

The potential importance of bacterial processes in regulating rate of lake acidification^{1,2}

C. A. Kelly

Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York 10964

John W. M. Rudd³

Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba R3T 2N6

R. B. Cook⁴

Lamont-Doherty Geological Observatory

D. W. Schindler

Freshwater Institute

Abstract

Rates of microbial reduction of O₂, Fe³⁺, Mn⁴⁺, NO₃⁻, and SO₄²⁻, and total generation of CO₂ and CH₄ were measured in the hypolimnia of three Canadian Shield lakes. Methanogenesis accounted for 72-80% of anoxic carbon generation, while sulfate reduction contributed 16-20%. The remainder of anoxic carbon generation (2-8%) originated from all of the other processes combined (nitrate, iron, and manganese reduction).

In lakes affected by acid deposition, inputs of sulfate and nitrate will increase, and it is expected that reducing power normally going to methane production will be diverted to nitrate and sulfate reduction. The last two reduction reactions can result in alkalinity production, whereas methane production does not. A model was developed to predict the significance of hypolimnetic alkalinity production which could result from these reactions in lakes with known hypolimnetic reducing power (methane production). The model showed that the hypolimnia of two ELA lakes which have been made eutrophic artificially could potentially produce enough persistent alkalinity to neutralize "typical" acid deposition, while a lake that was not eutrophic could not. Besides trophic state, other factors important in determining a lake's capability for hypolimnetic alkalinity production were watershed area : surface area ratio, the watershed retentions of H⁺, SO₄²⁻, NO₃⁻, and NH₄⁺, and the degree of precipitation of FeS in the sediment.

Atmospheric acid deposition delivers elevated levels of nitrate and sulfate ions, as well as hydrogen ions, to lake basins (Likens et al. 1977; Dillon et al. 1978). In lakes and soil, both of these anions may be reduced by bacteria which use them as electron acceptors in anoxic environments or by photosynthetic organisms which use them as nutrients. These reduction reactions result in the production

of alkalinity, i.e. they supplement geological sources of alkalinity and thus contribute to the acid-neutralizing ability of an ecosystem (Berner et al. 1970; Schindler et al. 1980; Hemond 1980; Goldman and Brewer 1980; Cook 1981). In lakes with low sources of mineral alkalinity, such as the Canadian Shield lakes, biologically produced alkalinity may be one of the few sources of neutralization. Although this phenomenon of biologically produced alkalinity is well documented, it remains to be shown whether it could be significant in low alkalinity lakes in offsetting the acidity of anthropogenic atmospheric deposition.

Bacterial nitrate and sulfate reduction require anoxic or near-anoxic conditions and oxidizable organic substrate. Other bacterial reactions which can occur un-

¹ This work was supported by NSF grants DAR 79-17291 and DAR 80-17639, and the Department of Fisheries and Oceans, Canada.

² Lamont-Doherty Geological Observatory Contribution.

³ To whom reprint requests should be sent.

⁴ Current address: Department of Meteorology, University of Stockholm, S-106 91 Stockholm, Sweden.

Table 1. Oxidative reactions for organic material of the Redfield composition (equations from Froelich et al. 1979).

$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}$	(1)
$\text{CO}_2:\text{O}_2 = 0.77$	
$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) + 236\text{MnO}_2 + 472\text{H}^+ \rightarrow 236\text{Mn}^{2+} + 106\text{CO}_2 + 8\text{N}_2 + \text{H}_3\text{PO}_4 + 366\text{H}_2\text{O}$	(2)
$\text{CO}_2:\text{Mn}^{2+} = 0.45$	
$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) + 84.8\text{HNO}_3 \rightarrow 106\text{CO}_2 + 42.4\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 + 148.4\text{H}_2\text{O}$	(3)
$\text{CO}_2:\text{NO}_3^- = 1.25$	
$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) + 424\text{FeOOH} + 848\text{H}^+ \rightarrow 424\text{Fe}^{2+} + 106\text{CO}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 + 742\text{H}_2\text{O}$	(4)
$\text{CO}_2:\text{Fe}^{2+} = 0.25$	
$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) + 106\text{H}^+ + 53\text{SO}_4^{2-} \rightarrow 106\text{CO}_2 + 16\text{NH}_3 + 53\text{H}_2\text{S} + \text{H}_3\text{PO}_4 + 106\text{H}_2\text{O}$	(5)
$\text{CO}_2:\text{SO}_4^{2-} = 2$	
$(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4) \rightarrow 53\text{CO}_2 + 53\text{CH}_4 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$	(6)
$\text{CO}_2:\text{CH}_4 = 1$	

der anoxic conditions and which use organic substrate are iron and manganese reduction, and methanogenesis (Table 1). These anoxic reactions have often been studied individually, but very few data are available on the relative importance of each reaction to total organic carbon oxidation. Because there is only a finite amount of organic substrate available in a lake, these various anoxic reactions are competitive: an increase in one can be expected to occur at the expense of another. The relative importance of each activity should be a function of the concentrations of reactants and products at a given moment, and any other environmental conditions that might favor one group over another, e.g. pH. Some of these bacterial reactions do not result in alkalinity production (e.g. methanogenesis), and, of those that do, the alkalinity may or may not be long lasting in the lake environment. Therefore, it is instructive to know the relative importance of these activities in freshwaters and also the potential for changes as the inputs of sulfate, nitrate, and hydrogen ions are increased.

The most obvious potential for change in anoxic bacterial activities as acid deposition increases is a shift from methanogenesis (Table 1, Eq. 6) to nitrate and sulfate reduction. Methane is produced in many lakes (Rudd and Taylor 1980),

and methane release accounted for 37–58% of the carbon regenerated from organic sediment input in five lakes with anaerobic hypolimnia (Kelly and Chynoweth 1981). The addition of nitrate or sulfate to a methanogenic system results in a shift of electron flow away from the production of methane to the reduction of nitrate or sulfate (Balderston and Payne 1976; Bryant et al. 1977; Winfrey and Zeikus 1977; Knowles 1979; Mountfort et al. 1980). It has also been shown that anoxic methane oxidation can occur, linked to reduction of sulfate or other electron acceptors such as iron or manganese, although the importance of this in freshwater systems seems to be small (Zehnder and Brock 1980). In either case, the net effect on the system is the same. Methane production has been measured in quite a few lakes (e.g. Rudd and Hamilton 1978; Strayer and Tiedje 1978; Kelly and Chynoweth 1980; Falton et al. 1980). However, such measurements have never been compared to the quantities of nitrate and sulfate delivered to lakes by acid deposition and the potential for change in anoxic bacterial communities. In addition, the quantities of nitrate and sulfate reduction which commonly occur in freshwater lakes are not well documented.

The two main purposes of this work were to provide comprehensive measure-

ments of the relative importance of the many different kinds of anoxic bacterial activities in several different lakes and to quantify the response of anoxic bacterial communities to elevated nitrate and sulfate concentrations associated with acid deposition, including the significance of this response to the acid-neutralizing capacity of a lake.

F. A. J. Armstrong, R. J. Flett, R. Hesslein, and P. Campbell provided criticisms and encouragement during the preparation of this paper. The ELA sampling crews and analytical staff headed by J. Penny and J. Prokopowich produced the DIC, O₂, H₂S, and NO₃⁻ data. Sulfate, iron, and manganese samples were analyzed at the Freshwater Institute chemistry laboratory.

Methods

Three ELA lakes (227, 226N, and 223) were used for this study. Lake 227 ($Z_{\max} = 10$ m) was made eutrophic experimentally in 1969 by adding P and N (Schindler and Fee 1974). It received 14 mmol P·m⁻² as H₃PO₄ and 450 mmol N·m⁻² as NaNO₃ each year from 1969 until 1975. In 1975, N additions were changed to 160 mmol·m⁻² with P loading remaining the same. The hypolimnion is anoxic (>4 m) during stratification. Lake 226N ($Z_{\max} = 14$ m) was made eutrophic experimentally in 1973 by adding P, N, and organic carbon fertilizer (Schindler 1974) and has received 10 mmol P·m⁻² as H₃PO₄, 129 mmol N·m⁻² as NaNO₃, and 288 mmol C·m⁻² as sucrose each year since 1975. Additions were only slightly different before 1975. Lake 226N becomes anoxic below 5 m during summer stratification. Lake 223 ($Z_{\max} = 14$ m) has been acidified experimentally since 1976 (Schindler et al. 1980). It received 373 mmol H₂SO₄·m⁻² in 1976, 196 mmol·m⁻² in 1977, 228 mmol·m⁻² in 1978, and 190 mmol·m⁻² in 1979, causing the epilimnetic pH to drop from 6.7 to 5.6. Lake 223 is anoxic below 12 m during stratification.

Hypolimnetic water samples were collected at 1–2-m intervals with a peristaltic pump. Samples were analyzed for total dissolved inorganic carbon, oxygen,

sulfate, sulfide, iron, and manganese according to the methods of Stainton et al. (1977). Methane concentration was determined as by Rudd et al. (1974).

Reduction rates of oxygen, sulfate, and nitrate were assumed to be equal to total loss of each chemical species from the hypolimnetic water column during summer stratification. There was no photosynthesis and very little oxygen at the depths used. Reduction of iron and manganese was estimated as the increase of total dissolved iron and manganese in the water column. The reduced species of these elements are quite soluble and the oxidized species very insoluble (Stumm and Morgan 1981). Methane and carbon dioxide production rates also were measured as release to the hypolimnetic water column. Not all of the reduced products are released into the water column, however; some portion remains "stored" in the porewater. The degree to which these release measurements may underestimate true production rates is probably small, due to the small volume of porewater available for storage. An exception is Fe²⁺ which is also stored in the sediments as FeS. FeS formation was estimated as the difference between SO₄²⁻ loss and H₂S return to the water column, and the iron reduction rates were corrected accordingly.

Hypolimnetic accumulation or loss of each chemical species was measured below 4 m in Lake 227 and below 5 m in 226N. Corrections for loss or gain by vertical diffusion across the 4- and 5-m planes were not significant because these depths were within the metalimnion where vertical diffusion rates are extremely low (5×10^{-4} cm²·s⁻¹; Quay et al. 1980).

Because the anoxic zone of Lake 223 began 3 m below the bottom of the thermocline, vertical diffusion corrections were necessary and were made from

$$F = -D \frac{dC}{dX}$$

where F is flux rate in mol·cm⁻²·s⁻¹, D is average eddy diffusion coefficient in cm²·s⁻¹ ($D = 2 \times 10^{-3}$ for 11–12 m, Lake 223; Quay 1977), and dC/dX is concentration gradient in mol·cm⁻³·cm⁻¹.

To relate the magnitude of these chemical changes to the relative importance of the various types of anoxic bacterial reaction, we computed the amount of organic carbon potentially mineralized by each reaction. For O_2 , SO_4^{2-} , NO_3^- , Fe^{3+} , and Mn^{4+} reduction, the amount of carbon mineralized was taken from the measured amount of electron acceptor reduced and the amount of CO_2 produced as predicted by the stoichiometry of the oxidation of organic material (Table 1). In methanogenesis, both CH_4 and CO_2 are the carbon-containing end products (Eq. 6: Table 1). For this reaction, the methanogenic CO_2 was taken to be the amount left after subtracting the CO_2 generated by all other reactions from the total.

There are some known reactions where reduction of an anoxic electron acceptor is linked to an inorganic oxidation, e.g. nitrate reduction with sulfide oxidation. However, the most abundant reduced species available in these lakes is carbon, and the occurrence of these anoxic inorganic oxidations is not detectable by a mass balance approach. Until otherwise shown, we are concluding that these reactions are minor.

It should be noted that not all of these reduction reactions are necessarily catalyzed by bacteria. For example, iron and manganese reduction can occur either biologically or chemically (Brock 1966). However, the electrons responsible for all the reduction reactions in sediments must be generated by microbial oxidation of organic material, as there is no other source of reducing power.

Results

Most of the changes in hypolimnetic masses of DIC, CH_4 , Fe^{2+} , Mn^{2+} , SO_4^{2-} , NO_3^- , H_2S , and NH_4^+ for Lakes 223, 226N, and 227 during summer stratification were linear with time throughout the measurement period (Figs. 1–3, Table 2). NO_3^- and O_2 , which were depleted early in the season, were exceptions. The shapes of the concentration profiles indicated that the major reaction site for all of these species was the sediment, as shown previously for CH_4 , DIC, and NH_4^+ (Hes-

slein 1980). It should be noted that these are mean rates for the whole hypolimnion and do not represent a true picture of concurrent reactions in a particular square meter of sediment. For example, sulfate was depleted more rapidly in deeper water because of the smaller ratio of water volume to sediment area. Because of this depletion, sulfate reduction rates deep in the hypolimnion may become very low late in summer compared to those in sediment in shallower water.

The total change in quantity of each species measured was computed for an 84-day period from mid-June to mid-September (Table 3). In all three lakes, DIC and CH_4 changed the most, followed by ammonium, sulfate, and iron in varying order. An exception was oxygen in 226N, which showed a fairly large change due to its high concentration in the hypolimnion at the beginning of June.

Anoxic metabolism predominated in the hypolimnia of all three lakes, with oxygen reduction accounting for only 22, 2.5, and 5.1% of total carbon metabolism in Lakes 226N, 227, and 223 (Table 4). In all three lakes, methanogenesis was the predominant anoxic microbial activity, accounting for 72–82% of total anoxic carbon mineralization. Sulfate reduction was the next most prevalent (16–20%), followed by iron, nitrate, and manganese reduction, with all three of these amounting to <2–8% of the totals in these lakes.

To further characterize the hypolimnetic metabolism in these lakes, we compared total CO_2 production, anoxic CO_2 production (CO_2 from all processes except O_2 reduction), and methanogenic CO_2 production to methane production ($CO_2:CH_4$: Table 5). Also, for Lake 226N, we made these calculations using three different depths as the upper level (5, 7, and 10 m). These data showed that CO_2 production was more important than methane production in the upper depths, largely because of the presence of oxygen between 5 and 7 m at the beginning of summer. Selection of the various upper levels did not greatly affect the calculated ratios of anoxic $CO_2:CH_4$ or methanogenic $CO_2:CH_4$.

Table 2. Rates of change of dissolved hypolimnetic species during 1979 summer stratification.

Species	Interval (No. of days)	Δ (mmol·m ⁻² ·d ⁻¹)	Linear fit, level of significance (%)
Lake 226N >5 m			
O ₂	27 Jun–20 Aug (54)	-5.9±0.27	1
	21 Aug–19 Sep (29)	0	—
SO ₄ ²⁻	25 Jun–23 Jul (28)	-1.7	*
	24 Jul–17 Sep (55)	-0.52	1
Fe ²⁺	27 Jun–19 Sep (84)	+1.1±0.07	1
Mn ²⁺	27 Jun–19 Sep (84)	0.14±0.04	5
NO ₃ ⁻	27 Jun–20 Aug (56)	-0.64±0.09	n.s.
	21 Aug–19 Sep (27)	0	—
DIC	27 Jun–19 Sep (84)	+8.1±1.2	5
CH ₄	27 Jun–19 Sep (84)	+5.0±0.67	1
NH ₄ ⁺	27 Jun–19 Sep (84)	+1.1±0.11	1
ΣH ₂ S	12 Jun–17 Sep (100)	0.34±0.02	1
Lake 227 >4 m			
O ₂	19 Jun–17 Jul (28)	-1.2	*
	18 Jul–11 Sep (85)	0	—
SO ₄ ²⁻	19 Jun–12 Sep (85)	-0.97±0.15	1
Fe ²⁺	19 Jun–12 Sep (85)	+0.60±0.15	n.s.
Mn ²⁺	19 Jun–11 Sep (84)	+0.043±0.008	5
NO ₃ ⁻	19 Jun–17 Jul (28)	-0.040	*
	18 Jul–11 Sep (56)	0	—
DIC	19 Jun–11 Sep (84)	+7.4±0.28	1
CH ₄	19 Jun–11 Sep (84)	+5.0±0.53	1
NH ₄ ⁺	19 Jun–11 Sep (84)	+1.7±0.07	1
ΣH ₂ S	21 Jun–12 Sep (83)	0.38±0.06	1
Lake 223 >12 m			
O ₂	18 Jun–16 Jul (28)	-1.2	*
	17 Jul–10 Sep (55)	-0.45	†
SO ₄ ²⁻	18 Jun–10 Sep (84)	-1.0±0.02	1
Fe ²⁺	18 Jun–13 Aug (56)	+2.4±0.10	5
	14 Aug–10 Sep (28)	+0.8	*
Mn ²⁺	18 Jun–10 Sep (84)	+0.13±0.01	5
NO ₃ ⁻	18 Jun–13 Aug (56)	-0.004±0.0002	5
	14 Aug–10 Sep (28)	0	—
DIC	18 Jun–10 Sep (84)	+7.6±0.37	1
CH ₄	18 Jun–10 Sep (84)	+3.2±0.13	1
NH ₄ ⁺	18 Jun–10 Sep (84)	+0.65±0.01	1
ΣH ₂ S	4 Jun–10 Sep (98)	+0.097±0.02	1

* Only two points.

† Vertical differential correction.

Discussion

Sequence of reduction processes—It is generally accepted that under standard conditions there is a sequence to the reduction processes, proceeding from O₂ reduction to methanogenesis (Table 1). A sequence in reduction processes was observed in these ELA lakes to some extent because reduction of O₂ and NO₃⁻ ceased before the end of the stratification period; however, all of the reactions proceeded simultaneously and usually linearly (Figs.

1–3, Table 2). This is probably caused primarily by spatial heterogeneity within the hypolimnion, and by the fact that the reactions were not occurring at standard concentrations.

Relative importance of the different types of reactions—In any lake the relative predominance of each type of hypolimnetic bacterial activity should be a function of the relative concentration of each different electron acceptor (O₂, NO₃⁻, etc.), the organic loading to the

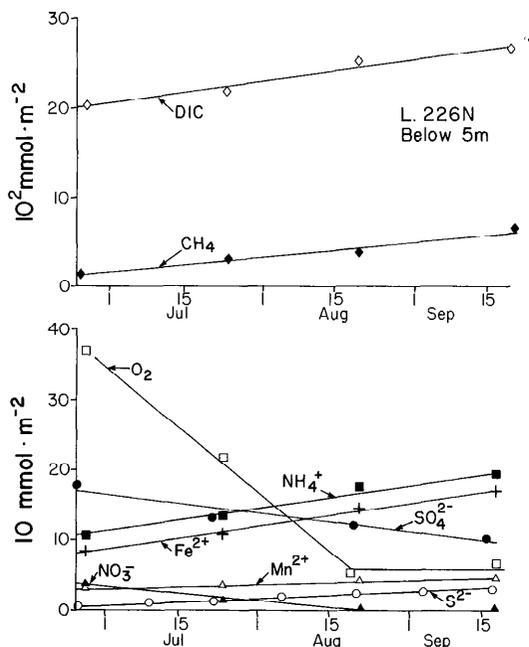


Fig. 1. Mass per unit area below 5 m in Lake 226N during summer 1979 of DIC, CH₄, O₂, NH₄⁺, NO₃⁻, SO₄²⁻, H₂S, Fe²⁺, and Mn²⁺.

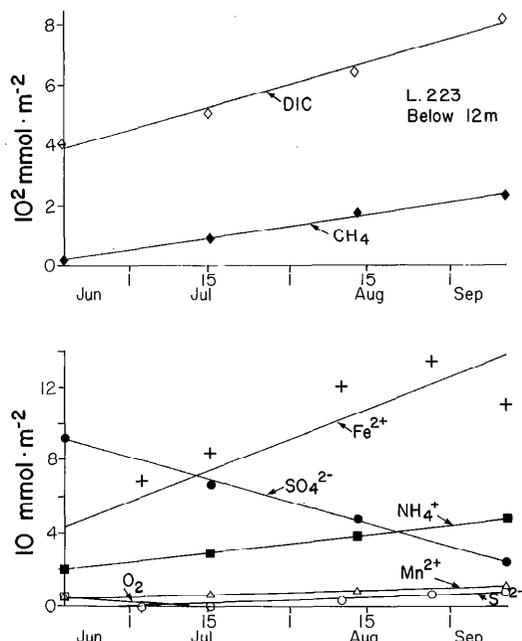


Fig. 3. As Fig. 1, but below 12 m in Lake 223. NO₃⁻ was too low to be shown.

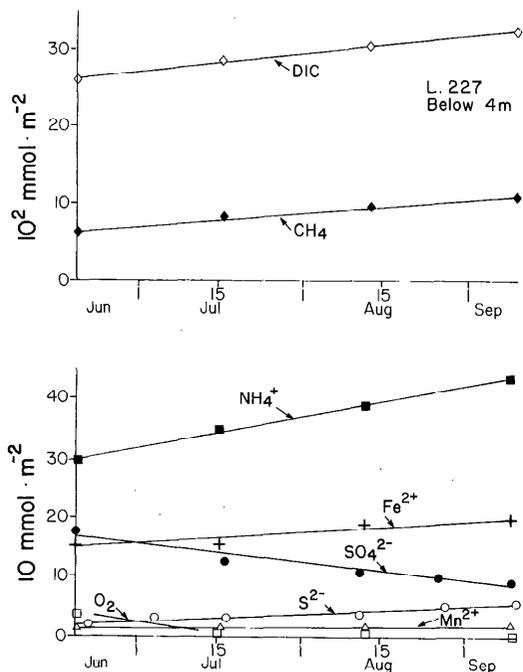


Fig. 2. As Fig. 1, but below 4 m in Lake 227. NO₃⁻ was too low to be shown.

sediments, and the duration of anoxic conditions following a circulation event—O₂ and NO₃⁻ reduction would be more prevalent just after complete circulation than late in summer. In the three lakes discussed here, the relative importance of each anoxic activity in summer 1979 was fairly constant from lake to lake (Table 4). Before acidification of Lake 223 (before 1976), rates of sulfate reduction were lower than in 1979 (Cook 1981). Spring circulation concentrations of SO₄²⁻ have been increased from the preacidification value of 40 μmol · liter⁻¹ to 115 (Cook 1981; Cook and Schindler in press). Thus, although CH₄ production was not measured before 1979, it probably played a larger role in anoxic metabolism in Lake 223 before acidification.

Few data are available on the entire spectrum of anoxic bacterial activities in other lakes, but there are several comparisons of methane production with sediment organic carbon input. In five mesotrophic to eutrophic lakes with anoxic

Table 3. Total changes of hypolimnetic dissolved chemical species in lakes 226N, 227, and 223 during 1979 summer stratification (84 days).

Species	Δ (mmol·m ⁻²)*		
	226N	227	223
O ₂	-320±15	-34	-59
Mn ²⁺	+12±3.1	+3.6±0.6	+11±1
NO ₃ ⁻	-36±5	-1.1	-0.36
Fe ²⁺	+92±0.6	+50±13	+157±56
SO ₄ ²⁻	-76±17	-82±13	-84±2
ΣH ₂ S	+28±2	+32±5	+8.1±2
NH ₄ ⁺	+92±9.2	+140±6	+55±0.8
CH ₄	+480±60	+420±24	+270±11
DIC	+680±100	+620±45	+640±31
Est.			
FeS†	48	50	76
C:N‡	13	7.4	17

* Values given are ±1 SD of the slope where linear regressions were possible and appropriate.

† Assumes that for each mole SO₄²⁻ reduced and not returned as ΣH₂S, 1 mole of FeS was formed in sediments.

‡ Ratio of total C generation (CO₂ + CH₄) to NH₄⁺ generation.

hypolimnia, methane release is linearly related to organic carbon input, with 36–58% of the input returned as methane (Kelly and Chynoweth 1981). These lakes include Mendota (Fallon et al. 1980), which has relatively high SO₄²⁻ concentrations (260 μmol·liter⁻¹ at fall circulation: Winfrey and Zeikus 1977), and 227, which is relatively low in SO₄²⁻ (about 40 μmol·liter⁻¹). Lake Mendota also has a higher organic input to the sediments (67.5 mmol C·m⁻²·d⁻¹ in summer 1977: Fallon et al. 1980) than Lake 227 (21 mmol C·m⁻²·d⁻¹ in summer 1970 and 1971: Schindler et al. 1973). This information gives some idea of the common magnitude of methanogenesis in the anoxic

Table 5. Ratios of ΣCO₂, anoxic CO₂, and methanogenic CO₂ production to CH₄ production.

Lake	ΣCO ₂ :CH ₄	Anoxic CO ₂ :CH ₄	Methanogenic CO ₂ :CH ₄	
226N	>5 m	1.4±0.4	0.90±0.4	0.44±0.24
	>7 m	1.0±0.4	0.85±0.4	0.55±0.17
	>10 m	0.7±0.3	0.70±0.3	0.46±0.17
227	>4 m	1.5±0.2	1.4±0.2	1.0±0.15
223	>12 m	2.4±0.3	2.2±0.3	1.4±0.15

portion of various lakes. Determination of the relative importance of the other anoxic activities requires data from a wider variety of lakes.

In addition to variations in the prevalence of each type of anoxic activity, the variation in the ratios of CO₂:CH₄ from methanogenesis (Table 5) is another way in which lakes or time periods seem to differ in anoxic bacterial metabolism. Methanogenic breakdown of a molecule containing the ratio of elements shown in Table 1 (Froelich et al. 1979) predicts an overall ratio for CO₂:CH₄ of 1. This is about the same as the ELA average, but the measured range was from 0.4 to 1.4 (Table 5). The 226N ratio was the most different from 1, but this same lake in 1978 showed a ratio of about 1.1 (C. Kelly and D. Schindler unpubl.). Thus, 1979 may have been an unusual year. This brings up the question of whether the elemental (C, H, O) composition of available organic substrates varies from that assumed in Table 1. Some evidence for this was seen in the variation of the C:N

Table 4. Relative carbon-mineralizing activity of different hypolimnetic bacterial reactions during 1979 summer stratification.

Reactions	C end products	Associated C mineralization (mmol·atoms C·m ⁻²)			% of anoxic C metabolism		
		226N	227	223	226N	227	223
O ₂ reduction*	CO ₂	250±12	26	45	—	—	—
Mn ⁴⁺ reduction*	CO ₂	5.4±1.4	1.6±0.3	5	0.6	0.2	0.6
NO ₃ ⁻ reduction*	CO ₂	45±6	1.4	0.45	5.0	0.1	0.05
Fe ³⁺ reduction*	CO ₂	23±0.15	13±3	39±14	2.5	1.3	4.6
SO ₄ ²⁻ reduction*	CO ₂	150±34	160±26	168±4	16	16	20
CH ₄ production†	CO ₂ + CH ₄	690±160	840±45	630±30	75	82	72

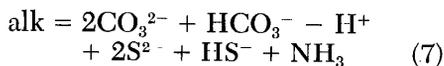
* Calculated using stoichiometry of equations in Table 1.

† Methanogenic CO₂ = total CO₂ - CO₂ from all other reactions; total carbon mineralized methanogenically = CH₄ + methanogenic CO₂.

ratio of degradation products ($\text{CO}_2 + \text{CH}_4$: NH_4^+) in the three lakes—7.4, 13, and 17 in 227, 226N and 223 (Table 3). Despite this, the anoxic CO_2 : CH_4 ratios now available have a mean value (1.0 ± 0.37) that is the same as the predicted ratio.

Knowledge of the mean and variability of the methanogenic CO_2 : CH_4 ratio could be useful in at least two ways. First, in highly alkaline lakes, hypolimnetic CO_2 production by bacteria is difficult to measure directly because chemical dissolution of sediment carbonates may obscure biological production. In these lakes, CH_4 production could be measured and then CO_2 production could be estimated from the methanogenic CO_2 : CH_4 ratio, plus the loss and accumulation of the various other CO_2 -producing reactants and products. Second, when rate of organic input to sediments is known and the proportion of total carbon metabolism going to CH_4 rather than to CO_2 has been more firmly established, this information will be useful in predicting the response of different lakes to acid deposition. This is because CH_4 production is the amount of carbon metabolism which could be shifted to nitrate or sulfate (or both) reduction. Here we measured CH_4 production rates directly and have used these data as predictors of the response of lakes to acid deposition. This is discussed in detail below.

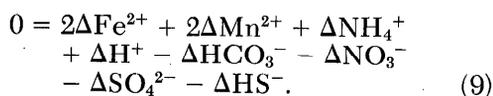
Lake buffering by anoxic microbial processes—Schindler et al. (1980) and Cook (1981) demonstrated that sulfate reduction coupled with FeS precipitation in the hypolimnion of artificially acidified Lake 223 increased the alkalinity and provided a source of neutralization for incoming hydrogen ions. The most common chemical species contributing to alkalinity in freshwater are



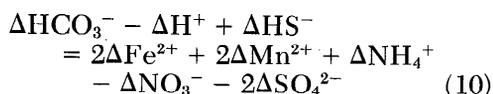
where all units are in moles. Silicates, borates, phosphates, and organic bases may also contribute to alkalinity, but usually only to a very small degree (Stumm and Morgan 1981). Also, at neutral or acid pH values, CO_3^{2-} , S^{2-} , and NH_3 are insignificant, so Eq. 7, for practical purposes, can be reduced to



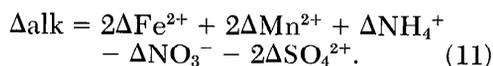
Production of CO_2 alone does not affect alkalinity, because its reaction with water adds equal amounts of H^+ and HCO_3^- . Nitrate reduction increases alkalinity by removing one equivalent of H^+ with each equivalent of NO_3^- (Eq. 3). Sulfate reduction also increases alkalinity in the same way (Eq. 5). Some of the H_2S produced can dissociate to HS^- and H^+ , but since each H^+ is now balanced by an HS^- , the alkalinity gain remains equal to the SO_4^{2-} loss, in equivalents. A general way of looking at all the changes that occur is to say that the net change of all positive and negative ions must be zero. Equation 9 expresses this for those ions undergoing significant changes in the hypolimnion during summer stratification:



Rearranging this gives



where all units are in moles. Combining Eq. 8 and 10 gives



The usefulness and validity of this approach has been demonstrated for the hypolimnion of Lake 223 by Cook (1981), who showed that the change in alkalinity predicted by the changes in ions shown in Eq. 10 is very similar to the change in alkalinity measured.

Much of the alkalinity produced by these reactions during stratification is not permanent. At fall overturn, when the water is circulated and oxygenated, Fe^{2+} and Mn^{2+} are rapidly oxidized and precipitated. NH_4^+ is more slowly oxidized to NO_3^- in oxic zones during winter, and then may be reduced again as winter anoxia develops (D. W. Schindler unpubl.). Thus, although Fe^{2+} , Mn^{2+} , and NH_4^+ production may be important during stratification, their oxidation at overturn

results in no permanent increase in alkalinity on an annual basis.

Bacterial denitrification (Eq. 3; Table 1) results in permanent alkalinity since the N_2 gas produced can escape to the atmosphere. Refixation of this N_2 by algae would be unlikely in lakes receiving large quantities of nitrate in acid precipitation, due to an unfavorably high N:P ratio (Flett et al. 1980). N_2 is not the only possible end product of denitrification. Under various conditions, including low pH and high NO_3^- , denitrification sometimes results in the formation of N_2O rather than N_2 (Firestone et al. 1980). N_2O may be further reduced or may escape to the atmosphere if it reaches surface waters. In a study of denitrification in Lake 227 water and sediments (Chan and Campbell 1980), N_2 was the principal product, with very little production of N_2O .

Sulfate reduction leads to permanent increases in alkalinity in the water only if the sulfide produced is permanently precipitated. ΣH_2S in the water oxidizes rapidly during fall circulation. During summer stratification, varying amounts of reduced sulfate are returned to the water column as dissolved sulfide—37% in 226N, 39% in 227, and only 10% in 223 (Table 3). The solubility of the sulfide is controlled by dissolved iron concentrations. The concentrations of both Fe^{2+} and ΣH_2S reach similar values in all three lakes, which become saturated with respect to FeS at the lower depths (Cook 1981). However, the hypolimnion of Lake 223 has a low ratio of water volume to sediment area compared to the other two lakes. Thus, the total amount of dissolved sulfide which the hypolimnetic water can hold per unit area of sediment is lower, and a higher proportion of the total sulfide is precipitated. This morphometric relationship is important in predicting future potentials for FeS formation. The supply rate of iron from the watershed may also become important as sediment iron becomes sequestered as FeS.

Once FeS has formed, its permanence depends on whether it is oxidized at fall or spring overturn. Sulfur budgets for Lake 223 (1976–1980) show large net an-

nual losses of S to the sediments (Schindler and Turner in press). Because the primary S input to Lake 223 sediments is via SO_4^{2-} reduction (Cook and Schindler in press), this net annual loss is good evidence for FeS permanence. The relationship of permanent FeS to the gross amount formed each year is yet to be determined.

Because we are most interested here in the production of alkalinity which is persistent, the model presented below includes only nitrate reduction, and sulfate reduction that does not lead to return of ΣH_2S to the water is represented in the equations below as $[\Delta SO_4^{2-} - \Sigma H_2S]$. The equation for persistent alkalinity formation becomes

$$\Delta \text{alk} = \Delta NO_3^- + 2[\Delta SO_4^{2-} - \Delta \Sigma H_2S]. \quad (12)$$

Model for estimation of acid deposition-induced alkalinity production by hypolimnetic microbial activities during summer stratification—As nitrate and sulfate inputs to a lake increase by acid deposition, the maximum quantities of these ions that can be reduced in the hypolimnion will be a function of the reducing power available from the microbial oxidation of organic carbon. Sulfate and nitrate inhibit methane production by successfully competing for electrons which would otherwise contribute to the formation of methane (Balderston and Payne 1976; Bryant et al. 1977; Knowles 1979). Thus, the reducing power available for increased alkalinity production by sulfate and nitrate reduction is equal to the reducing power currently used for methane production. If we assume constant reducing power, supplied by inputs of organic material to the sediments, the average hypolimnetic SO_4^{2-} concentrations which would completely inhibit methane production in Lakes 226N, 227, and 223 are 94, 140, and 270 $\mu\text{mol} \cdot \text{liter}^{-1}$. These are 2–3 times higher than present spring concentrations of SO_4^{2-} (Table 6). Concentrations in excess of these presumably would not be reduced during stratification and would not contribute to alkalinity production.

The above values for maximum reduc-

Table 6. 1979 spring circulation SO_4^{2-} and NO_3^- , 1979 SO_4^{2-} and $\Sigma\text{H}_2\text{S}$ changes in hypolimnion, and hypothetical acid deposition for Lakes 226N, 227, and 223 (in $\mu\text{eq}\cdot\text{liter}^{-1}$).

Lake	Watershed area* (A_w) ($\times 10^4 \text{ m}^2$)	Surface area (A_s) ($\times 10^4 \text{ m}^2$)	Total vol (V_L) ($\times 10^8$ liters)	1979 spring circ. concn.		1979 mean changes in hypolimnion		Input from hypothetical annual acid deposition†				
				SO_4^{2-}	NO_3^-	ΔSO_4^{2-}	$\Delta\Sigma\text{H}_2\text{S}$	H^+	SO_4^{2-}	NO_3^-	NH_4^+	
											H^+	NO_3^-
226N	40.2	8.3	4.7	80	8.2	34	13	19	66	8.1	11	5.3
227	29.4	5.0	2.2	114	0.53	53	21	26	100	12	15	7.3
223	135.2	27.3	19.5	204	0.87	187	18	15	53	7	8.4	4.2

* Does not include lake surface.

† Based on eastern Ontario precipitation content of $100 \mu\text{eq}\cdot\text{liter}^{-1} \text{H}^+$ and $80 \mu\text{eq}\cdot\text{liter}^{-1} \text{SO}_4^{2-}$ (Dillon et al. 1978), $35 \mu\text{eq}\cdot\text{liter}^{-1} \text{NO}_3^-$ and $35 \mu\text{eq}\cdot\text{liter}^{-1} \text{NH}_4^+$ (P. Dillon pers. comm.). Annual ELA precipitation = $70.5 \text{ cm}\cdot\text{yr}^{-1}$ (Newbury and Beaty 1980). This = $7.1 \times 10^4 \mu\text{eq} \text{H}^+$, $5.6 \times 10^4 \mu\text{eq} \text{SO}_4^{2-}$, $2.5 \times 10^4 \mu\text{eq} \text{NO}_3^-$ and NH_4^+ per m^2 . Watershed retention values for ELA were used and are in text.

ible sulfate were calculated on the assumption that only sulfate would increase. However, acid deposition contains both sulfuric and nitric acid. Further, the amounts of NO_3^- , SO_4^{2-} , and H^+ reaching a lake are modified during travel through the terrestrial catchment basin, so that runoff differs substantially in composition from precipitation falling directly onto the lake surface. Using our current knowledge of watershed chemistry and microbial processes, we have constructed a model which estimates the potential for hypolimnetic alkalinity production during summer in response to increased acid deposition. The major inputs to the model are current CH_4 production, lake area and volume, and watershed area. A first assumption of the model is that primary production (and therefore organic input to the sediments) will not change significantly. No such change has been observed in Lake 223 as the epilimnetic pH has been lowered from 6.7 to 5.6 (Schindler et al. 1980; Schindler 1980). Calculations are simplified as follows.

—The annual inputs are entered as though they occur at the time of spring circulation. This assumption is valid for the hypolimnion because, after the onset of thermal stratification, inputs of sulfate and nitrate from outside the lake are largely confined to the epilimnion. Inputs via groundwater flow are not a factor in granitic ELA basins.

—The hypolimnion is treated as a mixed box, without regard to effects arising

from varying concentration gradients; e.g. CH_4 production is expressed as a mean value ($\mu\text{mol}\cdot\text{liter}^{-1}$) for the whole hypolimnion.

—Only the period of summer stratification is treated; anoxia also develops in winter in all these lakes and should be included in future models when enough winter CH_4 production rates are available.

—Spring overturn is assumed to be complete.

First, we calculated the inputs of H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ with a "typical" eastern Ontario acid deposition composition of $100 \mu\text{eq}\cdot\text{liter}^{-1} \text{H}^+$ and 80 of SO_4^{2-} (Dillon et al. 1978), 35 of NO_3^- and of NH_4^+ (P. Dillon pers. comm.). The volume of rainfall was taken to be the ELA average of $70.5 \text{ cm}\cdot\text{yr}^{-1}$ (Newbury and Beaty 1980). Watershed retention values which have been measured for the Rawson Lake (ELA) watersheds are 90% for H^+ , -15% for SO_4^{2-} (Schindler et al. 1976), 83% for NO_3^- , and 96% for NH_4^+ (D. Schindler unpubl.).

The overall equation for the "acid deposition" inputs is

$$\begin{aligned} & \text{H}^+ + \text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ \\ & = [(A_w)(0.1\text{H}_p^+ + 1.15\text{SO}_4^{2-p} \\ & \quad + 0.17\text{NO}_3^- + 0.04\text{NH}_4^+) \\ & \quad + (A_s)(\text{H}_p^+ + \text{SO}_4^{2-p} + \text{NO}_3^- \\ & \quad + \text{NH}_4^+)]/V_L \quad (13) \end{aligned}$$

where H_i^+ , SO_4^{2-i} , etc. are lake inputs in $\mu\text{eq}\cdot\text{liter}^{-1}$, H_p^+ , SO_4^{2-p} , etc. are precipi-

tation values in $\mu\text{eq} \cdot \text{m}^{-2}$, A_w is watershed area in m^2 , A_s is lake surface area in m^2 , and V_L is lake volume in liters.

Second, the inputs in Eq. 13 are assumed to be equally distributed in the water at spring circulation. These input concentrations are then compared to the potential (P) for shifting hypolimnetic reducing power from methanogenesis to sulfate and nitrate reduction. In this shift, for each additional μeq of SO_4^{2-} reduced there would be one less μmol of CH_4 produced, and for each additional μeq of NO_3^- reduced there would be 1.5 less μmol of CH_4 produced.

$$P = \frac{(\text{SO}_4^{2-} + 1.5\sum\text{NO}_3^-)}{\Delta\text{CH}_4} \quad (14)$$

where P is the proportion of SO_4^{2-} and NO_3^- inputs that could potentially be reduced in the hypolimnion, $\sum\text{NO}_3^-$ is $\text{NO}_3^- + \text{NH}_4^+$ (assumes that the incoming NH_4^+ will be oxidized on reaching the lake), and ΔCH_4 is mean hypolimnetic methane production during summer stratification in $\mu\text{mol} \cdot \text{liter}^{-1}$.

If the nitrate and sulfate concentrations do not exceed the maximum that can be reduced (i.e. $P < 1$), then the additional input of these ions can be maximally utilized, and the potential for alkalinity production is expressed by

$$\Delta\text{alk} = (\text{SO}_4^{2-} - \sum\text{H}_2\text{S} + \text{NO}_3^-) \cdot \frac{V_H}{V_L} - \text{H}^+ + \frac{\text{H}^+ \cdot V_O}{V_L} \quad (15)$$

where Δalk is change in alkalinity in $\mu\text{eq} \cdot \text{liter}^{-1}$, for whole lake volume; SO_4^{2-} and NO_3^- are total spring circulation concentrations, including "normal" and acid inputs, in $\mu\text{eq} \cdot \text{liter}^{-1}$ (equation assumes that all SO_4^{2-} and NO_3^- in the hypolimnion will be reduced); $\sum\text{H}_2\text{S}$ is expected return of free sulfide to the water column (assumed to be the same as present day total return), in $\mu\text{eq} \cdot \text{liter}^{-1}$; V_H is anoxic hypolimnetic volume in liters; and V_O is outflow volume in liters.

If the nitrate and sulfate concentrations exceed the maximum that can be reduced (i.e. $P > 1$), then the potential for alkalinity production is expressed as

$$\Delta\text{alk} = \left[\frac{(\text{SO}_4^{2-} + \text{NO}_3^-)}{P} + (\text{SO}_4^{2-} + \text{NO}_3^- - \sum\text{H}_2\text{S}) \right] \cdot \frac{V_H}{V_L} - \text{H}^+ + \frac{\text{H}^+ \cdot V_O}{V_L} \quad (16)$$

where SO_4^{2-} and NO_3^- are current spring circulation concentrations in $\mu\text{eq} \cdot \text{liter}^{-1}$, and all other symbols are as above.

The results of the input calculations (Eq. 13) for Lakes 226N, 227, and 223 are expressed as hypothetical spring circulation values (Table 7). It should be noted that the H^+ input potentially derived from NH_4^+ oxidation was very significant (Table 6). If NH_4^+ retention were to decrease with greater NH_4^+ loading, then H^+ input from this source would be much greater (retention at current loading levels is extremely high—96% in ELA watersheds: D. Schindler unpubl.). This shows the importance of NH_4^+ inputs to lake acidification and of the watershed role in retaining these inputs. Inputs would be somewhat different for different types of watershed. For example, at Hubbard Brook, where loading rates have been much higher, the retention values measured are similar for H^+ (90%), SO_4^{2-} (-40%), and NH_4^+ (88%) but much less for NO_3^- (15%) (Likens et al. 1977). These data suggest that alkalinity production via NO_3^- reduction would be relatively more important at Hubbard Brook than at ELA. If an area such as ELA received much acid precipitation, watershed retention values for nitrogen might become more like those at Hubbard Brook.

The net hypolimnetic alkalinity production, as calculated with the "mixed hypolimnion" model presented above, was +34 $\mu\text{eq} \cdot \text{liter}^{-1}$ for Lake 226N, +52 for Lake 227, and -18 for Lake 223 (Table 7). Of course the hypolimnion is not mixed during stratification, and a more accurate model can be made by including the effect of the gradients in the hypolimnion. The nitrate gradient is not very important because essentially all of the hypolimnetic nitrate is reduced during summer stratification. However, sulfate tends to be completely depleted only at

Table 7. Estimation of hypolimnetic alkalinity production in Lakes 226N, 227, and 223 in response to increased H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ in rainfall.

Lake	Anoxic hypolimnetic vol (V_h) (10^6 liters)	V_h/V_L	V_o (10^6 liters)	Mean hypolimnetic CH_4 prod. summer 1979 ($\mu\text{mol} \cdot \text{liter}^{-1}$)	Hypothetical spring circ. concn*				Net whole-lake alk from hypolimnetic reductions*	
					H^+	SO_4^{2-}	NO_3^-	P	Mixed model	Approx gradient model
226N	1.6	0.34	1.8	95	30	146	22	0.90	+34	+5.0
227	0.80	0.36	0.86	137	41	214	20	0.94	+52	+10
223	0.18	0.0092	2.5	291	23	257	12	0.24	-18	-18

* In $\mu\text{eq} \cdot \text{liter}^{-1}$.

the lower hypolimnetic depths. At upper depths, where there is less sediment area per unit volume of water, sulfate is much less depleted. Modeling of this is somewhat complicated because each depth must be considered separately. Also, the rate of sulfate depletion should increase as concentrations increase (Cook and Schindler in press). An approximation can be made from the proportion of sulfate depleted in each hypolimnion during summer 1979 (Table 6): 43% of the total hypolimnetic sulfate in Lake 226N, 46% in 227 and 92% in 223. The higher percentage of depletion in Lake 223 is due in part to a greater ratio of sediment area to water volume in this hypolimnion. In addition, as sulfate concentrations in Lake 223 have been increased by additions of sulfuric acid, the residual sulfate concentrations in the hypolimnion at the end of summer have been lower (fig. 2; Schindler et al. 1980), suggesting increasing efficiency of removal.

With this approximation of the concentration gradient effect, our best estimates of hypolimnetic alkalinity production from this model show that complete neutralization of the H^+ inputs would occur in Lakes 226N and 227, but not in Lake 223 (Table 7, last column). Even though the net alkalinity production estimates in Lakes 226N and 227 were small and approximate, it should be remembered that only summer alkalinity production was included; the addition of winter reduction processes would increase the production estimate. Anoxia also occurs in

winter, and winter CH_4 production in Lake 227 is about equal to summer (Rudd and Hamilton 1978). Therefore, it may be possible for as much alkalinity production to occur in winter as in summer. Also, in winter, nitrate reduction may predominate over sulfate reduction (Sørensen et al. 1979) due to greater NO_3^- availability in the absence of algal activity. In contrast, SO_4^{2-} reduction occurs at lower rates in Lake 223 in winter than in summer (Cook and Schindler in press).

A factor not included in these models is the degree of completeness of spring circulation; we have assumed total mixing. Incomplete mixing would deliver less SO_4^{2-} and NO_3^- to the hypolimnion and decrease the potential for alkalinity production during that season. This happens occasionally at northern latitudes in continental areas where stratification develops soon after ice-out. For example, in Lake 226N from 1971 to 1979, total circulation (indicated by elevated NO_3^- concentrations at the lowest depth in May) was observed in 5 years, partial circulation in 2 years, and very little circulation in 1 year (D. Schindler unpubl.).

The ratio of the watershed area to the surface area is important in determining the ratio of $H^+ : SO_4^{2-}$ which enters the lake, because H^+ is retained in the watershed to a much greater degree than SO_4^{2-} . If H^+ and SO_4^{2-} entered the lake in equal quantities, then hypolimnetic reduction reactions could not possibly neutralize the H^+ because only part of the SO_4^{2-} enters a reducing environment. The

best condition for adequate neutralization of H^+ in the lake is a high ratio of $A_{10}:A_8$, resulting in high $SO_4^{2-}:H^+$ ratios entering the lake.

The ratio of the anoxic hypolimnetic volume to lake volume obviously greatly affects the neutralization capacity of hypolimnetic alkalinity production. In Lake 223, even though the reaction rates per square meter or per liter in the anoxic hypolimnion were very high, the alkalinity produced was almost insignificant when mixed into the whole lake volume (Table 7). Lake 223 is much less productive than 226N and 227, and most of the organic carbon input to the sediments seems to concentrate in a small central basin. In general, the ratio of anoxic hypolimnion to lake volume should be a function of total primary production (all other things being equal, such as morphology, etc.). The high potential for hypolimnetic alkalinity production in the two ELA lakes that were made eutrophic artificially suggests that phosphorus additions could be expected to have an ameliorating effect on lakes affected by acid rain. Additions of P to two eastern Ontario lakes have resulted in increased primary productivity and alkalinity and reduced concentrations of NO_3^- , possibly due to uptake by the algae of NO_3^- followed by burial, or denitrification in the sediments, or both (P. Dillon pers. comm.; Dillon et al. 1979). In Lake 227, which has been fertilized with both P and N since 1970, annual N loss (burial and denitrification) has been at least 24–70 $\mu\text{mol}\cdot\text{liter}^{-1}$ (D. Schindler unpubl., N_2 entering via fixation not included). If we assume that this loss is primarily from the NO_3^- pool, this would result in 24–70 $\mu\text{eq}\cdot\text{liter}^{-1}$ annual increase in alkalinity. This is much greater than the alkalinity production predicted for all hypolimnetic reactions in Lake 227, including denitrification (Table 7). Thus, adding P should enhance alkalinity production by reactions in addition to hypolimnetic ones, probably primarily burial of algal N and epilimnetic denitrification. The relative importance of these two processes of NO_3^- removal is not known. When more

is known about these, and when winter alkalinity production is added, the total potential for P-enhanced alkalinity production may be at least two times as great as that indicated by the summer hypolimnetic model presented here.

Research that would improve the predictability of microbial responses to acid deposition include determination of the magnitude of these reactions in epilimnetic sediments, the relative importance of permanent burial of N vs. denitrification and the effects of environmental changes (lowered pH, increased SO_4^{2-} , and NO_3^- concentrations) on the nitrate and sulfate reduction processes. In most lakes the epilimnetic sediment area is much larger than the hypolimnetic area and reactions occurring in the epilimnion tend to be more important on a whole-lake basis. In the epilimnetic sediments of three ELA lakes, including acidified 223, both NO_3^- and SO_4^{2-} in porewaters are at lower concentrations than in the water column, indicating reduction activity in the sediments (Rudd et al. unpubl.). However, the rates of these activities have not yet been measured. Quantification of epilimnetic sediment activities by mass balance is usually difficult because the ratio of sediment area to water volume is small, meaning that the effect of sediment activity on NO_3^- and SO_4^{2-} in the water is often small and within the error of measurement. This was not a problem in Lake 114, a shallow mesotrophic lake where depletion of NO_3^- and SO_4^{2-} under winter ice has been observed at both oxic and anoxic depths (D. Schindler unpubl.). In Lake 223, the sulfuric acid added has not lowered the pH as quickly as predicted (Schindler et al. 1980). About half of the unexpected buffering in 1976 and 1977 could be accounted for by "missing sulfate," and the greatest part of this sulfate was lost from epilimnetic and metalimnetic waters. The potential for epilimnetic microbial buffering should be further investigated, especially with respect to rates of activities and the factors determining these rates.

It has been argued that rates of bacterial activity might decrease during lake

acidification (e.g. Hendrey et al. 1976). However, the effect of lowered pH on sediment sulfate and nitrate reduction is not established. Some experiments show that low pH can slow or inhibit both reactions (Connell and Patrick 1968; Muller et al. 1980). Other experiments do not show inhibition (Bartlett et al. 1979; Gilliam and Gambrell 1978). Thus, there may be organisms in lake sediments which can perform these reactions at low pH.

Anoxic hypolimnetic microbial processes are obviously not in themselves a "cure" for acidification. Lakes 226N and 227 are highly productive through additions of phosphorus, and the large blooms of algae which develop would not be considered desirable lake management. However, we have considered quantitatively here only anoxic bacterial processes that occur in the summer hypolimnion. The winter period, epilimnetic algal and bacterial activities, and other chemical or biological reactions may also contribute to neutralization. Thus, there may be intermediate levels of productivity that could result in significant neutralization of acid deposition. The primary questions about the feasibility of such an approach to acid amelioration are the permanence and continuation of FeS precipitation over many years and the total degree to which denitrification and burial of N can be enhanced on an annual basis.

References

- BALDERSTON, W. L., AND W. J. PAYNE. 1976. Inhibition of methanogenesis in salt marsh sediments and whole-cell suspensions of methanogenic bacteria by nitrogen oxides. *Appl. Environ. Microbiol.* **32**: 264-269.
- BARTLETT, M. S., L. C. BROWN, N. B. HANES, AND N. H. NICKERSON. 1979. Denitrification in freshwater wetland soil. *J. Environ. Qual.* **8**: 460-464.
- BERNER, R. A., M. R. SCOTT, AND C. THOMLINSON. 1970. Carbonate alkalinity in pore waters of anoxic marine sediments. *Limnol. Oceanogr.* **15**: 544-549.
- BROCK, T. D. 1966. *Principles of microbial ecology*. Prentice-Hall.
- BRYANT, M. P., L. L. CAMPBELL, C. A. REDDY, AND M. R. CRABILL. 1977. Growth of *Desulfovibrio* in lactate or ethanol media low in sulfate in association with H_2 -utilizing methanogenic bacteria. *Appl. Environ. Microbiol.* **33**: 1162-1169.
- CHAN, Y. K., AND N. E. CAMPBELL. 1980. Denitrification in Lake 227 during summer stratification. *Can. J. Fish. Aquat. Sci.* **37**: 506-512.
- CONNELL, W. E., AND W. H. PATRICK, JR. 1968. Sulfate reduction in soil: Effects of redox potential and pH. *Science* **159**: 86-87.
- COOK, R. B. 1981. The biogeochemistry of sulfur in two small lakes. Ph.D. thesis, Columbia Univ. 246 p.
- , AND D. W. SCHINDLER. In press. The biogeochemistry of sulphur in an experimentally acidified lake. *Proc. 5th Int. Symp. Environ. Biogeochem.* Stockholm.
- DILLON, P. J., AND OTHERS. 1978. Acidic precipitation in south-central Ontario: Recent observations. *J. Fish. Res. Bd. Can.* **35**: 809-815.
- , N. D. YAN, W. A. SCHEIDER, AND N. CONROY. 1979. Acidic lakes in Ontario, Canada: Characterization, extent and responses to base and nutrient additions. *Arch. Hydrobiol. Bcih. Ergeb. Limnol.* **13**: 317-336.
- FALLON, R. D., S. HARRITS, R. S. HANSON, AND T. D. BROCK. 1980. The role of methane in internal carbon cycling in Lake Mendota during summer stratification. *Limnol. Oceanogr.* **25**: 357-360.
- FIRESTONE, M. K., R. B. FIRESTONE, AND J. M. TIEDJE. 1980. Nitrous oxide from soil denitrification: Factors controlling its biological production. *Science* **208**: 749-751.
- FLETT, R. J., D. W. SCHINDLER, R. D. HAMILTON, AND N. E. CAMPBELL. 1980. Nitrogen fixation in Canadian Precambrian Shield lakes. *Can. J. Fish. Aquat. Sci.* **37**: 494-505.
- FROELICH, P. N., AND OTHERS. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**: 1075-1090.
- GILLIAM, J. W., AND R. P. GAMBRELL. 1978. Temperature and pH as limiting factors in loss of nitrate from saturated Atlantic coastal plain soils. *J. Environ. Qual.* **7**: 526-532.
- GOLDMAN, J. C., AND P. G. BREWER. 1980. Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity. *Limnol. Oceanogr.* **25**: 352-357.
- HEMOND, H. F. 1980. Biogeochemistry of Thoreau's Bog, Concord, Massachusetts. *Ecol. Monogr.* **50**: 507-526.
- HENDREY, G. R., K. BAALSURUD, T. TRAAEN, M. LAAKE, AND G. RADDUM. 1976. Acid precipitation: Some hydrobiological changes. *Ambio* **5**: 224-227.
- HESSLEIN, R. H. 1980. Whole-lake model for the distribution of sediment-derived chemical species. *Can. J. Fish. Aquat. Sci.* **37**: 552-558.
- KELLY, C. A., AND D. P. CHYNOWETH. 1980. Comparison of in situ and in vitro rates of methane release in freshwater sediments. *Appl. Environ. Microbiol.* **40**: 287-293.
- , AND ———. 1981. The contribution of temperature and organic input in controlling

- rates of sediment methanogenesis. *Limnol. Oceanogr.* **26**: 891-897.
- KNOWLES, R. 1979. Denitrification, acetylene reduction, and methane metabolism in lake sediment exposed to acetylene. *Appl. Environ. Microbiol.* **38**: 486-493.
- LIKENS, G. E., F. H. BORMANN, R. S. PIERCE, J. S. EATON, AND N. M. JOHNSON. 1977. Biogeochemistry of a forested ecosystem. Springer.
- MOUNTFORT, D. O., R. A. ASHER, E. L. MAYS, AND J. M. TIEDJE. 1980. Carbon and electron flow in mud and sandflat intertidal sediments at Delaware Inlet, Nelson, New Zealand. *Appl. Environ. Microbiol.* **39**: 686-694.
- MULLER, M. M., V. SUNDMAN, AND J. SKUJINS. 1980. Denitrification in low pH spodosols and peats determined with the acetylene inhibition method. *Appl. Environ. Microbiol.* **40**: 235-239.
- NEWBURY, R. W., AND K. G. BEATY. 1980. Water renewal efficiency of watershed and lake combinations in the ELA region of the Precambrian Shield. *Can. J. Fish. Aquat. Sci.* **37**: 335-341.
- QUAY, P. D. 1977. An experimental study of turbulent diffusion in lakes. Ph.D. thesis, Columbia Univ. 194 p.
- , W. S. BROECKER, R. H. HESSLEIN, AND D. W. SCHINDLER. 1980. Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes. *Limnol. Oceanogr.* **25**: 201-218.
- RUDD, J. W., AND R. D. HAMILTON. 1978. Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism. *Limnol. Oceanogr.* **23**: 337-348.
- , ———, AND N. E. CAMPBELL. 1974. Measurement of microbial oxidation of methane in lake water. *Limnol. Oceanogr.* **19**: 519-524.
- , AND C. D. TAYLOR. 1980. Methane cycling in aquatic environments. *Adv. Aquat. Microbiol.* **2**: 77-150.
- SCHINDLER, D. W. 1974. Eutrophication and recovery in experimental lakes: Implications for lake management. *Science* **184**: 897-898.
- . 1980. Experimental acidification of a whole lake: A test of the oligotrophication hypothesis, p. 370-374. *In Ecological impact of acid precipitation. Symp. Proc. SNSF Project, Oslo.*
- , AND E. J. FEE. 1974. Experimental Lakes Area: Whole-lake experiments in eutrophication. *J. Fish. Res. Bd. Can.* **31**: 937-953.
- , AND OTHERS. 1973. Eutrophication of Lake 227 by addition of phosphate and nitrate: The second, third and fourth years of enrichment, 1970, 1971, and 1972. *J. Fish. Res. Bd. Can.* **30**: 1415-1440.
- , R. W. NEWBURY, K. G. BEATY, AND P. CAMPBELL. 1976. Natural water and chemical budgets for a small Precambrian lake basin in central Canada. *J. Fish. Res. Bd. Can.* **33**: 2526-2543.
- , AND M. A. TURNER. In press. Physical, chemical and biological responses of lakes to experimental acidification. *Water Air Soil Pollut. (Proc. Am. Meteorol. Soc.-Can. Meteorol. Oceanogr. Soc. Conf., Albany.)*
- , R. WAGEMANN, R. B. COOK, T. RUSZCZYNSKI, AND J. PROKOPOWICH. 1980. Experimental acidification of Lake 223, Experimental Lakes Area: Background data and the first three years of acidification. *Can. J. Fish. Aquat. Sci.* **37**: 342-354.
- SØRENSEN, J., B. B. JØRGENSEN, AND N. P. REVSBECH. 1979. A comparison of oxygen, nitrate, and sulfate respiration in coastal marine sediments. *Microb. Ecol.* **5**: 105-115.
- STANTON, M. P., M. J. CAPEL, AND F. A. ARMSTRONG. 1977. The chemical analysis of fresh water, 2nd ed. *Fish. Mar. Serv. Can. Misc. Spec. Publ.* **25**. 166 p.
- STRAYER, R. F., AND J. M. TIEDJE. 1978. Kinetic parameters of conversion of methane precursors to methane in a hypereutrophic lake sediment. *Appl. Environ. Microbiol.* **36**: 330-340.
- STUMM, W., AND J. J. MORGAN. 1981. *Aquatic chemistry*, 2nd ed. Wiley-Interscience.
- WINFREY, M. R., AND J. G. ZEIKUS. 1977. Effect of sulfate on carbon and electron flow during microbial methanogenesis in freshwater sediments. *Appl. Environ. Microbiol.* **33**: 275-281.
- ZEHNDER, A. J., AND T. D. BROCK. 1980. Anaerobic methane oxidation: Occurrence and ecology. *Appl. Environ. Microbiol.* **39**: 194-204.

Submitted: 19 June 1981

Accepted: 18 March 1982