THE SIGNIFICANCE OF IN-LAKE PRODUCTION OF ALKALINITY

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ABSTRACT. Alkalinity production in terrestrial and aquatic ecosystems of Canada, the U.S.A., Norway and Sweden is calculated from either strong acid titrations or budgets for base cations and strong acid anions, using mass-balance budgets. Where alkalinity budgets for lakes and their catchments are calculated in acid-vulnerable geological settings, in-lake processes often contribute more to lake alkalinity than yield from terrestrial catchments. Nitrate and sulfate removal, and Ca exchange with sediments are the predominant alkalinity generating mechanisms in lakes.

Nitrate and sulfate removal rates increase as the concentrations of NO_3^- and SO_4^{2-} in lake water increase, so that in-lake acid neutralizing capacity increases as acid deposition increases. Both processes occur in sediments overlain by oxic waters, at rates which seem to be controlled primarily by diffusion.

1. INTRODUCTION

While the transfer of alkalinity from sediments to overlying waters has been known for decades (for example, Mortimer, 1941-42; Hutchinson, 1957), early authors did not quantitatively relate in-lake alkalinity production to other sources in a lake's watershed. Even so, it is curious that limnology texts (for example, Ruttner, 1959; Wetzel, 1975) and summaries of the effects of acid precipitation (for example, NRCC, 1981; Norton, 1982; Driscoll and Newton, 1985) have assumed that the alkalinity of lakes would be derived primarily from ion exchange and weathering of terrestrial soils and rocks.

In all of the above cases, standard weathering reactions were assumed to predominate in alkalinity production. The first illustrations of the importance of biological buffering in lakes by sulfate reduction in lakes were by Hongve (1978), Schindler (1978), and Schindler et al. (1980). Schindler and Turner (1982), Cook and Schindler (1983), and Cook et al. (1986) showed the quantitative

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importance of sulfate retention, and deduced that reduction and transfer of S to sediments was responsible. Schindler and Turner (1982), Kelly and Rudd (1984), and Cook et al. (1986) showed that sediments overlain by oxic water still reduced and retained sulfate. Kelly et al. (1982) showed that alkalinity generation was also related to biological productivity in lakes. Kilham (1982) found that sulfate removal and nitrate uptake completely neutralized H^+ input to Weber Lake, Michigan, and Hemond (1980) found similar results for Thoreau's Bog, Massachusetts. Baker et al. (1984), showed that alkalinity production was important in softwater lakes of Florida, Minnesota and Wisconsin. Carignan (1985) showed that fluxes of alkalinty from the sediments of Clearwater Lake in eastern Ontario could neutralize most of the acid inputs. Rudd et al. (1986a) showed that sulfate reduction and denitrification in epilimnetic sediments were important sources of alkalinity in low pH lakes from eastern Canada, the Adirondacks, and Norway. Schindler et al. (1985) and Schuurkes (1985) showed that the effect of N input on the alkalinity of freshwaters depended on the ionic form of N. van Breemen et al. (1982) show similar properties for terrestrial soils, and van Breemen et al. (1984) showed that acid-sensitive terrestrial watersheds yielded very little alkalinity. Several papers at the Muskoka '85 conference also have illustrated the importance of in situ alkalinity generation (Schiff and Anderson, 1985; Dillon and LaZerte, 1985; Jeffries et al., 1985). The topic was also discussed in detail at a pre-conference workshop sponsored by the Ontario Ministry of Environment.

This paper summarizes what is known about in-lake alkalinity generation from mass-balance studies, and compares the importance of in-lake processes with inputs to lakes for terrestrial catchments in determining the alkalinity balance of lakes.

2. METHODS

Studies of alkalinity generation in both lake and terrestrial ecosystems may be done by mass-balance, using any of three sets of measurements: 1) titratable alkalinity, 2) HCO_3^- plus H^+, or 3) budgets for individual base cations and strong acid anions. In method 3) it is assumed that the sum of all cations must equal the sum of all anions to maintain charge balance. In surface waters which typify acid sensitive areas:

$$H^+ + Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ = HCO_3^- + SO_4^{2-} + Cl^- + NO_3^-. \quad (1)$$

Because alkalinity may be defined as:

$$Alk = HCO_3^- - H^+ \quad (2)$$

in typical acid sensitive waters alkalinity will equal the difference between basic cations and strong acid anions:

$$Alk = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+} - (SO_4^{2-} + Cl^{-} + NO_3^{-}). \quad (3)$$

Aluminum (Al^{3+}) and organic anions (A^{-}) also contribute to alkalinity budgets in some lakes, but their role depends on the pH range of individual lakes and the pK_a values of different organic acids. Their entire role in the buffering process is not completely understood at present. Space does not allow their inclusion here, but calculations based on a few sites indicate that while Al^{3+} and A^{-} may be important in some lakes, their omission does not affect our general conclusions. ESSA (1986) review the problem.

If the inputs (I), outputs (O) and change in storage in the lake (ΔM) of the individual base cations and strong acid anions in Equation (3) are combined in mass balance calculations, the changes in a lake's alkalinity resulting from various ionic reactions can be calculated. Expressed as alkalinity production (P_a):
For base cations:

$$P_a = O + \Delta M - I \quad (4)$$

and for strong acid anions:

$$P_a = I - (\Delta M + O). \quad (5)$$

In general, release of base cations and removal of strong acid anions in an ecosystem are alkalinity producing reactions, exemplified by Ca^{2+} exchange, and removal of sulfate and nitrate. Conversely, removal of base cations such as ammonium, re-oxidation of reduced S and nitrification in ecosystems would consume alkalinity.

With the exception of uptake and release of nutrients by plankton, most in situ alkalinity production or consumption occurs in or near sediment surfaces (Carignan, 1985; Rudd et al., 1986b; Schiff and Anderson, 1985, 1986). Both geochemical processes (precipitation, adsorption, dissolution, and desorption) and biological mechanisms (sulfate reduction, sulfate ester formation, denitrification, assimilation of nitrate and ammonium) can affect alkalinity. Both iron sulfides and organic sulfides are sinks for the reduced S, although the latter seem to be more important in the long-term (Landers et al., 1983; Nriagu and Soon, 1985; Rudd et al., 1986b). Reviews of pertinent aquatic reactions are given by Schnoor and Stumm (1985), Cook et al. (1986) and Rudd et al. (1986b). Analogous expressions for soils are given by van Breemen et al. (1982, 1984).

Terrestrial alkalinity production may be calculated in a matter analogous to that for freshwater lakes (Equation (4) or (5)). While ΔM is seldom known, it appears reasonable to disregard it for this comparison, because long-term fluxes of chemicals from catchments do not usually show uni-directional changes, unless they have been disturbed very recently (Likens et al., 1977; Bayley and Schindler, 1986). Further discussion is given by van Breemen et al. (1984). The outflow of alkalinity from terrestrial catchments, called the yield in this paper, must be known in order to calculate the alkalinity budgets of lakes. I use the term production in the same way in both terrestrial and aquatic ecosystems, to designate the change in alkalinity occurring during passage of water through the system. In terrestrial ecosystems, this is yield-precipitation input. Similar studies were done by van Breemen et al. (1983, 1984) for terrestrial systems without reference to their contribution to lakes.

3. RESULTS

3.1. Terrestrial alkalinity production

Complete ion budgets for 33 terrestrial watersheds in acid-sensitive regions of Canada, Scandinavia and the U.S. were selected from the literature or contributed by scientists at the Muskoka '85 conference (see Table I for sources). North American sites produced from -20 to 193 meq m^{-2} yr^{-1} of alkalinity, with all but two sites producing less than 90 meq m^{-2} yr^{-1}. Scandinavian sites ranged from 9 to 112 meq m^{-2} yr^{-1}. There appeared to be no relationship between alkalinity production and deposition of H^+. This was not unexpected, because the reactivity of soils and bedrock in watersheds, the duration of interaction between water and soil, and the acidity of precipitation (i.e. its potential for weathering or ion-exchange reactions) should all affect the production of alkalinity. Furthermore, Stuanes (1980) has shown that increased yields of base cations from terrestrial plots did not occur until artificial acid precipitation had a pH less than 3. Fölster (1985) demonstrated that weathering rates in acid-sensitive areas receiving acid precipitation could not be distinguished from historical values. van Breemen et al. (1984) found a large variation in the ions affecting proton budgets of different watersheds.

Reactions involving release of Ca^{2+} or Mg^{2+}, or retention of NO_3^- were the most important mechanisms producing terrestrial alkalinity. Na^+ release was significant at a few sites. In addition, retention of SO_4^{2-} was significant in watersheds containing a high proportion of wetland, e.g., the ELA NE Subbasin, the Mersey River, Storgama STE03, and the Swedish watersheds. This retention is lower during periods of drought (Bayley et al., 1985).

Many of the watersheds appeared to export more sulfate than they received. The highest discrepancies were for watersheds near Sudbury, where recent reductions in sulfate emissions are likely to have caused non-steady state conditions. Negative values for other watersheds may indicate that input of S is underestimated, which appears to be a widespread problem (Johnson, 1985; Jeffries et al., 1984; Dillon and LaZerte, 1985). The high chloride losses from some sites (Sudbury and Scandinavia) are inexplicable, but deserve further research because they are too high and too numerous to be caused by errors in budget calculations. They represent important consumers of alkalinity, as shown in Table I.

TABLE I
Production of alkalinity by various ionic reactions in acid-sensitive terrestrial watersheds, as calculated from Equations (4) and (5). Values are in meq m^{-2} yr^{-1}. Aluminum and organic acids are ignored. Negative values indicate alkalinity removal.

Description	P_a due to: Release of					Removal of			ΣP_a by addition cations	ΣP_a by removal acid anions	ΣP_a
	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-			
CANADA											
ELA, Ontario[a]											
NW Subbasin	7	8	6	3	-15	-16	13	3	9	0	9
NE "	4	5	5	2	-15	12	15	5	1	32	33
E "	14	8	8	2	-15	- 1	14	4	17	17	34
Saqvaqjuac, N.W.T.[b]	58	23	34	5	not done	-37	not done	-38	120*	- 75*	45*
Muskoka, Ontario											
Harp Lake[c]											193***
Watershed 3[d]	54	34	11	2	-31	-28	29	-10	70	- 9	61
" 3A[d]	66	37	5	1	-31	-42	16	- 1	78	- 27	51
" 4[d]	44	28	7	2	-30	-27	34	- 2	51	5	56
" 5[d]	57	38	6	3	-30	-63	34	- 5	74	- 34	40
Plastic Lake[c]											-20***
Sudbury, Ontario[e]											
Clearwater 1	73	36	- 7	2	-25	-121	37	2	79	- 82	- 3
" 2	298	75	76	6	-25	-128	37	-341	430	-432	- 2
" 3	65	30	21	2	-26	-107	38	- 6	92	- 75	17
" 4	147	52	16	4	-22	-114	36	-124	197	-202	- 5
Middle	141	84	10	8	-28	-236	36	- 23	215	-223	- 8
Nelson 1	91	31	- 2	2	-22	-118	33	1	100	- 84	16
2	100	30	0	1	-22	-127	36	- 2	109	- 93	16
3	82	30	- 3	2	-22	- 88	34	- 1	89	- 55	34
4	129	54	5	5	-22	-171	35	0	171	-136	35
5	124	60	5	6	-18	-162	32	0	177	-130	47
6	110	88	4	5	-22	-123	34	6	185	- 83	102
Nova Scotia											
Mersey River[f]	12	12	21	1	-12	20	34	0	34	54	88
USA											
Hubbard Brook, NH[g]	58	21	24	2	-14	- 32	4	6	91	- 22	69
NORWAY											
Storgama STE01[h]	131	40	66	15	- 92	- 62	79	- 35	130	- 18	112
" STE03[h]	44	20	25	8	- 96	46	87	- 36	1	97	98
Birkenes[i]	59	25	54	2	- 48	- 60	45	- 52	92	- 67	25
Storgama[i]	32	11	19	5	- 25**	- 22	27	- 10	42	- 5	37
Gulen[i]	5	6	12	1	- 7	0	7	- 15	17	- 8	9
Todalen[i]	9	2	- 2	1	- 3	0	2	5	7	7	14
Långtjern 02[j]	31	7	5	- 1	no data	14	24	0	42*	38	80
" 03[j]	25	9	6	- 1	no data	13	24	0	39*	37	76*
SWEDEN											
Solmyren[k]	60	27	11	3	- 13	5	12	0	88	17	105
Vuoddasbäcken[k]	32	21	15	1	- 12	36	11	0	57	47	104
Lilla Tivsjön[k]	42	22	7	0	- 12	6	11	0	59	17	76

*excludes NO_3^- and/or NH_4^+
**estimated
***by Gran alkalinity mass-balance
[a] Schindler et al., 1986; [b] Welch, 1986; [c] Dillon and Lazerte, 1985; [d] NRCC, 1981; [e] Jeffries et al., 1984; [f] Kerekes, 1980; [g] Likens et al., 1977; [h] Braekke, 1981 (sub-basins of total Storgama watershed); [i] Overrein et al., 1980; [j] Wright, 1983; [k] Calles, 1983

To put the above acid-sensitive catchments in perspective, I calculated partial alkalinity budgets for calcareous catchments from data for Ca^{2+}, Mg^{2+}, Na^+, K^+ and SO_4^- which were summarized by Likens et al. (1977). As expected, alkalinity production in such watersheds was very high (up to 420 meq m^{-2} yr^{-1} at Carnation Creek, BC and 1313 meq m^{-2} yr^{-1} at Walker Branch, TN), and dominated by Ca^{2+} yield. Certain soils (i.e. Walker Branch) also retain sulfate, apparently by chemical adsorption rather than by sulfate reduction and precipitation as in lakes and bogs (Johnson and Todd, 1983). Either mechanism contributes to alkalinity production.

3.2. Terrestrial alkalinity yield

Because yield is the sum of terrestrial production and precipitation inputs, it will be lower than production in regions where precipitation has negative alkalinity, which is the case for all sites considered here. For the same acid-vulnerable watersheds summarized in Table I, the range in yield was -87 to 171 meq m^{-2} yr^{-1} (Table II). Watersheds in most high-deposition areas had alkalinity yields ranging from -50 to 50 meq m^{-2} yr^{-1}. ELA and Storgama also had low yields, despite low acid deposition. Values from Harp Lake, Ontario, watersheds in northern and central Sweden, and Saqvaqjuac, N.W.T. were over 100 meq m^{-2} yr^{-1}, perhaps indicating the presence of some calcareous material in the drainages.

3.3. Aquatic alkalinity production

Alkalinity production calculated from Gran alkalinity budgets for the lakes available varied by less than 3x with the exception of the Sault Ste. Marie sites, even though the regions encompassed receive deposition which varies by almost an order of magnitude in H^+, SO_4^{2-} and NO_3^-. Where both Gran alkalinity and ion-balance methods could be used, the agreement between methods was reasonably good, as one would expect if organic anions are relatively unimportant (Table III).

Ca^{2+} exchange, and removal of NO_3^- and SO_4^{2-} were the most important in situ processes producing alkalinity. Ca^{2+} exchange was much higher at the Sault Ste. Marie sites, which have small amounts of calcareous tills and lie in greenstone geology. Lake 302N, experimentally acidified with HNO_3, had a much higher rate of NO_3^- removal than the rest. Also, lakes 223 and 302S, to which H_2SO_4 was added, had the highest rates of SO_4^{2-} removal. SO_4^{2-} appeared to be exported, rather than retained in the Sault Ste. Marie lakes, although inputs may be underestimated due to high dry deposition in the area (Jeffries et al., 1984). Exchange for H^+ or biological uptake of other cations (Mg^{2+}, K^+, NH_4^+) may significantly affect alkalinity budgets, but are of lesser importance (Schindler et al., 1986; Cook et al., 1986; Jeffries et

TABLE II
The yield (Output) of various ions, from the terrestrial watersheds in Table 1. Σ alkalinity yield = total base cation yield − total strong acid anion yield. Data are in meq alkalinity m^{-2} yr^{-1}.

Description	Yield of								Σ base cation yield	Σ base acid anion yield	Σ alk. yield
	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-			
CANADA											
ELA, Ontario											
NW Subbasin	22	15	11	5	0	39	2	4	53	45	8
NE "	20	12	10	3	0	11	0	2	45	13	32
E "	29	15	13	5	0	24	1	3	62	28	34
Saqvaqjuac, N.W.T.	150	24	41	5	not done	42	not done	45	220*	87*	133*
Muskoka, Ontario											
Harp Lake											125***
Watershed 3	84	41	26	6	2	99	8	2	159	109	50
" 3A	97	44	20	5	1	113	21	- 6	167	128	39
" 4	74	36	22	5	2	98	4	- 6	139	96	43
" 5	87	45	21	6	2	134	3	- 3	161	134	27
Plastic Lake											-87***
Sudbury, Ontario											
Clearwater 1	100	42	28	7	1	193	1	9	178	203	- 25
" 2	324	80	104	10	1	202	2	352	519	556	- 37
" 3	91	36	36	6	0	180	1	16	169	197	- 28
" 4	172	58	51	9	3	176	2	135	293	313	- 20
Middle	178	92	46	10	2	320	4	36	328	360	- 32
Nelson 1	114	38	25	6	2	187	2	9	185	198	- 13
2	123	36	28	4	1	197	0	6	192	203	- 11
3	106	37	24	6	2	156	2	6	175	164	11
4	152	60	32	8	1	239	1	8	253	248	5
5	163	66	32	10	4	230	4	8	275	242	33
6	132	94	32	8	1	192	2	14	267	208	59
Nova Scotia											
Mersey River	30	34	121	6	0	73	1	114	191	188	3
USA											
Hubbard Brook, NH	68	26	32	5	2	112	28	14	133	154	-21
NORWAY											
Storgama STE01	160	59	135	23	24	312	47	116	401	475	-74
" STE03	73	39	94	16	20	204	39	80	242	323	-81
Birkenes	72	43	133	8	5	164	8	133	261	305	-44
Storgama	39	15	33	7	not done	78	13	27	94	118	-24
Guelen	10	22	78	3	1	29	2	91	114	122	- 8
Todalen	13	8	23	2	1	9	1	25	47	35	12
Längtjern 02	38	11	15	3	15**	49	1	11	82	61	21
" 03	32	12	17	2	16**	50	1	11	79	62	17
SWEDEN											
Solmyren	82	34	25	6	1	14	1	8	148	23	125
Vuoddásbacken	55	28	29	4	1	7	2	8	117	17	100
Lilla Tivsjön	59	27	15	2	1	8	1	6	104	15	89

*excludes NO_3^-, NH_4^+
**inputs are wet plus dry, rather than bulk ppt.
***by Gran alkalinity mass-balance

TABLE III
A summary of in-lake production of alkalinity and alkalinity generation by the three most commonly-important ionic reactions in acid-sensitive lakes. Data included are from mass-balance studies of either Gran alkalinity or ion balance, mesocosm mass balance studies, and pore-water studies. All data are in meq alkalinity m^{-2} yr^{-1}.

	Gran alkalinity	Ion balance alkalinity	Ca^{+2} exchange	NO_3^- removal	SO_4^{2-} removal
Whole-lake mass balance studies					
CANADA					
ELA - Lake 239[a]	118	92	29	19	39
Lake 223[b]	333	364	76	19	368
Lake 302S[c]	248	182	14	21	168
Lake 302N[c]	244	260	11	149	81
Muskoka					
Plastic Lake[d]	170	148	negligible	34	70
Harp Lake[d]	208	200	negligible	52	71
Sault Ste. Marie[e]	313	531	466	49	-110
So. Batchawana Lake	765	677	585	86	- 43
Turkey Lake					
USA					
Florida					
McCloud Lake[f]	-	-	-	17-20	26-34
NORWAY					
Langtjern[g]	-	111	43	17	57

[a] Schindler *et al.* (1986) - natural lake in low deposition area.

[b] Cook *et al.* (1986) - lake experimentally acidified to pH 5.1 with H_2SO_4. Data are 1981-83 average.

[c] Schindler *et al.* (1986 unpublished data) - Lake 302S was experimentally acidified to pH 5.6 with H_2SO_4, Lake 302N was experimentally acidified with the same amount per unit volume of HNO_3.

[d] P. Dillon and Lazerte (1985) - natural lakes in high deposition area.

[e] D. Jeffries *et al.* (1984) - natural lakes with some calcareous material, moderately acid deposition. Values may include input from groundwater seepage.

[f] Baker and Brezonik (1985a), Baker *et al.* (1984) - seepage lake, moderately acid deposition.

[g] Wright (1983) - natural lake in high deposition area.

al., 1985). Under anoxic conditions, diffusion of redox-sensitive species (Fe^{2+}, Mn^{2+}) from sediments may cause temporary increases in alkalinity, but this disappears at overturn, when the Fe^{2+} and Mn^{2+} are re-oxidized.

3.4. The role of terrestrial yield and *in situ* production in determining lake alkalinity

If *in situ* production were negligible, the alkalinity of a lake should be equal to the sum of average yield from the terrestrial basin and precipitation input to the lake surface, divided by the average outflow volume of the lake (Schindler *et al.*, 1986; Dillon *et al.*, 1985). Where the necessary measurements have been made, lakes always have much higher alkalinities than these theoretical calculations, illustrating the importance of *in situ* processes (Table IV). Similar conclusions could be reached for lakes in the Sudbury area, but because of recent reductions in regional sulfate

TABLE IV
Theoretical and observed alkalinity in acid-sensitive lakes, where theoretical alkalinity = (terrestrial yield + precipitation input) ÷ lake outflow volume . Alkalinity data in μeq L^{-1}.

Lake	τ, yr	Terrestrial drainage area / Lake area	Theoretical alkalinity	Observed alkalinity	Reference
Lake 239	6.2	6	73	150	Schindler *et al.*, 1986
Lake 223	8.7	6[a]	12	80	Schindler *et al.*, 1980; Cook *et al.*, 1986
Harp Lake	2.5	7	13	64	Dillon and Lazerte, 1985
Plastic Lake	3.0	3	- 75	8	Dillon and Lazerte, 1985
Langtjern	0.2	20	25	35	Wright, 1983
Lake McCloud	1.3	19	-133	0	Baker *et al.*, 1984

[a] Excluding drainage of upstream lakes.

emissions, these lakes are not at steady-state with respect to deposition (Dillon and LaZerte, 1985). Some have also been contaminated by road salt (Dillon *et al.*, 1986). We therefore have not included them in our comparison.

The role of *in situ* processes becomes still more important as lakes acidify. Addition of H_2SO_4 to ELA lakes 223 and 302S caused an almost linear increase in SO_4^{2-} reduction, with corresponding alkalinity production (Cook and Schindler, 1983; Schindler, 1985; Kelly and Rudd, 1984). In waters acidified with H_2SO_4, SO_4^{2-} removal became the dominant alkalinity-generating process, furnishing 92% of alkalinity production (Cook *et al.*, 1986; Schindler *et al.*, 1986). Likewise, addition of HNO_3 to Lake 302 North caused increased alkalinity production (Table III), largely due to increased denitrification (Rudd *et al.*, 1986a). While there are no data documenting long-term responses of terrestrial watersheds to increased acidification, it is unlikely that alkalinity export would increase, so that *in situ* processes will increase in relative importance in aquatic alkalinity budgets as lakes acidify.

4. DISCUSSION

In many acid-sensitive regions, terrestrial watersheds are unlikely to be the predominant alkalinity source for lakes (Table II). In some cases, they are actually consumers of alkalinity. For example, the average alkalinity yield from Hubbard Brook is 21 meq m^{-2} yr^{-1}, that from the Mersey River, NS is only +3, Norwegian watersheds range from -81 to +21, and 7 of 11 Sudbury watersheds have negative alkalinity yields. While terrestrial alkalinity yields from Sweden, Muskoka and ELA are slightly higher, in all cases aquatic alkalinity generation is too important to be ignored in budget calculations.

Sulfate retention appears to be a function of SO_4^{2-} concentration (Cook and Schindler, 1983; Schindler, 1985), which is in turn a function of sulfate input and water renewal (Baker and Brezonik, 1985b; Kelly et al., 1986). But the concentration of sulfate and nitrate alone does not appear to be sufficient to predict the rates of sulfate and nitrate reduction among lakes. The concentration of degradable organic substrate in near-surface sediments where sulfate reduction and denitrification occur is also important (Rudd et al., 1986a). Because of the dependence of a lake's acid neutralizing capacity on these biological reactions, it is presently impossible to predict the vulnerability of lakes to acidification from easily-measurable chemical, physical or geological characteristics alone. It follows that water column alkalinity is not necessarily a good indicator of the acid neutralizing capacity (ANC) of lakes, because alkalinity generated by sulfate and nitrate reduction increases when concentrations of these two ions are increased.

Clearly, alkalinity budgets in both terrestrial watersheds and lakes are partly a function of the composition of precipitation. For example, input and consumption of NH_4^+ can be expected to have the same effect on ecosystems as input of H^+, i.e. alkalinity consumption, (Vollenweider, 1963; Hunt and Boyd, 1981; Schindler et al., 1985; Schuurkes, 1985; van Breemen et al., 1982):

$$\begin{array}{lll} NH_4^+ & \rightarrow & NH_3 + H^+ \\ & & \downarrow \\ & & \text{plants.} \end{array} \qquad (6)$$

A brief survey of the literature reveals that NH_4^+ concentrations in precipitation ranged from 17 to 173% of H^+ (see, for example, Likens et al., 1977). In most of the ecosystems studied, ammonium removal is nearly 100%. The sum of ammonium input plus H^+ input should be a better index of the acidification potential of precipitation on ecosystems than H^+ alone. Evaluating the effect of biologically-reactive anions in precipitation is more difficult, because of the wide variation in efficiencies of utilization by different ecosystems. Likens et al. (1977) present data for Hubbard Brook which suggest that the efficiency of terrestrial ecosystems at generating alkalinity may decrease as nitrate deposition increases, because nitrate retention by the terrestrial watershed decreased markedly in the 1960's and 1970's.

Lakes with larger terrestrial catchments will usually have higher rates of water renewal, which would be expected to reduce the retention of sulfate and nitrate as has been shown for nutrients in eutrophication (Dillon, 1975; Vollenweider, 1976; Schindler et al., 1978). This would result in a lower retention of alkalinity by the lake (Baker and Brezonik, 1985b; Kelly et al., 1986). Also, in systems where alkalinity yield from terrestrial basins is positive, lakes with larger terrestrial basins should have a higher proportion of their alkalinity originate outside the lake (Table V). However, even in Langtjern, with a terrestrial:lake surface ratio of 20 and a

TABLE V
A comparison of terrestrial and aquatic alkalinity production and terrestrial yield at several sites. All values are by Gran titration, in meq m^{-2} yr^{-1}.

	Terrestrial production	Terrestrial yield	Aquatic production
239	26	16	118
Harp	193	125	208
Plastic	-20	-87	170
Langtjern	93	19	57

water renewal time of 0.2 yr, 25% of the alkalinity in the system is generated within the lake. Clearly, even lakes with very short water renewal times can have a substantial part of their alkalinity generated in situ.

The number of data sets which are complete enough to allow calculation of separate alkalinity budgets for lakes and their watersheds is small, and the above conclusions must be regarded as tentative until checked more widely. However, studies of in situ alkalinity using other methods generally confirm my conclusions. Alkalinity exchange between sediments and overlying waters have been calculated by using flux-gradient calculations for ions in pore water (Baker et al., 1984; Carignan, 1985; Schiff and Anderson, 1985), and by changes in mass during periods when precipitation, inflow and outflow are negligible (Schindler and Turner, 1982). Alkalinity generation can also be measured in smaller scale experiments with isotopic tracers (Rudd et al., 1986a) and by mesocosm studies (Schiff and Anderson, 1986).

There were some exceptions worthy of discussion. Rudd et al. (1986a) found that reoxidation of S in sediments of Lake Hovvatn, Norway, destroyed much of the alkalinity which had been produced by sulfate reduction. However, high rates of nitrate reduction were important generators of alkalinity. Nitrate removal was very high in the Adirondacks, but negligible in Muskoka. Schiff and Anderson (1985) pointed out that while steep gradients of Fe^{2+}, Mn^{2+} and NH_4^+ usually occurred in lake sediments, they did not contribute greatly to the alkalinity of overlying water, because of reprecipitation of Fe and Mn at the sediment surface and biological uptake of NH_4^+. This point is not considered in earlier treatments.

Published watershed models to date have not included in-lake processes, although some modelling groups have indicated that recent revisions of models will include them. Such models clearly need to include in-lake processes in order to accurately predict changes in alkalinity for a wide variety of lake types.

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