explainable by shifts in acid anion concentrations, at sites with high acid loading—is qualitatively consistent with the depletion of exchangeable bases from catchment soils. Acid loading accelerates base cation leaching to runoff more than it accelerates base cation release by mineral weathering, because weathering rates of silicate minerals (which predominate in acid-sensitive catchments) generally increase as  $[\text{H}^+]^m$  with  $m$  between 0 and 1 (8, 15, 16); whereas equilibrium porewater concentrations (and thus leaching rates) of Ca and Mg are roughly proportional to  $[\text{H}^+]^2$  (11). Therefore, progressive acidification of soils and runoff can occur, even under

constant or declining acid deposition, wherever acid loading and biomass uptake are sufficient to remove bases from catchments faster than they are resupplied by mineral weathering and atmospheric deposition (11).

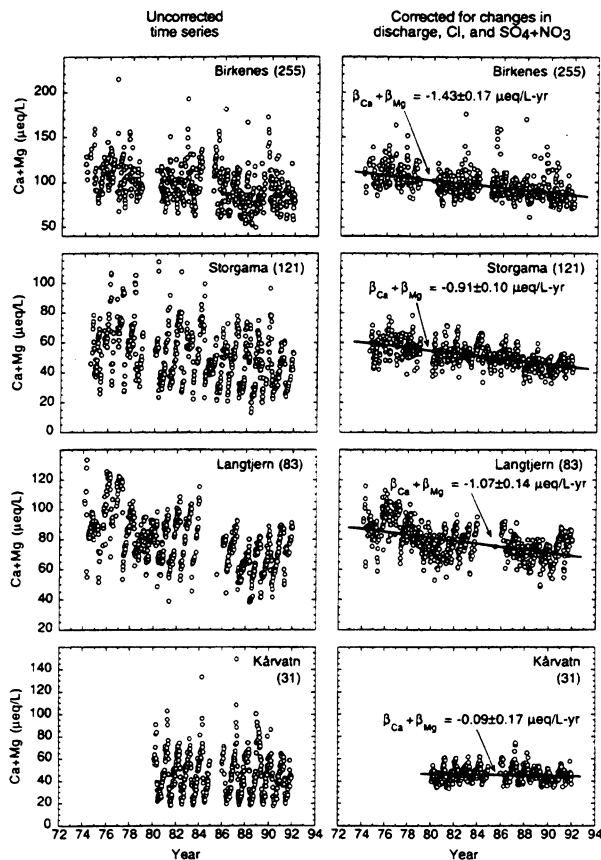
We hypothesize that the observed persistent losses ( $\beta$ ) of Ca and Mg from runoff are caused by depletion of exchangeable bases, resulting from accelerated base cation leaching under high acid loading. This hypothesis suggests two related questions. First, how rapidly would exchangeable Ca and Mg need to be lost from catchment soils to account for the observed runoff trends? Second, has acid loading accelerated base cation leaching enough to account for the inferred rates of loss of exchangeable Ca and Mg at these sites? We consider these issues in turn.

Depletion of exchangeable bases from catchments should produce long-term trends ( $\beta$ ) that are geochemically predictable (11) by expressions of the form

$$\frac{\beta_{\text{Ca}}}{\text{Ca}} = \frac{\partial \text{Ca} / \partial t}{\text{Ca}} = (1 - F_{\text{Ca}}) \alpha \frac{dX_{\text{Ca}} / dt}{X_{\text{Ca}}} \quad (3)$$

where  $\beta_{\text{Ca}}/\text{Ca}$  is the percentage rate of change in runoff calcium concentrations (corrected for acid anion effects, flow effects, etc.),  $(dX_{\text{Ca}}/dt)/X_{\text{Ca}}$  is the percentage depletion rate of exchangeable Ca from catchment soils,  $F_{\text{Ca}}$  is calculated by eq 2, and  $\alpha$  is a dimensionless coefficient expressing how changes in  $X_{\text{Ca}}$  affect the activity of the adsorbed phase.  $\alpha$  can be calculated from eqs 33–35 of ref 11.  $\alpha$  approaches 1 for soils with low base saturation; for our sites,  $\alpha$  ranges from 1.01 to 1.07. The net mass balance for exchangeable Ca,  $dX_{\text{Ca}}/dt$ , can also be written as the balance between Ca inputs from deposition ( $D_{\text{Ca}}$ ) and mineral weathering ( $W_{\text{Ca}}$ ) and losses to net biomass uptake ( $B_{\text{Ca}}$ ) and runoff ( $\text{Ca} \cdot q$ ), yielding

$$\frac{\beta_{\text{Ca}}}{\text{Ca}} = \frac{\partial \text{Ca} / \partial t}{\text{Ca}} = (1 - F_{\text{Ca}}) \alpha \frac{D_{\text{Ca}} + W_{\text{Ca}} - B_{\text{Ca}} - \text{Ca} \cdot q}{X_{\text{Ca}}} \quad (4)$$



**FIGURE 2.** Concentrations of calcium and magnesium in weekly runoff samples at Norwegian sites. Number in parentheses following catchment name is average acid loading (non-seasalt sulfate plus nitrate), in  $\text{mequiv m}^{-2} \text{yr}^{-1}$ . Raw time series (left-hand plots) are dominated by fluctuations in acid anion concentrations and discharge, obscuring long-term trend. Underlying time trends (right-hand plots) are revealed by correcting for variations in flow, Cl, and  $\text{SO}_4 + \text{NO}_3$  via the formula  $\gamma(t) = \gamma - \eta(\log(q) - \log(\bar{q})) - \gamma(\text{Cl} - \bar{\text{Cl}}) - \phi(\text{SO}_4 + \text{NO}_3 - \bar{\text{SO}}_4 - \bar{\text{NO}}_3)$ , where  $\gamma(t)$  is the underlying time trend in the concentration  $\gamma$ , and  $\eta$ ,  $\gamma$ , and  $\phi$  are multiple regression coefficients from eq 1.  $\gamma(t)$  expresses how  $\gamma$  would vary with time if flow and acid anion concentrations were held constant at the average values  $\log(\bar{q})$ ,  $\bar{\text{Cl}}$ ,  $\bar{\text{SO}}_4$ , and  $\bar{\text{NO}}_3$ .

where  $q$  is the water flux in runoff (a consistent set of units is  $q$  in  $\text{m}^3/\text{yr}$ , Ca in  $\mu\text{equiv/L}$ ,  $X\text{Ca}$  in  $\text{mequiv/m}^2$ ; and  $D_{\text{Ca}}$ ,  $W_{\text{Ca}}$ , and  $B_{\text{Ca}}$  in  $\text{mequiv m}^{-2} \text{yr}^{-1}$ ). Equations 3 and 4 are derived from premises similar to those embodied in common catchment acidification models, but unlike typical simulation models, these equations show the relationships of interest explicitly. Equations 3 and 4 say that if acid anion concentrations and discharge are held constant, any imbalance between inputs and outputs of Ca or Mg (expressed as a percentage of exchangeable Ca or Mg) should produce a proportional percentage change in runoff Ca and Mg concentrations where the constant of proportionality is approximately  $1 - F_{\text{Ca}}$  or  $1 - F_{\text{Mg}}$ .

From a catchment mass balance, we could estimate the rate of change of exchangeable bases and use eq 3 to predict the resulting runoff trends. Here we do the reverse: given the observed trends, we estimate the rate of base cation depletion required to produce them. Using eq 3, we calculate that the observed trends ( $\beta$ ) at Birkenes, Storgama, and Langtjern are consistent with the depletion of exchangeable Ca and Mg from catchment soils at rates of 24–47  $\text{mequiv m}^{-2} \text{yr}^{-1}$  (Table 4).

**TABLE 4**

**Exchangeable Cation Pools and Estimated Depletion Rates**

	Birkenes	Storgama	Langtjern	Kårvatn
<b>Acid Deposition (<math>\text{mequiv m}^{-2} \text{yr}^{-1}</math>)</b>				
NSS $\text{SO}_4 + \text{NO}_3$	$255 \pm 17$	$121 \pm 9$	$83 \pm 6$	$31 \pm 1$
<b>Exchangeable Cations Stored in Catchment Soils (<math>\text{mequiv/m}^2</math>)<sup>a</sup></b>				
XCa	$1158 \pm 179$	$675 \pm 109$	$1437 \pm 263$	$879 \pm 186$
XMg	$380 \pm 53$	$205 \pm 44$	$255 \pm 37$	$504 \pm 114$
<b>Depletion of Exchangeable Cations Consistent with Observed Runoff Trends (<math>\text{mequiv m}^{-2} \text{yr}^{-1}</math>)<sup>b</sup></b>				
Ca	$26 \pm 6$	$20 \pm 4$	$43 \pm 11$	$8 \pm 10$
Mg	$7 \pm 1$	$4 \pm 1$	$4 \pm 1$	$-2 \pm 2$
<b>Increase in Cation Leaching Rates Due to Acid Loading (<math>\text{mequiv m}^{-2} \text{yr}^{-1}</math>)<sup>c</sup></b>				
Ca	$39 \pm 4$	$26 \pm 3$	$27 \pm 3$	$7 \pm 1$
Mg	$9 \pm 2$	$6 \pm 1$	$8 \pm 1$	$3 \pm 1$

<sup>a</sup> Area-weighted averages of 120–330 soil cores taken from 25 to 40 widely distributed sampling locations in each catchment; exchangeable cations extracted with 1 M KCl and analyzed by atomic absorption. <sup>b</sup> Estimated from runoff trends using eq 2 and data in Tables 1 and 3 (see text). <sup>c</sup> Estimated as non-seasalt sulfate flux times  $F_{\text{Ca}}$  and  $F_{\text{Mg}}$  (Table 3); for Mg, either this estimate or non-seasalt Mg flux, whichever is smaller, is used. All quantities reported as mean  $\pm$  standard error.

Is this rate of depletion consistent with the expected effects of acid loading on Ca and Mg leaching rates? Theoretical arguments and experimental data (6, 11, 17) show that, over time scales of weeks to years, changes in runoff acid anion concentrations produce roughly proportional changes in base cation concentrations where the constant of proportionality is approximately the buffer slope  $F$  (Table 3). Thus, we can estimate how much acid loading has accelerated Ca and Mg leaching at our sites by multiplying the non-seasalt  $\text{SO}_4$  flux in runoff by  $F_{\text{Ca}} + F_{\text{Mg}}$  (we ignore the effect of  $\text{NO}_3$  loading because  $\text{NO}_3$  deposition has primarily been taken up by biomass, and runoff  $\text{NO}_3$  concentrations have been low). In this way, we estimate that acid loading has elevated Ca and Mg fluxes in runoff by 32–48  $\text{mequiv m}^{-2} \text{yr}^{-1}$  at Birkenes, Storgama, and Langtjern (Table 4). These increases in Ca and Mg leaching are more than sufficient to produce the observed trends  $\beta_{\text{Ca}}$  and  $\beta_{\text{Mg}}$ , except at Langtjern where they are nearly, but not quite, large enough. As mentioned above, the time series for Langtjern is somewhat uneven, leading to a probable overestimate in  $\beta_{\text{Ca}}$  and  $\beta_{\text{Mg}}$  and thus in depletion rates calculated from eq 3.

Long-term declines in runoff base cations have previously been found at Birkenes and at Plastic Lake, Ontario, and were attributed to soil acidification (18, 19). However, in both cases the base cation trends accompanied declining sulfate concentrations (18, 20), so it was unclear how much the base cation losses reflected simple shifts in equilibrium, depletion of exchangeable bases, or both. Here, we have subtracted the effects of acid anion concentrations, thus clarifying the underlying trends ( $\beta$ ) and showing that they are not explainable by shifts in catchment equilibria. We have also shown that the observed trends are quantitatively consistent with the rates of base cation depletion that should accompany the levels of acid loading at our sites.

Declining trends in base cations, like those in Figure 1, have also been observed at Hubbard Brook, NH, by Driscoll et al. (21), who attributed them to changes in base cation deposition. At our sites, changes in deposition cannot

explain the observed long-term loss of base cations from runoff. Table 2 shows the trends in volume-weighted annual average runoff and precipitation concentrations for major ions at the four sites. The precipitation concentrations have been adjusted for dry deposition and evapo-concentration (assuming Cl is a conservative tracer of both processes), so that if trends in deposition were transmitted directly to runoff, the two trends in Table 2 would be equal. Instead, the declines in runoff Ca + Mg are 10 times larger than the declines in deposition flux at Birkenes and Storgama and three times larger than the changes in deposition flux at Langtjern. Although base cation deposition may be decreasing at our sites, the deposition trends are not statistically significant, nor are they quantitatively adequate to account for the runoff trends we have observed. Even the Hubbard Brook data are ambiguous, as Dillon (22) has pointed out, since base cation deposition declined during the first half of the 25-yr record (but not the second), whereas runoff concentrations declined during the second half (but not the first). By contrast, our hypothesis—that excess leaching of base cations should result in declining base cation concentrations, whether or not base cation deposition is changing—is quantitatively consistent with the data from our sites and also has been shown to be consistent with the Hubbard Brook data as well (11).

Long-term losses of exchangeable Ca and Mg from forest soils have been directly measured by repeat soil sampling at several sites in Europe and Scandinavia (23–25). There is currently considerable debate over whether the observed losses of Ca and Mg from soils are caused by increases in base cation leaching, increases in biomass uptake, or both (23). Although we cannot definitely exclude this possibility, we have no evidence for significant biomass accumulation at any of our sites over the period. Furthermore, our runoff chemistry trends are consistent with expected rates of base cation leaching by acid deposition, both at Birkenes, which is forested, and at Storgama, which has few trees. This suggests a clear relationship between acid loading and base cation depletion, but no clear role for biomass uptake at our sites.

### Effect of Reductions in Acid Deposition

We have shown that although acid deposition in southern Norway is declining, runoff water quality has not measurably improved, because acid loading is still high enough to cause depletion of exchangeable bases and long-term progressive acidification. So has anything been gained by emission reductions to date? To measure the effects of emission controls, one should *not* compare current conditions with those before emission controls; instead, one should compare current conditions with those that would have existed at present if emission controls had not been implemented. By this latter standard, emission controls have clearly been beneficial. Although water quality has not improved over time (because long-term base cation depletion has offset the effects of reductions in acid loading), water quality has not deteriorated as it would have if acid deposition had remained constant.

How rapidly would alkalinity have been lost under constant acid loading? The  $\beta$  coefficient in eq 1 measures the long-term trends (here attributed to depletion of exchangeable bases) expected under constant acid anion concentrations. The values of  $\beta_{Ca}$  and  $\beta_{Mg}$  shown in Table 3 indicate that, under constant acid loading, runoff alkalinity would have declined at roughly  $-1.4$ ,  $-0.9$ , and  $-1.1$   $\mu\text{equiv}$

$\text{L}^{-1} \text{yr}^{-1}$  at Birkenes, Storgama, and Langtjern, respectively (dashed lines, Figure 1). The actual alkalinity trends, if any, are much smaller. So, although acid loading reductions over the period have not reversed acidification at Birkenes, Storgama, and Langtjern, they have prevented substantial loss of alkalinity that would otherwise have occurred.

How much have reductions in acid deposition contributed to preventing alkalinity loss? Multiplying the trend in runoff concentrations of  $\text{SO}_4 + \text{NO}_3$  by  $(F_{Ca} + F_{Mg} - 1)$  to correct for the partially offsetting effects on Ca and Mg (dotted lines, Figure 1), we estimate that reductions in  $\text{SO}_4 + \text{NO}_3$  have improved alkalinity by 1.3, 0.6, and 0.3  $\mu\text{equiv L}^{-1} \text{yr}^{-1}$  at Birkenes, Storgama, and Langtjern, respectively, compared to the trends that would have occurred under constant acid loading. Thus, acid loading reductions have largely compensated for the effects of base cation depletion at these sites.

### Implications for Reversibility of Acidification

If, as our data show, reductions in acid loading are needed simply to hold runoff alkalinity constant, what does this imply for efforts to reverse catchment acidification? Our results imply that runoff alkalinity can be improved in two ways: by reducing acid loading *rapidly* enough to offset the effects of progressive acidification from base cation depletion and by reducing acid loading *far* enough to bring base cation leaching rates into balance with rates of base cation supply.

Immediate improvements in runoff water quality can be achieved by reducing acid loading rapidly enough to compensate for ongoing progressive acidification. Our calculations above show that acid loading reductions over the period of record at our catchments have offset significant deterioration in water quality that would otherwise have occurred (Figure 1). Here, we show two ways to estimate the rate that acid loading must be reduced to produce net improvements in runoff alkalinity. Assuming that non-seasalt sulfate ( $\text{SO}_4^*$ ) is the major acid anion of concern, that seasalt loading and discharge are roughly stable over time, and that nitrate is relatively unimportant, the condition required to raise runoff alkalinity is

$$\frac{d\text{SO}_4^*}{dt}(F_{Ca+Mg} - 1) + \beta_{Ca+Mg} \geq 0 \quad (5)$$

where  $F_{Ca+Mg} - 1$  represents the effect of changes in  $\text{SO}_4^*$  on alkalinity, net of equilibrium changes in Ca and Mg. This can be solved directly for the rate of  $\text{SO}_4^*$  decrease needed to stabilize or improve alkalinity

$$\frac{d\text{SO}_4^*}{dt} \leq \frac{\beta_{Ca+Mg}}{1 - F_{Ca+Mg}} \quad (6)$$

where both  $\beta$  and  $d\text{SO}_4^*/dt$  are negative, indicating that  $\text{SO}_4^*$  must decline faster than  $\beta_{Ca+Mg}/(1 - F_{Ca+Mg})$  in order to offset long-term depletion of Ca and Mg from the catchment. Using Table 3, we calculate that stabilizing runoff alkalinity would require decreasing non-seasalt sulfate concentrations in runoff by approximately  $2.4 \pm 0.3$   $\mu\text{equiv L}^{-1} \text{yr}^{-1}$  at Birkenes and  $1.8 \pm 0.2$   $\mu\text{equiv L}^{-1} \text{yr}^{-1}$  at Storgama. This corresponds to reductions in  $\text{SO}_4^*$  loading of  $2.8 \pm 0.4$  and  $1.7 \pm 0.3$   $\text{mequiv m}^{-2} \text{yr}^{-1}$  at the two sites, assuming no long-term adsorption or desorption of sulfate from catchment soils (at these sites, deposition and runoff

fluxes of SO<sub>4</sub> agree to within 10–20%, indicating little retention or release of sulfate).

Many catchments lack sufficiently detailed time series to reliably estimate the trend  $\beta_{Ca+Mg}$  as required in eq 6. At such sites,  $\beta_{Ca+Mg}$  can be approximated from eq 3 under the assumption that the net depletion rate of base cations will be approximately the non-seasalt sulfate flux scaled by  $F_{Ca+Mg}$ :

$$\beta_{Ca+Mg} = (Ca + Mg)(1 - F_{Ca+Mg})\alpha \frac{-SO_4^* \cdot F_{Ca+Mg} \cdot q}{XCa + XMg} \quad (7)$$

Combining eqs 6 and 7 yields an estimate of the rate of change in SO<sub>4</sub><sup>\*</sup> required to stabilize runoff alkalinity as a percentage of current SO<sub>4</sub><sup>\*</sup>

$$\frac{dSO_4^*/dt}{SO_4^*} \leq -\alpha F_{Ca+Mg} \frac{(Ca + Mg) \cdot q}{XCa + XMg} \quad (8)$$

Expressing  $dSO_4^*/dt$  as a percentage of SO<sub>4</sub><sup>\*</sup> means that eq 8 is equally applicable to sulfate concentrations and fluxes. From eq 8, we estimate that SO<sub>4</sub><sup>\*</sup> loading reductions of 2–3% per year would be needed to stabilize runoff alkalinity at Birkenes, Storgama, and Langtjern (3.3 ± 0.5, 1.8 ± 0.3, and 1.3 ± 0.3  $\mu\text{equiv L}^{-1} \text{yr}^{-1}$ , respectively, corresponding to loading reductions of 3.8 ± 0.7, 1.7 ± 0.4, and 0.8 ± 0.2 mequiv m<sup>-2</sup> yr<sup>-1</sup>, respectively). As sulfate loading is reduced, we would expect roughly proportional reductions in the rates of base cation depletion. Thus, the rate of loading reductions needed to offset progressive acidification will decrease as sulfate loading itself decreases, although as a percentage of current loading the rate is likely to remain roughly constant.

Estimates derived from eqs 6 and 8 cannot be considered as more than rough approximations. However, at our sites these equations yield results that are consistent with one another and broadly consistent with the rates of SO<sub>4</sub><sup>\*</sup> decrease that, in the actual catchment time series, have prevented substantial deterioration of runoff alkalinity.

Permanent stabilization of runoff water quality can only be achieved by reducing acid loading far enough that the base cation leaching rate comes into balance with base cation supply from atmospheric deposition and weathering. Determining this "critical load" that catchments can sustain over the long term requires reliable estimates of base cation release by mineral weathering (24, 26, 27). Our analysis does not permit a precise estimate of critical loads, but it suggests that they are probably well below current acid loading at our sites. For example, Table 4 indicates that at Birkenes and Storgama, the long-term runoff chemistry trends imply a base cation depletion rate that is roughly 70–75% of the rate expected from leaching by non-seasalt sulfate (at Langtjern, the runoff chemistry trends are too uncertain for this calculation to be made reliably). This suggests that mineral weathering offsets roughly 25–30% of base cation leaching [approximately 8–15 mequiv m<sup>-2</sup> yr<sup>-1</sup>, broadly consistent with the  $\approx 10$  mequiv m<sup>-2</sup> yr<sup>-1</sup> estimated by strontium isotope techniques (28) for the Buskbäcken catchment in central Sweden], which in turn implies that halting progressive acidification at these sites would require reducing acid loading by approximately 70–75% from the levels of the mid-1980s.

Our analysis is not primarily intended to define critical loads, but instead to show that water quality also depends on how quickly the critical load is reached. At catchments

where exchangeable bases are being progressively depleted, water quality may deteriorate significantly before the critical load is reached if acid loading is not reduced quickly enough. Conversely, if acid loading is reduced as rapidly as indicated by eq 6 or eq 8, then water quality can be maintained at current levels as the critical load is achieved.

Reversing acidification—rather than simply halting it—requires reducing acid loading (and thereby base cation leaching rates) below the critical load, so that over time weathering can replenish base cations depleted from the catchment's ion-exchange pools. This recovery process is likely to be slow. As the calculations above indicate, weathering rates at these sites may be roughly one-third of the base cation depletion rates inferred over the period of record. Thus, even if base cation leaching rates were reduced to nearly zero, weathering would only replace base cations about one-third as quickly as they have been depleted. Because base cation depletion has been ongoing at these catchments for several decades, permanent recovery should be expected to take several times longer than this.

## Conclusions

At three acid-impacted Norwegian catchments, runoff concentrations of SO<sub>4</sub> + NO<sub>3</sub> declined by 20–25% from the late 1970s to the early 1990s (Figure 1), mirroring similar declines in acid deposition (Table 2). However, runoff water quality did not measurably improve because decreases in runoff SO<sub>4</sub> + NO<sub>3</sub> were offset by roughly equivalent declines in runoff Ca + Mg (Figure 1, Table 2). A fourth site, subject to relatively little acid loading, showed no significant trends.

Four lines of evidence support the hypothesis that the observed loss of Ca and Mg from runoff is largely caused by depletion of exchangeable bases from catchment soils under high acid loading. First, long-term declines in Ca + Mg persist even when the effects of changes in acid loading, seasalt loading, and discharge are subtracted (Figure 2, Table 3). Second, the largest long-term losses in Ca and Mg ( $\beta$ , Table 3) occur at the sites with the highest acid loading. Third, changes in Ca and Mg deposition are too small to explain the observed losses from runoff (Table 2). Fourth, the long-term trends ( $\beta$ ) imply rates of base cation depletion that are quantitatively consistent with base cation leaching rates expected from the levels of acid loading at these sites (Table 4).

Although runoff water quality has not markedly improved over the period of record, reductions in acid deposition have offset significant acidification that would otherwise have taken place. Under constant acid deposition, our sites would have lost approximately 0.9–1.4  $\mu\text{equiv/L}$  of alkalinity per year (dashed lines, Figure 1) due to ongoing base cation depletion. Instead, under declining acid deposition, alkalinity has remained roughly constant (although at Langtjern, a clear trend is difficult to discern). If exchangeable bases were not being depleted from the catchments, the observed reductions in SO<sub>4</sub> + NO<sub>3</sub> would have resulted in net improvements in alkalinity of 0.3–1.3  $\mu\text{equiv L}^{-1} \text{yr}^{-1}$  (dotted lines, Figure 1).

Where exchangeable bases are being depleted faster than they can be resupplied from mineral weathering, continuous reductions in acid loading are required simply to maintain constant runoff alkalinity. We estimate that sulfate loading reductions of more than 2–3% per year are required to offset base cation depletion and improve runoff alkalinity at these sites. Permanently restoring pre-



acidification water quality requires reducing acid loading, and thus base cation leaching, enough that mineral weathering can replace exchangeable bases depleted from catchment soils. Because silicate weathering rates are low compared to rates of base cation leaching under acid deposition, permanent recovery from base cation depletion will be slow.

Large, rapid reductions in acid deposition can improve runoff water quality, as acid exclusion experiments have demonstrated (29). Our results show that more modest reductions in acid loading, like those experienced to date in southern Norway and elsewhere, may be sufficient to limit—but not necessarily reverse—acidification of some acid-sensitive waters.

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