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Prediction of biological acid neutralization in acid-sensitive lakes

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Abstract. Sulfate and nitrate removal, and the resulting sulfuric and nitric acid neutralization within acid-sensitive lakes, were predicted from a simple model requiring knowledge only of water residence time, mean depth, and average mass transfer coefficients for nitrate and sulfate removal. The model applies to lakes with oxic hypolimnia which are typical of acid-sensitive lakes. Average mass transfer coefficients for sulfate and nitrate were obtained by two independent methods which agreed well with each other. A model such as this is necessary for predicting the rates at which different lakes acidify and recover from acidification, and explains why lakes with short water residence times are especially susceptible to acidification.

Introduction

Recent research has shown that sources of acid neutralization in lakes include within-lake processes, as well as the weathering of terrestrial rocks and soils (Schindler et al., 1980; Kilham, 1982; Kelly and Rudd, 1982; Schindler et al., 1986). While several models adequately describe terrestrial processes affecting acid inputs to lakes (Christopherson et al., 1982; Schnoor and Stumm, 1985; Cosby et al., 1985; Gherini et al., 1985), so far no model has been derived to predict within-lake acid neutralization. Different lakes have been observed to exhibit widely different degrees of acid neutralization within the lake (e.g., Galloway et al., 1983; Cook et al., 1986). Therefore, a model of in-lake neutralization processes is essential if we are to understand and to predict the rates at which different lakes acidify under known levels of acidic precipitation. Here we present a simple model which accurately predicts, for tested lakes, the consumption of H^+ by two biologically-mediated processes. These processes, the biological removal of sulfate and nitrate in lakes, can be important in acid-sensitive lakes (Schindler et al., 1985; Cook et al., 1986; Rudd et al., in press-a). The model requires only two measurements, water residence time and mean depth, plus the use of average mass transfer coefficients for sulfate and nitrate which are presented in this paper.

Removal of sulfate is thought to occur largely by reduction of sulfate to sulfide in sediments (Cook and Schindler, 1983), resulting in the formation of organic sulfur compounds and iron sulfides (Nriagu and Soon, 1985; Rudd et al., in press-b). The process occurs in hypolimnetic (Ingvorsen and Brock, 1982; Cook and Schindler, 1983) and in epilimnetic sediments (Kelly and Rudd, 1984; Rudd et al., in press-a). Sulfate uptake into algae followed by sedimentation may also contribute to overall removal (David and Mitchell, 1985). In the case of nitrate, both algal uptake and bacterial denitrification are potentially major removal mechanisms (Rudd et al., in press-a). The chemistry of H^+ removal by these mechanisms has been explained previously (e.g., Berner et al., 1970; Goldman and Brewer, 1980; Cook et al., 1986).

The biological-alkalinity production model presented below has been constructed for and is applicable to only the narrowly defined group of lakes whose characteristics cause them to be acid-sensitive. These lakes have small sources of geochemical neutralization in their basins and thus biological neutralization mechanisms can be the most important souce of acid neutralization (Cook et al. 1986). These lakes also tend to be low in primary productivity (Schindler, 1980) and thus they have small or no anoxic zones during stratification. Lakes of higher productivity tend to have large anoxic hypolimnia and would require a somewhat different model than the one described in this paper. However, such lakes are less acid sensitive (Kelly et al. 1982) and so are not of as much concern as the group of lakes treated by our model.

Development of this model was prompted by our observation that when removal rates of sulfate and nitrate by sediment processes were measured directly at the sediment-water interface, these rates were similar in a variety of acidified lakes including drainage lakes in southern Ontario, northwestern Ontario, the Adirondack Mountains (New York), and southern Norway (Rudd et al., in press-a) and in a seepage lake in northern Wisconsin (this ms.). However, in some of these lakes, there was little or no measurable removal of sulfate or nitrate from the water column, while in other lakes, the removal of these ions from the water column was easily detectable. From knowledge of differences in water residence times of these lakes we hypothesized that the contact time of the water with sediments should be a crucial factor in determining the proportion of sulfate and nitrate removed from the water as it passes through the lake. We have tested this hypothesis using equations previously developed for prediction of removal of phosphorous within lakes (Vollenweider, 1969 and 1976; Dillon and Rigler, 1974), and comparing these predictions with measured removal of sulfate and nitrate.

Methods

Sulfate and nitrate mass transfer coefficients were calculated in two ways: by mass balance, which measures total removal by all processes, and by direct measurement of sulfate reduction and denitrification at the sediment-water interface.

Mass balance data for nitrate and sulfate were obtained from measurements of concentrations and volumes of inflows and outflows for each lake. Detailed descriptions of data collection and calculation methods for Experimental Lakes Area lakes (223, 239, 302N, 302S) are given in Schindler et al. (1976), and for Harp and Plastic lakes in Scheider et al. (1979). Direct runoff and precipitation into Dart's lake is insignificant in its water budget (Schafran and Driscoll, 1987). Therefore mass balance calculations were made on only river flow. For Crystal Lake, a seepage lake, water inflow consisted of direct precipitation (90%) and groundwater (10%). Concentrations of nitrate and sulfate in both inflows were measured. Outflow from Crystal Lake was entirely by seepage and was measured by difference from detailed water budget data (S. Gherini unpub. data). The sulfate budget for Lake Malawi was calculated from concentrations of sulfate and volumes of river inflow and precipitation to Lake Malawi as well as river outflow.

The mass balance data were used in a model which relates whole lake removal to the water residence time, mean depth, and mass transfer coefficients of nitrate or sulfate. The unknowns in our data set were the mass transfer coefficients. The assumptions of the following model are: 1) nitrate and sulfate removal processes are in steady state with the inputs, and 2) nitrate and sulfate removal rates are first order reactions. The second assumption is supported by Andersen (1977), Cook and Schindler (1983), and Kelly and Rudd (1984) who found that nitrate and sulfate reduction rates increased in lakes with increasing concentration of each specie.

At steady state the removal of nitrate or sulfate by in-lake processes is expressed by:

$$R = \frac{\text{mass in-mass out}}{\text{mass in}} \qquad \text{(Eq. 1)}$$

where R = the removal coefficient (the proportion of incoming mass which is removed from the water column, either to the sediments or to the atmosphere or to a new form within the water column)

Eq. 1 can be written as $R = 1 - (\text{mass out}/\text{mass in})$. At steady state, mass in = mass out + mass lost within the lake ($I = O + S$). Using areal units (where the frame of reference is 1 m^2 of lake surface), mass out = $q_a \times [C]$, where q_a = average areal outflow of water ($m \cdot yr^{-1}$) and $[C]$ = concentration in the lake in $ueq \cdot m^{-3}$. Mass in = $(q_a \times [C]) + (S \times [C])$, where s = mass transfer coefficient in $m \cdot yr^{-1}$ and $(S \times [C])$ = removal rate in $ueq \cdot m^{-2} \cdot yr^{-1}$. Thus, $R = 1 - ((q_a \times [C])/((q_a \times [C]) + (S \times [C])))$ which reduces to eq. 2 below

$$R_S = 1 - \frac{q_a}{q_a + S_S} \qquad R_N = 1 - \frac{q_a}{q_a + S_N} \qquad \text{(Eq. 2)}$$

where R_S and R_N = sulfate and nitrate removal coefficients
q_a = average areal outflow ($m \cdot yr^{-1}$)
S_S and S_N = mass transfer coefficients for sulfate and nitrate ($m \cdot yr^{-1}$)

Calculation of q_a can be done from the mean depth divided by water residence time, or outflow or divided by area:

$$q_a = \frac{\bar{z}}{\tau_w} \quad \text{or} \quad q_a = \frac{OF}{A} \qquad \text{(Eq. 3)}$$

where $\bar{z}$ = mean depth (m) OF = outflow ($m^3 \cdot yr^{-1}$)
τ_ω = water residence time (yr) A = lake area (m^2)

Combining equations 2 and 3:

$$R_S = \frac{S_S}{(\bar{z}/\tau_w) + S_S} \qquad R_N = \frac{S_N}{(\bar{z}/\tau_w) + S_N} \qquad \text{(Eq. 4)}$$

To help in understanding this equation, think of a 1 m^2 water column of mean depth 5 m. Then, $\bar{z}/\tau_w$ is the height of this column that is displaced by new water each year, i.e. if τ_w = 5 yr, 1 m of water is displaced. The mass transfer coefficient is the height of the column from which nitrate or sulfate is removed each year.

Independent estimates of the mass transfer coefficients for nitrate and sulfate were calculated from direct measurements of concentrations and rates of loss in the sediments as follows:

$$S_S = \frac{f}{[SO_4^{2-}]} \qquad S_N = \frac{f}{[NO_3^-]} \qquad \text{(Eq. 5)}$$

where $[SO_4^{2-}]$, $[NO_3^-]$ = concentration ($ueq \cdot m^{-3}$)
f = measured sulfate reduction or denitrification rate ($ueq \cdot m^{-2} \cdot yr^{-1}$)

Sulfate reduction rate was measured by calculating the flux across the sediment-water interface from the SO_4^{2-} concentration gradient and the diffusion coefficient for SO_4^{2-} at each particular site, as determined by measurement of diffusion of ^3H_2O into the sediment (Rudd et al., in press-a). For most of the lakes this was done during summer. An annual rate was estimated by multiplying the summer rate by 0.5. This factor was determined over a two-year period by following the persistence of reduced ^{35}S in the epilimnetic sediments of Lake 302S (Rudd et al., in press-b).

Denitrification rates were measured by assaying the production of ^{15}N-labeled N_2 from $^{15}NO_3^-$ as described by Rudd et al. (in press-a). In one lake, 302N, the rate of denitrification was measured in the epilimnetic

Table 1. Removal coefficients for sulfate (R_S) and nitrate (R_N) in lakes of various water retention times were calculated from Eq (1) using mass balance data. Mass transfer coefficients for sulfate (S_S) and nitrate (S_N) were calculated from Eq (4) using mass balance data

Lake	Budget years	$\bar{Z}$ m	τ_w yr	$[NO_3^-]$ $\mu eq \cdot L^{-1}$	R_N	S_N[4] $m \cdot yr^{-1}$	$[SO_4^{2-}]$ $\mu eq \cdot L^{-1}$	R_s	S_S[4] $m \cdot yr^{-1}$
Dart's[6]	1982–84	7.1	0.06	20	0.07	8.9	150	U.D.[5]	–
Langtjern[1,7]	1972–78	2.4	0.20	2	0.36	6.8	82	0.05	0.63
Woods[2,6]	1978–80	3.5	0.61	19	–	–	126	U.D.	–
Panther[2,6]	1978–80	3.9	0.72	23	–	–	123	U.D.	–
Harp[8]	1980–84	12.4	2.35	6.5	0.58	6.8	180	0.09	0.52
Plastic[8]	1980–84	8.0	3.83	1.4	0.81	10.7	140	0.19	0.66
302N[9]	1981–84	5.7	5.8	19	0.70	2.3	70	0.45	0.80
239[9]	1981–83	10.9	6.2	3	0.88	12.9	62	0.20	0.44
302S[9]	1981–84	5.1	8.3	2	0.98	–[12]	120	0.39	0.39
223[9]	1976–84	7.1	8.7	1	0.98	–[12]	210	0.4	0.55
Crystal[10]	1984	10.6	25	0.5	0.99	–[12]	75	0.50	0.42
Malawi[11]	1980–81	290[3]	770	–	–	–[12]	58	0.92	4.4

[1] Wright, 1983.

[2] Galloway et. al., 1983.

[3] Hecky, 1984.

[4] The average S_S for 8 lakes (excluding Dart's, Woods, and Panther because R_s was undetected, and Malawi for reasons discussed in the text) was $0.54 \pm 0.13 m \cdot yr^{-1}$ for SO_4^{2-}. The average S_N for Dart's, Langtjern, Harp, Plastic, and 239 which had detectable summer epilimnetic nitrate was $9.2 \pm 2.6 m \cdot yr^{-1}$.

[5] Undetectable.

[6] Adirondack Mountains.

[7] Southern Norway.

[8] Southern Ontario.

[9] Experimental Lakes Area.

[10] Northern Wisconsin.

[11] East Africa.

[12] Not applicable to model in this paper — see text.

Table 2. Measured rates of sulfate reduction* on given dates, and estimates of annual mass transfer coefficients for sulfate (summer rate × 0.5)

Lake	Sampling Depth (m)	Date	SO_4^{2-} $\mu eq \cdot L^{-1}$	SO_4^{2-} reduction rate $\mu eq \cdot m^{-2} \cdot d^{-1}$	Annual S_S $m \cdot yr^{-1}$
302S	1.5	Aug. 1984	136	498	0.65**
223	4	Jul. 1983	236	426	0.33
114	2	Sept. 1981	128	215	0.31
Twitchell	1	Jun. 1984	92	222	0.44
Big Moose	3.5	Jul. 1983	150	400	0.49
Woods	1.5	Jun. 1984	126	362	0.52
Dart's	2.5	Jun. 1984	108	126	0.21
Red Chalk	2	Sept. 1982	176	150	0.16
Chubb	1.5	Sept. 1982	172	270	0.29
Plastic	3.0	Sept. 1982	146	91	0.11
Crystal	6	Jun. 1985	66	100	0.56
					$\bar{x} = 0.36 \pm 0.17$

*Rudd et al., in press-a.

**For L.302S using data from 27 epilimnetic samplings in all seasons for 1981–85, S_s was 0.32 ± 0.19 m/yr.

sediments seven times over a one year period. It was found that the rate on an annual basis was 64% of the average summer rate (unpub. data). This factor was used to estimate an annual rate in the other lakes based on summer measurements of denitrification.

Results and discussion

In lakes where R_N and/or R_S have been measured, removal coefficients for nitrate and sulfate were found to increase with increasing water residence time (Table 1). The removal of nitrate was much greater than was the removal of sulfate, approaching the high efficiencies that have previously been observed for phosphorous removal in lakes (Dillon, 1975). Near complete removal of sulfate occurred in only one lake which had a very long water residence time of 200 years (Table 1).

An average mass transfer coefficient for sulfate of $0.54 \pm 0.13\, m \cdot yr^{-1}$ (± 1 S.D.) was calculated using Eq. 4 and data from eight lakes where there was detectable sulfate removal (Table 1). Dart's, Woods, and Panther Lakes were not included in the calculation of this coefficient because sulfate removal could not be detected with the mass balance approach, as would be expected for these very short water residence time lakes (Table 1). Lake Malawi was also not included because of its large anoxic hypolimnion which is atypical of acidified lakes (see later discussion). For the 8 lakes which were used, the fairly narrow range for the mass transfer coefficients (± 20%, 1 S.D.) indicated a consistent pattern for acidified lakes.

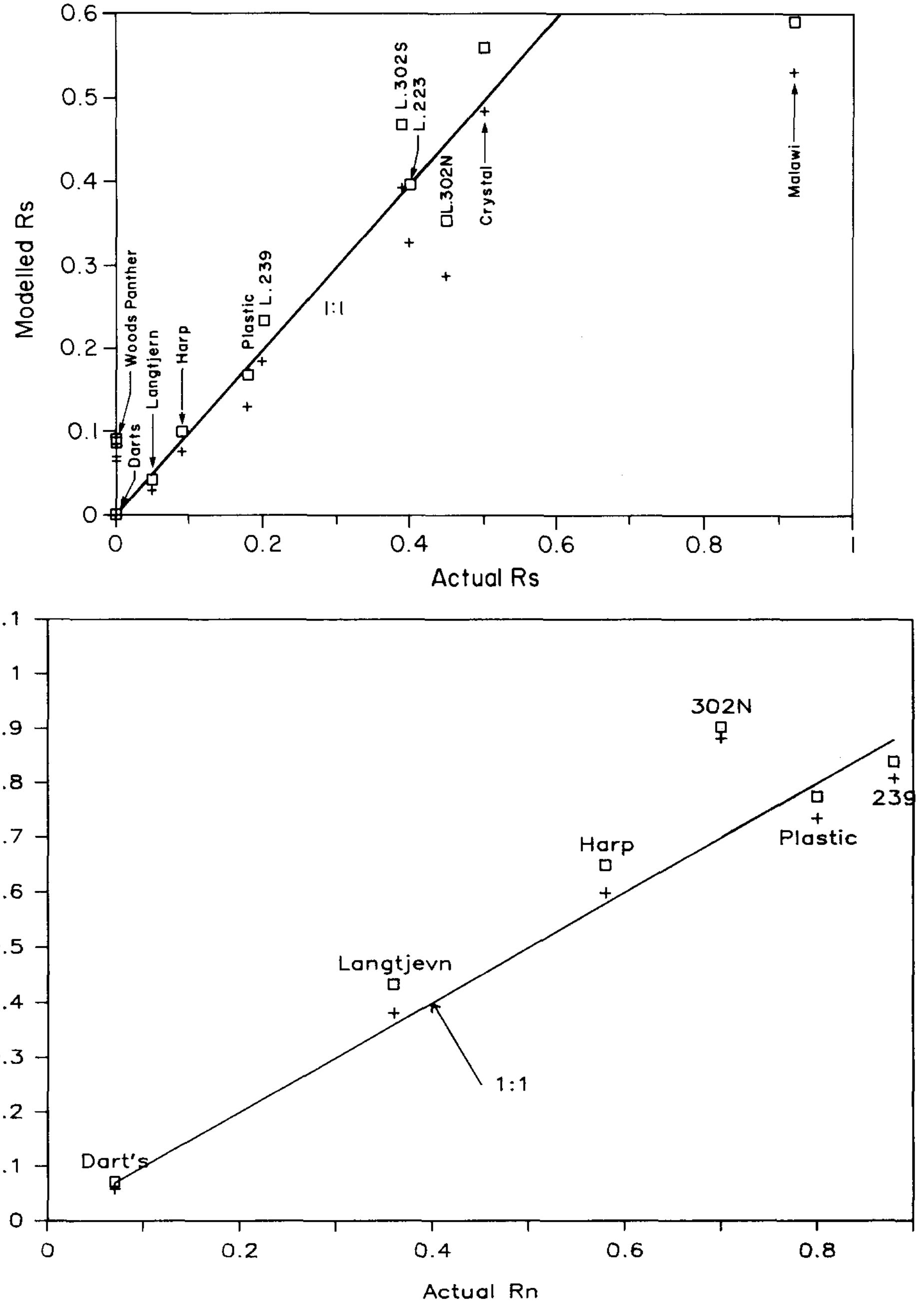

Figure 1. A comparison of actual coefficients of removal for sulfate (R_S) and nitrate (R_n) and modelled removal coefficients. The modelled removal coefficients were calculated using either average mass transfer coefficients obtained from the chemical budgets of lakes (□) or mass transfer coefficients obtained from measurements of rates of sulfate reduction or denitrification (+).

Use of the direct measurement data for sulfate flux at the sediment-water interface resulted in a value for the mass transfer coefficient for sulfate of 0.4 ± 0.2 $m \cdot yr^{-1}$ (± 1 S.D.) for 10 acidified North American lakes (Table 2). This value is slightly below the one derived from mass balance data, perhaps because the mass balance estimate includes some loss of sulfate to the sediments by algal uptake and sedimentation as well as by sulfate reduction in the sediments. Nevertheless, use of either value for the mass transfer coefficient in Eq. (4) resulted in modelled sulfate removal coefficients for the whole lake that agreed closely with the removal coefficients measured by mass balance (Figure 1a).

Variations in mean depth, water residence time, and the mass transfer coefficient are all important mathematically in the model. In practice, however, the wide variation in water residence time for lakes in our data set explained most of the observed variation in sulfate removal. For example, water residence times varied by 3 orders of magnitude even without considering the long water residence time of Lake Malawi. In contrast, mean depths varied by a factor of only 5 and sulfate concentrations and removal rates (used to determine the mass transfer coefficients) varied by factors of 3 and 5, respectively (Table 1). It should be noted that τ_w can vary greatly in some lakes from year to year, and the prediction of removal coefficients is best done using an average τ_w for several years covering the range of precipitation levels for a particular region.

This sulfate removal model is not useful for all lakes. For example, sulfate was almost completely removed from Lake Malawi (Table 1) even though the model predicted a retention coefficient of about 0.25 (Figure 1a). One obvious difference between Lake Malawi and the other lakes is that a large percentage (58%) of the surface area of Lake Malawi is permanently underlaid by anoxic water (Hecky, 1984). The mass transfer coefficient calculated from the lake budget data was very large (4.4 $m \cdot yr^{-1}$). This type of value may be more representative of mass transfer coefficients across an oxic/anoxic interface within the water column where diffusion rates would be much faster than across the sediment-water interface. This idea is supported by the measured S_s of 5.48 $m \cdot yr^{-1}$ for Lake 227 (Cook, 1981). Both Lake Malawi and Lake 227 have anoxic hypolimnia beginning at the bottom of the epilimnion. Other lakes with much smaller and deeper anoxic zones in the hypolimnion which begin several meters below the bottom of the thermocline e.g. Lakes 223, 302N and 302S, could be modelled successfully (Figure 1). The model presented here appears to apply to levels of productivity below those which result in the establishment of a large anoxic hypolimnion.

Nitrate removal was also related to water residence time (Table 1). However, calculation of values for S_N for all of the lakes suggested that they should be grouped into two categories: lakes with undetectable summer NO_3^- and lakes with detectable summer NO_3^-. In lakes where there was no detectable NO_3^- in the summer surface water, the values for

Table 3. Measured rates of denitrification on given dates, and estimates of annual mass transfer coefficients (S_N) for nitrate calculated as the summer rate × 0.64*

Lake	Sampling Depth (m)	Date	NO_3^- $\mu eq \cdot L^{-1}$	Denitrif. by ^{15}N $\mu eq \cdot m^{-2} \cdot d^{-1}$	Annual S_N $m \cdot yr^{-1}$
Dart's	2.5	Jun. 1984	20	556	6.5
Twitchell	1.0	Jun. 1984	13.4	484	8.3
Big Moose	3.5	Jun. 1984	23	602	6.1
Woods	1.5	Jun. 1984	17.3	376	5.1
Sagamore	2.5	Jun. 1984	7.4	406	12.7
Hovattn	2.5	Sept. 1984	13.4	368, 454	7.2
Little Hovattn	2.5	Sept. 1984	10	266, 232	5.8
					$\bar{x} = 7.4 \pm 2.6$

*For 302N, denitrification measured by ^{15}N at epilimnetic sites on an annual basis was 0.64 of the summer rate (J. Rudd and M. Holoka, unpubl. data).

S_N were very high ($30–40 m \cdot yr^{-1}$) and were not included in Table 1 because these lakes probably have algal (water column) uptake as the dominant removal mechanism, and our model was not designed to predict algal activity. For example, in L. 227, which has little detectable NO_3^- in the summer surface water, 98% of the nitrate is removed by algal uptake (Chan and Campbell, 1980), and values for S_N from the mass balance budgets ranged from $43–504 m \cdot yr^{-1}$ (unpublished data). In contrast, many of the acidified lakes sampled had easily detectable NO_3^- in the surface waters during summer ($7–23 ueq \cdot l^{-1}$, Table 3). In these lakes the values for S_N (from mass balance data) were much lower, averaging 9.2 ± 2.6 (± 1 S.D.) $m \cdot yr^{-1}$ (Table 1). This average valueis in agreement with mass transfer coefficients calculated from direct measurements of denitrification using ^{15}N ($7.4 \pm 2.6 m \cdot yr^{-1}$, ± 1 S.D., Table 3). The fact that both methods of calculating S_N resulted in similar values suggests that, for lakes that have excess nitrate in the epilimnion during summer stratification, most of the permanent removal of nitrate is done by denitrification.

For acidified lakes which have detectable nitrate in the surface waters (Table 1), the use of either value of S_N (9.2 or $7.4 m \cdot yr^{-1}$) in the model (Eq. 4) resulted in close agreement between actual and predicted retention coefficients of nitrate (Figure 1b). Thus it appears that both nitrate and sulfate removal in acidified lakes can be successfully modelled with this approach.

The value of a mass transfer coefficient reflects the rate of a process compared to the available concentration. It is not necessarily indicative of the order of importance of each reaction in terms of total mass removed from the lake. In the case of algal uptake of NO_3^-, the mass transfer coefficient is high but total uptake is limited by phosphorus availability, and this total can probably not be increased much if NO_3^- inputs increase due to acidic precipitation. Denitrification is slower but is first order with

NO_3^-. Thus, as NO_3^- concentration increases the mass of NO_3^- removed by denitrification will increase. Similarly, in comparing denitrification and sulfate reduction, both rates and concentrations must be considered. Where NO_3^- is very low in concentration, sulfate reduction will be more important in terms of mass of H^+ removed even though it is a slower process. Where NO_3^- is available, however, its faster removal may result in greater neutralization even though its concentration is lower than the concentration of SO_4^{2-} in the same lake (Tables 2 and 3). This last case has been examined in several acidified lakes where denitrification was estimated to be 6 times more important than sulfate reduction on an annual basis (Rudd et al., in press-a). The model presented in this article will be of use to lake managers for predicting future acceptable atmospheric loadings of sulfuric and nitric acid to acid-sensitive lakes. The following equation is suggested which is derived from Eq. 2:

$$AN = L\left[\frac{1}{OF/A} - \frac{1}{(OF/A) + S}\right] \qquad \text{(Eq. 6)}$$

where: AN = neutralization of acid ($ueq \cdot m^{-3}$)
L = areal sulfate or nitrate loading ($ueq \cdot m^{-2} \cdot yr^{-1}$)
OF = lake outflow ($m^3 \cdot yr^{-1}$)
A = lake area (m^2)
S = mass transfer coefficient for NO_3^- (7.4–9.2) or SO_4^{2-} (0.4–0.54 $m \cdot yr^{-1}$).

This simple relationship enables calculation of biological acid neutralization in lakes with inputs of only lake area, average annual outflow, and sulfate and nitrate loading. In the case of nitrate, one must also know whether it is detectable in summer. If it is not, alkalinity production should be equal to loading and it is not necessary to model it. If there is detectable nitrate, then the above model applies. Annual outflow is easily obtainable from precipitation measurements and drainage basin yields of water (Newbury and Beaty, 1980). This loading model is useful for sulfate on its own in geographical areas where the terrestrial watershed does not retain sulfate (e.g., northeastern U.S., Galloway et al., 1983, and the Canadian Shield, Schindler et al., 1976). Because significant quantities of sulfate are retained in some systems (e.g., Cosby et al., 1985) and nitrate is retained to varying degrees (e.g., Likens et al., 1977), a general model for acid neutralization due to removal of these two ions requires that the model presented here be linked in series to a terrestrial model.

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References

Andersen, J.M. 1977. Rates of denitrification of undisturbed sediment for six lakes as a function of nitrate concentration, oxygen, and temperature. Archive fur Hydrobiologie 80:147–159.

Berner, R.A., M.R. Scott, and C. Thomlinson. 1970. Carbonate alkalinity in pore waters of anoxic marine sediments. Limnology and Oceanography 15:544–549.

Chan, Y.K., and N.E.R. Campbell. 1980. Denitrification in Lake 227 during summer stratification. Canadian Journal of Fisheries and Aquatic Sciences 37:506–512.

Christopherson, N., H.M. Seip, and R.F. Wright. 1982. A model for stream water chemistry at Birkenes, Norway. Water Resources Research 18:977–996.

Cook, R.B., 1981. The biogeochemistry of sulfur in two small lakes. Ph.D. thesis, Columbia University, p. 48.

Cook, R.B., and D.W. Schindler. 1983. The biogeochemistry of sulphur in an experimentally acidified lake. Environmental Biogeochemistry Ecological Bulletin (Stockholm) 35:115–127.

Cook, R.B., C.A. Kelly, D.W. Schindler, and M.A. Turner. 1986. Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. Limnology and Oceanography 31:134–148.

Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright. 1985. Time scales of catchment acidification. Environmental Science and Technology 19:1144–1149.

David, M.B. and M.J. Mitchell. 1985. Sulfur constituents and cycling in waters, seston, and sediments of an oligotrophic lake. Limnology and Oceanography 30:1196–1207.

Dillon, P.J. 1975. The phosphorus budget of Cameron Lake, Ontario: The importance of flushing rate to the degree of eutrophy of lakes. Limnology and Oceanography 20:28–39.

Dillon, P.J. and F.H. Rigler. 1974. A test of a simple nutrient budge model predicting the phosphorus concentration in lake water. Journal of the Fisheries Research Board of Canada 31:1771–1778.

Galloway, J.N., C.L. Schofield, N.E. Peters, G.R. Hendrey, and E.R. Altwicker, 1983. Effect of atmospheric sulfur on the composition of three Adirondack lakes. Canadian Journal of Fisheries and Aquatic Sciences 40:799–806.

Gherini, S.A., L. Mok, R.J.M. Hudson, G.F. Davis, C.S. Chen, and R.A. Goldstein 1985. The ILWAS model: formulation and application. Water Air Soil Pollution 26:425–459.

Goldman, J.C. and P.G. Brewer. 1980. Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity. Limnology and Oceanography. 25:352–357.

Hecky, R.E. 1984. African lakes and their trophic efficiencies: a temporal perspective. In: Trophic Interactions Within Aquatic Ecosystems, D.G. Meyers and J.R. Strickler (eds.), AAAS Selected Symposium. pp. 405–448.

Ingvorsen, K., and T.D. Brock. 1982. Electron flow via sulfate reduction and methanogenesis in the anaerobic hypolimnion of Lake Mendota. Limnology and Oceanography. 27:559–564.

Kelly, C.A., J.W.M. Rudd, R.B. Cook, and D.W. Schindler. 1982. The potential importance of bacterial processes in regulating rate of lake acidification. Limnology and Oceanography 27:868–882.

Kelly, C.A. and J.W.M. Rudd. 1984. Epilimnetic sulfate reduction and its relationship to lake acidification. Biogeochemistry 1:63–77.

Kilham, P. 1982. Acid precipitation: its role in the alkalization of a lake in Michigan. Limnology and Oceanography 27:856–867.

Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton, and N.M. Johnson. 1977. Biogeochemistry of a forest ecosystem. Springer-Verlag, New York. 135 pp.

Newbury, R.W. and K.G. Beaty. 1980. Water renewal efficiency of watershed and lake combinations in the ELA region of the Precambrian shield. Canadian Journal of Fisheries and Aquatic Sciences. 37:335–341.

Nriagu, J.O. and Y.K. Soon. 1985. Distribution and isotopic composition of sulfur in lake sediments of northern Ontario. Geochimica et Cosmochimica Acta 49:823–834.

Rudd, J.W.M., C.A. Kelly, V. St. Louis, R.H. Hesslein, A. Furutani, M.H. Holoka. Microbial consumption of nitric and sulfuric acids in acidified north temperate lakes. Limnology and Oceanography (in press-a).

Rudd, J.W.M., C.A. Kelly and A. Furutani. The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. Limnology and Oceanography (in press-b).

Schafran, G.C. and C.T. Driscoll. 1987. Spatial and temporal variations in aluminum chemistry of a dilute acidic lake. Biogeochemistry, 3: 105–119.

Scheider, W.A., J.J. Moss, and P.J. Dillon. 1979. Measurement and uses of hydraulic and nutrient budgets. In: Lake restoration. Proceedings National Conference, August 1978, Minneapolis, Minnesota, EPA 440/5-79-001 pp. 77–83.

Schindler, D.W. 1980. Experimental acidification of a whole lake: A test of the oligotrophication hypothesis, p. 370–374. In: Ecological impact of acid precipitation. Proceedings of International Conference SNSF Project.

Schindler, D.W., R.W. Newbury, K.G. Beaty, and P. Campbell. 1976. Natural water and chemical budgets for a small Precambrian lake basin in central Canada. Journal of the Fisheries Research Board of Canada 33:2526–2543.

Schindler, D.W., R. Wagemann, R.B. Cook, T. Ruszczyunski, and J. Prokopowich. 1980. Experimental acidification of Lake 223, Experimental Lakes Area: Background data and the first three years of acidification. Canadian Journal of Fisheries and Aquatic Sciences 37:342–354.

Schindler, D.W., M.A. Turner, M.P. Stainton, and G.A. Linsey. 1986. Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian Shield. Science 232:844–847.

Schnoor, J.L. and W. Stumm. 1985. Acidification of aquatic and terrestrial systems. In: Chemical Processes in Lakes, W. Stumm (ed.), John Wiley and Sons. pp. 311–338.

Vollenweider, R.A. 1969. Moglichkeiten und Grenzen elementarer Modelle der Stoffbilanz von Seen. Archiv fur Hydrobiologie 66:1–36.

Vollenweider, R.A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. Memorie dell'Instituto Italiano di Idrobiologia 33:53–83.

Wright, R.F. 1983. Input-output budgets at Langtjern, a small acidified lake in southern Norway. Hydrobiologia 101:1–12.