Dynamic Model of in-Lake Alkalinity Generation

LAWRENCE A. BAKER AND PATRICK L. BREZONIK

Department of Civil and Mineral Engineering, University of Minnesota, Minneapolis

In-lake alkalinity generation (IAG) is important in regulation of alkalinity in lakes with long residence times, particularly seepage lakes. An IAG model based on input/output modeling concepts is presented that describes budgets for each ion involved in alkalinity regulation by a single differential equation that includes inputs, outputs, and a first-order sink term. These equations are linked to an alkalinity balance equation that includes inputs, outputs, IAG (by sulfate and nitrate reduction), and internal alkalinity consumption (by ammonium assimilation). Calibration using published lake budgets shows that rate constants are generally similar among soft water lakes ($k_{SO_4} \approx 0.5$ m/yr; $k_{NO_3} \approx 1.3$ yr^{-1}; $k_{NH_4} \approx 1.5$ yr^{-1}). Sensitivity analysis shows that predicted alkalinity is sensitive to water residence time, but less sensitive to modest changes in rate constants. The model reflects the homeostatic nature of internal alkalinity generation, in which internal alkalinity production increases with increasing acid input and decreases with decreasing acid inputs of HNO_3 or H_2SO_4.

INTRODUCTION

Atmospheric H$^+$ inputs to watersheds are neutralized largely by mineral weathering and other biogeochemical reactions. Because of this, watershed residence time has been recognized as an important determinant in acidification of drainage lakes [*Gherini et al.*, 1985]. However, for many lakes there is limited interaction between precipitation and the soil system. Of particular interest is a subclass of seepage lakes known as groundwater recharge lakes (GRL) [*House*, 1985]. Alkalinity inputs from groundwater may not be sufficient to neutralize precipitation H$^+$ inputs to these lakes; hence in-lake biogeochemical processes are important in regulating lake water alkalinity. Groundwater recharge lakes are common in northern Wisconsin and Florida and are considered particularly susceptible to acidification [see *Eilers et al.*, 1983; *Hendry and Brezonik*, 1984; L. A. Baker et al., Alkalinity regulation in soft water Florida lakes, submitted to *Water Resources Research*, 1987 (hereinafter LAB et al., 1987)].

Two examples are Vandercook Lake, Wisconsin, and McCloud Lake, Florida. Vandercook Lake receives 2.5% of its water input from subsurface groundwater inputs and the rest from precipitation to the lake surface. Even though the groundwater is well buffered (alkalinity = 400 μeq/L), it neutralizes only 45% of the atmospheric H$^+$ inputs to the lake surface [*Lin et al.*, 1987]. At McCloud Lake, subsurface seepage (mean alkalinity = 125 μeq/L) contributed 10% of the total water input and neutralized 33–37% of atmospheric H$^+$ input to the lake surface [*Baker et al.*, 1986a]. In both lakes, in-lake biogeochemical processes contributed more alkalinity than did groundwater inputs.

Nevertheless, because our awareness of the significance of in-lake alkalinity generation (IAG) is very recent, most models to predict lake acidification [e.g., *Henriksen*, 1980; *Gherini et al.*, 1985; *Thompson*, 1982] focus on terrestrial acid neutralization processes. In-lake alkalinity generation is included in the trickle-down model [*Schnoor and Stumm*, 1985] as a zero-order term; we will show that this may lead to considerable error in estimating response to acid inputs.

The objective of this paper is to describe a relatively simple model of IAG that can be used to predict lake water alkalinity from known inputs of major ions. This model was developed

by *Baker et al.* [1985a] to analyze acidification of Florida seepage lakes, but at that time few data were available for calibration. Calibration of the sulfate component was given by *Baker et al.* [1986b]. This paper presents calibration of other model components, model verification, and application.

THEORETICAL DEVELOPMENT

The model is based on alkalinity/electroneutrality concepts [*Cook et al.*, 1986] and input/output modeling concepts analogous to those used in development of nutrient loading models [*Vollenweider*, 1975]. The intent was to develop a model that is simple in structure and has modest data requirements so that it can be used on a regional scale.

The IAG model is composed of a series of linked differential equations in which the alkalinity balance is calculated as the sum of alkalinity inputs and internal alkalinity generation minus outflows and internal alkalinity consumption. Budgets for ions that participate in alkalinity generating or consuming reactions are represented by differenctial equations that include loading, outflow, change in storage, and a sink/source term (see Rationale subsection):

$$d[SO_4^{2-}]/dt = (1/V)\{J_{SO_4} - [SO_4^{2-}](S_o + k_{SO_4}A)\} \tag{1}$$

$$d[NO_3^-]/dt = (1/V)\{J_{NO_3} - [NO_3^-](S_o + k_{NO_3}V)\} \tag{2}$$

$$d[NH_4^+]/dt = (1/V)\{J_{NH_4} - [NH_4^+](S_o + k_{NH_4}V)\} \tag{3}$$

$$d[\textstyle\sum M^+]/dt = (1/V)\{J_m - [\textstyle\sum M^+]S_o + \textstyle\sum W_iA - \textstyle\sum D_iA\} \tag{4}$$

where [i] is the concentration of i in milliequivalents per cubic meter, V is the lake volume in cubic meters, A is the lake area in square meters, S_o is the outflow in cubic meters per year, J_i is the loading of constituent i in milliequivalents per year, k_{SO_4} is the first-order loss term for SO_4^{2-} in meters per year, k_{NO_3} is the first-order loss constant for NO_3^- in yr^{-1}, k_{NH_4} is the first-order loss constant for NH_4^+ in yr^{-1}, W_i is the weathering rate for ion i in meq/(m^2 yr), D_i is the areal deposition rate for ion i in meq/(m^2 yr), and [$\sum M^+$] is the total concentration of weatherable cations in milliequivalents per cubic meter.

These are in turn linked to an alkalinity budget equation in which the alkalinity balance is represented by inputs, outputs, three source terms (sulfate reduction, nitrate immobilization, and cation production), and a sink term (immobilization of NH_4^+):

$$d[alk]/dt = 1/V\{J_{alk} - S_o[alk] + k_{SO_4}A(SO_4^{2-}]$$
$$+ V(k_{NO_3}[NO_3^-] - k_{NH_4}[NH_4^+]) + \textstyle\sum W_iA - \textstyle\sum D_iA\} \tag{5}$$

Input terms in these equations represent total loading from all sources (wet plus dry atmospheric inputs plus stream and groundwater inputs) to the lake. Inputs of alkalinity, SO_4^{2-}, NO_3^-, NH_4^+, and major cations therefore must be obtained from field measurements or by a separate watershed model.

Rationale

The sulfate model assumes that internal losses are first order with respect to $[SO_4^{2-}]$ and proportional to lake surface area. These assumptions reflect the fact that most sulfate losses occur by sulfate reduction in sediments (even when the overlying water is oxic) and that loss rate is controlled by diffusion into the sediment. This conclusion is supported by three type of evidence: (1) pore water profiles from several dozen lakes [Rudd et al., 1986a; Baker et al., 1986a; Perry, 1987; Brezonik et al., 1987], which consistently show depletion of sulfate within 5 cm below the sediment-water interface; (2) sediment-water microcosm and mesocosm studies, which show that added H_2SO_4 is removed from the water column [Perry et al., 1986a, b; Kelly and Rudd, 1984; Schiff and Anderson, 1987; Perry, 1987]; and (3) $^{35}SO_4^{2-}$ labeling experiments, which provide direct evidence of reduction within sediments [Rudd et al., 1986b; L. A. Baker, unpublished data, 1986]. Although some soft water lakes, such as lake 223 [Cook et al., 1986] have well-developed hypolimnia in which sulfate reduction occurs, most do not, and most or all of the in-lake sulfate reduction that occurs takes place in surficial sediments. Accordingly, sulfate losses are modeled on the basis of lake surface area (which for practical purposes is the same as sediment surface area).

The conclusion that sulfate reduction rates are diffusion controlled is based on observations of pore water profiles in acidification experiments. If sulfate reduction is diffusion limited, then gradients in pore water $[SO_4^{2-}]$ should become steeper as $[SO_4^{2-}]$ in the overlying water column increases. Observations in experimental enclosures show that this is the case: Pore water sulfate gradients were much steeper in enclosures that were acidified to pH 4.5 with H_2SO_4 than in control enclosures in Little Rock Lake, Wisconsin, but the depth to reach minimum concentrations remained unchanged with acid additions [Perry, 1987]. Kelly and Rudd [1984] showed a similar relationship between pore water gradients in acidified lake 223 and control lakes. According to Fick's first law, fluxes to the sediment are directly proportional to pore water gradients; it follows that fluxes are proportional to lake water $[SO_4^{2-}]$. We also have found that sulfate fluxes are relatively insensitive to temperature (i.e., temperature coefficients are low), which supports the argument that reduction rates are diffusion controlled (rather than limited by biological reduction rate) [Perry et al., 1986a]. The hypothesis that sulfate reduction is first order is further supported by experiments in laboratory microcosms [Hongve, 1978, Kelly and Rudd, 1984; Baker et al., 1985b; Perry et al., 1986a, b; Perry, 1987], in situ mesocosms [Perry, 1987; Schiff and Anderson, 1987], and whole lakes [Cook et al., 1986]. In all of these experiments, sulfate losses were directly proportional to $[SO_4^{2-}]$ in the overlying water.

Nitrate sinks are modeled as a first-order process in which depletion depends upon lake water $[NO_3^-]$ and volume. This assumes that assimilation by phytoplankton is the major mechanism of depletion (hence depletion is proportional to lake volume). This contrasts with the approach taken by Kelly et al. [1987], in which denitrification in surficial sediments was assumed to be the major mechanism of depletion (hence nitrate depletion was proportional to surface area). While their data show denitrification occurs in sediments of many soft water lakes, several lines of evidence support the contention that assimilatory reduction is a more important nitrate sink in most lakes where internal alkalinity generation is important. First, lakes in which IAG is important typically are oligotrophic, have long residence times, and receive most of their nutrients from atmospheric deposition. In the set of lakes used to calibrate the nitrate model, for example, mean $[NO_3^-]$ was only 4 μeq/L (mean $[NO_3^-]$ in the lakes used by Kelly et al. was twice as high). Additional support comes from the observation that the mean N:P ratio in atmospheric deposition in Florida (15:1) [Hendry and Brezonik, 1980] is similar to algal nutrient requirements and also to sediment N:P ratios for 10 soft water lakes in this region that receive most of their nutrient input from atmospheric inputs (mean, 21:1, range, 14:1–28:1) [Flannery et al., 1982]. The similarity of N:P ratios in atmospheric inputs and lake sediments suggests that there is no depletion of N relative to P and therefore that denitrification is a minor sink. Data of Armstrong et al. [1987] also show that denitrification is not important in Crystal Lake, Wisconsin. In this oligotrophic lake, the N:P ratio in sediment traps (16:1) was nearly the same as that of buried sediment (13:1).

Ammonium sinks are also modeled as a first-order, volume-dependent process, because assimilatory reduction by phytoplankton is the major sink for this ion.

The cation balance equation includes two in-lake process terms. The weathering component ($\sum W_i A$) contributes cations to the water column by dissolution of minerals, which are brought into the lake from the terrestrial drainage area [see Lerman and Brunskill, 1971]. In general, mineral weathering is a pH-sensitive process that has fractional-order dependence upon $[H^+]$ [Schnoor and Stumm, 1985], but in the pH range of interest (down to 4–4.5), the pH effect is slight for many minerals and weathering rates may be independent of pH. The second component is an in-lake deposition term ($\sum D_i A$), which represents sediment accumulation of cations which enter the lake in ionic form and are then assimilated by plankton and deposited to the sediment. Although a portion of this material is recycled, evidence suggests that long-term sediment accumulation may be an important sink for major cations, particularly Ca^{2+} [Baker et al., 1987]. In some Florida soft water lakes with little or no groundwater input, calcium is depleted in lake water relative to atmospheric inputs (LAB et al., 1987).

Although we have some understanding of processes that consume or produce cations within lakes, there are insufficient data to calibrate this component of the model. Very few lake budgets accurately measure in-lake cation production. For seepage lakes the problem of constructing accurate cation budgets is particularly troublesome, because even when groundwater is a small part of the overall water input, it may contribute a large fraction of the Ca^{2+} and other cations. For example, groundwater was only 2% of the water input to Vandercook Lake, but contributed 38% of the input Ca^{2+} [Lin et al., 1987]. Because there is considerable uncertainty in estimates of groundwater inputs (of the order of 100% [see Wentz et al., 1986a]) there also is considerable uncertainty in estimates of cation inputs and thus uncertainty in calculating sink/source terms by differences in ion balances.

Steady State Solutions

If we assume steady state conditions ($dC_i/dt = 0$), (1)–(5) can be rearranged to solve for steady state concentrations. The

TABLE 1. Morphometric and Hydrologic Characteristics of Study Lakes

Lake	Location	Reference	Area, ha	Volume, 10^6 m^3	t_w,* years	Hydrologic Type
Gardsjon	SW Sweden	*Hultberg* [1985]	31	1.5	1.1	Drainage
Langtjern	Norway	*Wright* [1983]	23	0.6	0.2	Drainage
Lake 239	experimental lakes area (ELA), Ontario	*Schindler et al.* [1986]	54	5.7	10.8	Drainage
Harp	Dorset, Ont.	P. Dillon, personal communication, 1986	67	8.3	2.9	Drainage
Plastic	Dorset, Ont.	P. Dillon, personal communication, 1986	33	2.6	3.0	Drainage
South	Herkimer Co., N.Y.	*Mitchell et al.* [1985]	202	2.6	2.0	Drainage
Lake 223†	ELA, Ontario	*Cook et al.* [1986]	27	1.9	10.6	Drainage
McCloud	Putnam Co., Fla.	*Baker et al.* [1986a]	5	0.13	9.6	Seepage
Magnolia	Putnam Co., Fla.	*Baker et al.* [1985a]	82	6.4	28.1	Seepage
Vandercook	Vilas Co., Wis.	*Lin et al.* [1987]	40	140	3.7	Seepage
Round	Northern Wis.	*Wentz et al.* [1986a, b]	15	1.2	87	Seepage
East 8 Mile	Northern Wis.	*Wentz et al.* [1986a, b]	15	0.43	17.6	Seepage
Little Rock‡	Vilas Co., Wis.	L. A. Baker, unpublished data, 1987	18	0.62	8.2	Seepage

*t_w is outflow/lake volume.

†Acidified for 7 years.

‡Currently being experimentally acidified, but budgets are for preacidification phase.

equations can be transformed further by dividing the top and bottom of their right sides by A. This transformation accomplishes two purposes: (1) inputs are expressed as areal loading rates (L_i, meq/(m^2 yr)), and (2) outflow S_o is replaced by z/t_w, where z is mean depth in meters and t_w is water residence time in years.

$$[SO_4^{2-}]_{ss} = L_{SO_4}/(z/t_w + k_{SO_4})$$ (6)

$$[NO_3^-]_{ss} = L_{NO_3}/(z/t_w + k_{NO_3}z)$$ (7)

$$[NH_4^+]_{ss} = L_{NH_4}/(z/t_w + k_{NH_4}z)$$ (8)

$$[\textstyle\sum M^+]_{ss} = (L_{M+} + \textstyle\sum W_i - \textstyle\sum D_i)/z/t_w$$ (9)

$$[alk]_{ss} = (L_{alk} + IAG)/(z/t_w)$$ (10)

where

$$IAG = k_{SO_4}[SO_4^{2-}] + k_{NO_3}[NO_3^-]z$$

$$- k_{NH_4}[NH_4^+]z - \textstyle\sum D_i + \textstyle\sum W_i$$

Predicted Retention of Ions

The model can be used to predict the fraction of each substance that is lost (or generated) by internal processes:

$$R_{SO_4} = 100k_{SO_4}/(k_{SO_4} + z/t_w)$$ (11)

$$R_{NO_3} = 100k_{NO_3}/(1/t_w + k_{NO_3})$$ (12)

$$R_{NH_4} = 100k_{NH_4}/(1/t_w + k_{NH_4})$$ (13)

$$R_{\sum Mi} = 100(\textstyle\sum D_i - \textstyle\sum W_i)/L_i$$ (14)

CALIBRATION

In order for this model to be useful, coefficients of individual processes (k_{SO_4}, k_{NH_4}, k_{NO_3}, W_i and D_i) for various lakes must be determined. For application on a regional basis the coefficients must be reasonably consistent among lakes. To calibrate the model, we compiled complete or partial ion budgets for 14 lakes. Hydrologic and morphometric character-

istics of the lakes are shown in Table 1, and data needed for model calibration and testing are shown in Table 2.

The calibration data set consists entirely of soft water lakes that are susceptible to acidification or are actually acidified. Seven are drainage lakes having $t_w = 0.2$–10.8 years. The rest are groundwater recharge lakes that lack channeled surface inlets or outlets and generally have $t_w > 10$ years. Over 90% of the water input to these lakes comes from direct precipitation; as a result, all of the groundwater recharge lakes except East Eight Mile have alkalinities <150 μeq/L.

The quality of ion budgets for these lakes varies. In general, the best budgets are for drainage lakes with gauged inflows and outflows that have been monitored for several years. In contrast, ion budgets for seepage lakes generally are less precise for several reasons: (1) the measurement period often is short relative to t_w, and errors in change in storage of ions may be significant compared with input and output terms; (2) dry deposition inputs are appreciable [see *Baker et al.*, 1986a], and there are no completely satisfactory methods for measuring these; and (3) as noted above, there is considerable uncertainty in groundwater inputs and outflows. The last problem leads to errors in both calculated ion inputs and water residence times.

Lakes were excluded from the calibration set if in-lake retention was <5% of the inputs for a given ion, because it was thought that retention values lower than this may simply be the result of errors in budget calculations. A second criterion for rejection was clear violation of the steady state assumption. This criterion resulted in the rejection of lake 223 (which was experimentally acidified with H_2SO_4) from the k_{SO_4} calibration set.

Calibration was done by rearranging (11)–(13) to calculate internal loss coefficients for each lake:

$$k_{SO_4} = R_{SO_4}z/t_w(100 - R_{SO_4})$$ (15)

$$k_{NO_3} = R_{NO_3}/t_w(100 - R_{NO_3})$$ (16)

$$k_{NH_4} = R_{NH_4}/t_w(100 - R_{NH_4})$$ (17)

TABLE 2. Data Used in Model Calibration

Lake	t_w, years	z, m	Sulfate				Nitrate				Ammonium			
			L_{SO_4}	$[SO_4^{2-}]$	R_{SO_4}	k_{SO_4}	L_{NO_3}	$[NO_3^-]$	R_{NO_3}	k_{NO_3}	L_{NH_4}	$[NH_4^+]$	R_{NH_4}	k_{NH_4}
Gardsjon	1.1	4.8	897	208	2	···*	64	8.4	42	0.7	52	3.1	74	2.54
Lake 239	10.8	10.5	182	124	21	0.26	22	2.6	87	0.6	17	4.7	76	0.30
Langtjern	0.2	2.0	1035	82	6	0.57	48	2.0	36	2.8	···	···	···	···
Lowery	17.4	4.9	59	74	75	0.84	23	4.0	109	···*	17	2.5	89	0.45
Magnolia	28.1	7.8	59	65	82	1.28	23	4.5	114	···*	17	2.9	95	0.68
McCloud	9.6	2.5	69	69	44	0.20	19	4.5	95	2.1	13	5.0	93	1.34
Harp	2.9	12.3	820	165	9	0.41	89	6.3	58	0.5	33	···	91	3.41
Plastic	3.0	8.0	372	140	19	0.62	41	1.5	80	1.3	27	1.5	82	1.48
Vandercook	3.8	3.5	46	88	45	0.75	21	7.0	126	···†	19	5.0	110	···†
Little Rock	8.2	3.5	40	54	48	0.24	···	···	···	···	···	···	···	···
East 8 Mile	17.6	2.9	33	58	53	0.19	···	···	···	···	···	···	···	···
Round	101.7	8.0	54	46	83	0.39	···	···	···	···	···	···	···	···
South	2.0	13.0	842	106	4	···*	···	···	···	···	···	···	···	···
Lake 223	10.6	7.2	629	193	36	···*	···	···	···	···	···	···	···	···

Loadings as meq/(m² yr), concentrations in microequivalents per liter, and retention R in percent. Loadings include atmospheric inputs, streams, and groundwater.

*Calculated value not used in computing mean. See text.
†Value of k undefined because retention >100%.

Sulfate Model

Calibration of the sulfate model (equation (15)) resulted in a mean k_{SO_4} of 0.52 ± 0.34 m/yr. This value is slightly higher than the value of 0.46 m/yr that we reported earlier [Baker et al., 1986b], because several lake budgets were added to the data set or modified. Magnolia Lake (Florida) had the highest k_{SO_4} (1.28 m/yr), while East Eight Mile Lake (Wisconsin) had the lowest k_{SO_4} (0.19 m/yr) (Table 2). Our mean k_{SO_4} is very close to the mean value of 0.54 m/yr recently reported by Kelly et al. [1987] for a slightly different set of lakes.

The relatively low value of mean k_{SO_4} (compared with phosphorus model coefficients of 8–16 m/yr) implies that sulfate loss is diffusion controlled. This can be demonstrated by calculating the diffusion velocity (v_p) [Lerman, 1979]:

$$v_p = D_c/L \qquad (18)$$

where D_c is the effective diffusion coefficient in centimeters squared per second and L is the length to reaction zone in centimeters. For the high-porosity gyttja that is common in many soft water lakes, Rudd et al. [1986a] showed that $D_c \approx 5 \times 10^{-5}$ cm²/s. The depth to minimum $[SO_4^{2-}]$ (approximately equal to L in (18)) for pore water profiles from a wide variety of lakes is 2–7 cm [Rudd et al., 1986a; Perry, 1987; Baker et al., 1986a; Brezonik et al., 1987]. This distance does not change appreciably with acidification, and it also appears to be somewhat less variable within a given lake (L. A. Sherman et al., manuscript in preparation, 1987). Substituting these values into (18) gives $v_p = 0.2$–0.7 m/yr, which is similar in magnitude to k_{SO_4} calculated from lake budgets.

As seen in Figure 1a, there is a good fit between modeled retention and measured retention. A linear regression of predicted versus measured retention gave the relationship

$$R_p = 7.9 + 0.9R_m \qquad (19)$$

($r^2 = 0.83$, $n = 11$, and $p < 0.001$).

When all lakes are included (Figure 1b), the regression equation of predicted versus measured areal sulfate sinks using all lakes ($n = 14$) is

$$F_p = 5.8 + 1.15F_m \qquad (20)$$

($r^2 = 0.88$, $n = 14$, and $p < 0.001$). This regression is not statistically meaningful, however, because it is driven largely by one lake (223), which has much a much higher sulfate sink than

any other lake (because it was experimentally acidified with H_2SO_4). Furthermore, calculated areal fluxes for lakes with low retention values are likely to be unreliable because internal sinks (input minus output) are small relative to inputs or outputs; small errors in the input/output (I/O) terms can therefore lead to large errors in calculated areal fluxes. If lake 223 and the two lakes with sulfate retention <5% of input
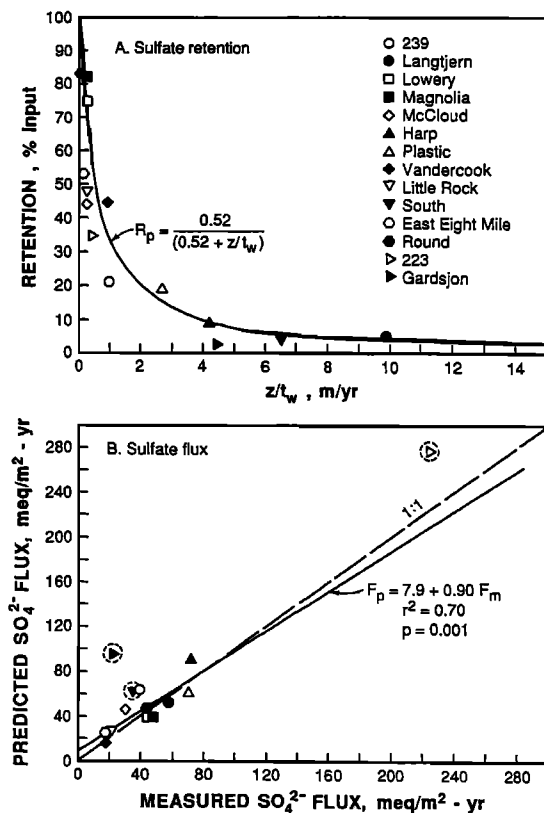

Fig. 1. (a) Sulfate retention as a function of water residence time. Line shows predicted R_{SO_4} from model. The regression equation between measured and predicted retention is $R_p = 7.9 + 0.9R_m$ ($r^2 = 0.83$ and $p < 0.001$). (b) Predicted versus measured sulfate fluxes for calibration data set.

(Gardsjon and South) are excluded from the data set, the resulting regression is

$$F_p = 7.9 + 0.90F_m \qquad (21)$$

($r^2 = 0.70$, $n = 11$, and $p = 0.0014$).

Nitrate Model

For the nine lakes in the data set with nitrate budgets, mean k_{NO_3} was 1.33 ± 0.94 yr^{-1} (Table 2). The model predicts retention as a function of t_w reasonably well (Figure 2a); the relationship between measured and predicted nitrate retention is described by the relationship

$$R_p = 27 + 0.61R_m \qquad (22)$$

($r^2 = 0.63$ and $p = 0.011$).

The relatively low r^2 occurs in part because several lakes (Lowery, Magnolia, and Vandercook) had nitrate retention values > 100%, indicating measurement errors or deviations from the steady state assumption. Nitrate retention predicted by the model of Kelly et al. [1987] also is shown in Figure 2a. In order to plot nitrate retention as a function of t_w with their model, we assumed a mean depth of 5 m (approximately the mean depth of our study lakes) and used their calibrated model constant of 9.2 m/yr (with the same approach, we computed a mean k_{NO_3} of 6.8 m/yr for our data set). As shown in Figure 2a, predictions using the two approaches are similar. For example, at $t_w = 1$ year, our model predicts 56% retention and the Kelly et al. model predicts 64% retention; at

$t_w = 5$ years, predicted retentions are 87% and 90%, respectively.

Regression analysis shows that the nitrate model predicts sinks with reasonable accuracy (Figure 2b); most lakes except Harp fall very close to the 1:1 line. It is not obvious why the predicted nitrate sink in Harp Lake is 40% higher than the measured value, particularly since this lake is near and morphometrically similar to Plastic Lake, for which the predicted nitrate sink is nearly identical to the measured sink (Figure 2b).

Ammonium Model

The ammonium model was calibrated using data from seven lakes for which suitable data were available; mean k_{NH_4} was 1.5 ± 1.2 yr^{-1}. Modeled ammonium retention is close to measured retention (Figure 3a). The relationship between predicted and measured ammonium retention was

$$R_p = 52.2 + 0.39R_m \qquad (23)$$

($r^2 = 0.14$, $n = 7$, and $p = 0.35$). The regression relationship is not statistically significant, but this does not indicate that the model is inappropriate. The poor regression relationship occurs because all of the lakes that have ammonium budgets have long residence times and high measured retention values. Thus the lack of statistical significance in the regression relationship occurs primarily because there is very little spread among data points. The model correctly predicts retention values that are close to measured values. The average difference between measured and predicted ammonium retention
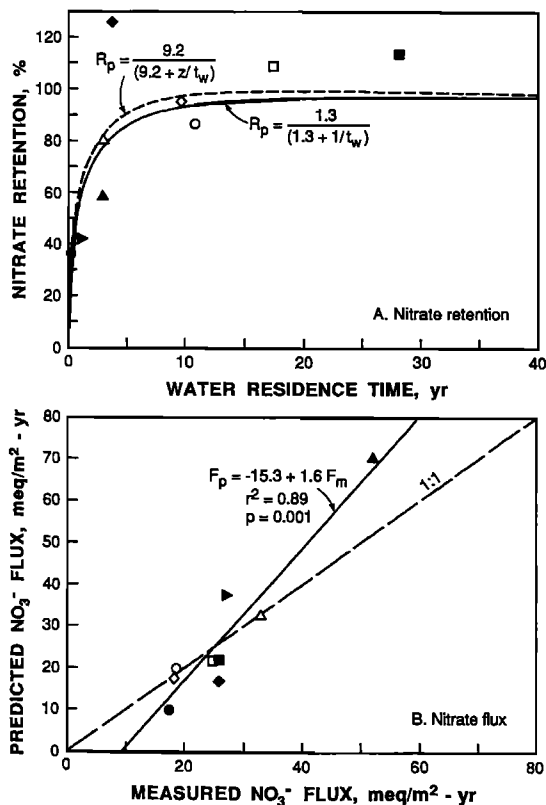

Fig. 2. (a) Nitrate retention as a function of water residence time. Lines show predicted R_{NO_3} from this model and from model of Kelly et al. [1987]; note that models predict similar retention values. The regression equation between measured and predicted retention for our model is $R_p = 27 + 0.61R_m$ ($r^2 = 0.63$ and $p = 0.011$). (b) Predicted versus measured nitrate fluxes for calibration lakes.
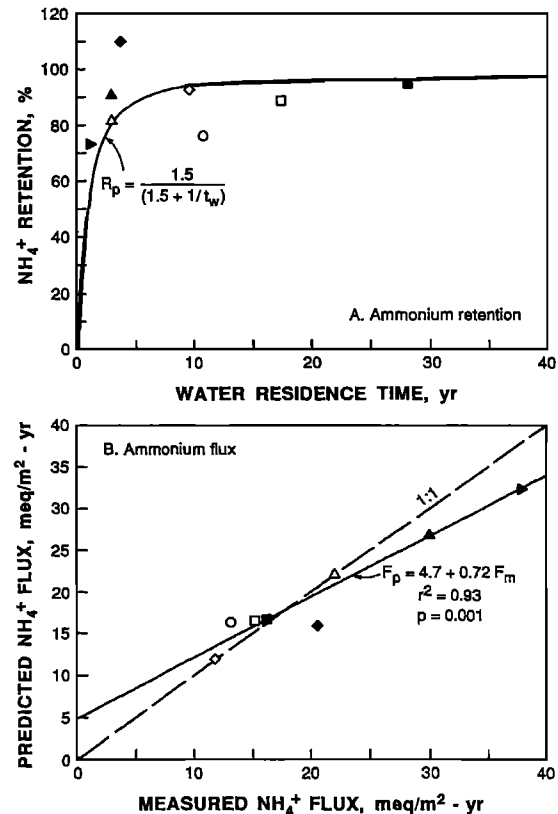
Fig. 3. (a) Ammonium retention as a function of water residence time. Line shows predicted R_{NH_4}. The regression equation between measured and predicted NH$_4^+$ retention is $R_p = 52 + 0.39R_m$ ($r^2 = 0.14$ and $p = 0.35$). The low r^2 and p levels occur in part because all retention values are > 70%. (b) Predicted versus measured ammonium fluxes for calibration lakes.

TABLE 3. Predicted Versus Measured Alkalinity for Eight Soft Water Lakes

| Lake | z, m | t_w, years | L_{SO_4} | L_{NO_3} | L_{NH_4} | L_{alk} | Model Predictions | | Measured Values | | |
							IAG	[alk]	IAG Gran Budget	IAG $C_b - C_a$ Budget	[alk]
Gardsjon	4.8	1.1	897	64	52	−205	92	−26	···	64	−21
Lake 239	10.5	10.8	182	22	52	275	31	315	39	25	378
Harp	12.3	2.9	820	89	33	23	125	35	188	99	64
Plastic	8.0	3.0	372	41	27	−155	66	−33	166	80	3
McCloud	2.5	9.6	69	19	13	−39	51	45	33	25	−32
Magnolia	7.8	28.1	59	23	17	−45	43	−8	44	−6	7
Lowery	4.9	17.4	59	23	17	−45	43	−8	46	−3	6
Vandercook	3.5	3.7	46	21	19	−11	16	6	33	−12	20

All loadings and IAG in meq/(m² yr); alkalinity in microequivalents per liter.

was 2%, and the maximum difference was 25%. The model shows that ammonium retention increases from 43% at t_w = 0.5 year, to 94% at t_w = 10 years.

Predicted and measured in-lake ammonium fluxes agree very well (Figure 3b). The slope of the regression line is 0.72, somewhat less than the expected slope of 1.0, but the r^2 value is high (0.93) and the relationship is highly significant ($p = 0.001$).

MODEL VERIFICATION

The calibrated model was used to predict alkalinity in eight lakes that had complete budgets for sulfate, nitrate, and ammonium (Gardsjon, lake 239, Harp, Plastic, McCloud, Lowery, Magnolia, and Vandercook) (Table 3). All of these lakes except Gardsjon had measured alkalinity budgets. For Gardsjon, alkalinity production was estimated from the balance of strong acids (C_a) and strong bases (C_b) retained within the lake:

$$\Delta alk \approx C_b - C_a = \Delta Ca^{2+} + \Delta Mg^{2+} + \Delta K^+ + \Delta Na^+$$
$$+ \Delta NH_4^+ - \Delta SO_4^{2-} - \Delta NO_3^- - \Delta Cl^- \quad (24)$$

$C_b - C_a$ budgets were also available for lake 239 and Harp, Plastic, and Vandercook lakes. Estimates of in-lake cation sinks are uncertain for the Florida seepage lakes, and alkalinity production could not be estimated by this method.

In general, model predictions of IAG agree well with measured IAG determined by either measured alkalinity budgets or by "$C_b - C_a$" budgets (Table 3 and Figure 4a). The exceptions are Harp and Plastic lakes, in which IAG rates determined by Gran alkalinity budget are higher than predicted from the model. There are at least two possible explanations for these discrepancies. First, the steady state assumption may be violated, since the chemical status of both lakes is changing in response to decreasing acid deposition [P. J. Dillon, personal communication, 1987]. A second possibility is that reactions not included in the model, such as retention of organic anions, are responsible for additional alkalinity production. Predicted IAG for these two lakes agree reasonably well with alkalinity production calculated from (24), indicating that the model is correct with respect to predictions of alkalinity production and consumption by strong acid and base reactions.

Model predictions of lake water alkalinity also agree reasonably well with measured values (Figure 4b). To illustrate the importance of IAG, lake water alkalinity also was calculated by setting IAG = 0 (e.g., no in-lake alkalinity production). For lakes with relatively short residence times, IAG has a fairly minor effect on lake water alkalinity. For example,

predicted alkalinity for Gardsjon (t_w = 1.1 year) was −26 μeq/L, but in the absence of IAG, alkalinity would be −47 μeq/L. By contrast, the model predicts an alkalinity of −8 μeq/L for Magnolia Lake, Florida (t_w = 28 years, measured alkalinity = 7 μeq/L), but in the absence of IAG its alkalinity would be −163 μeq/L. These results illustrate the importance of including internal alkalinity generation in acidification models for lakes with long residence times.

SENSITIVITY ANALYSIS

A sensitivity analysis was conducted to determine the effect of changing t_w and model coefficients on predicted alkalinity, $[alk]_p$. The model was used to predict alkalinity in a hypothetical lake with $z = 5$ m, $t_w = 10$ years, no groundwater inputs, and atmospheric inputs typical of northern Minnesota. As shown in Table 4, $[alk]_p$ was 13 μeq/L for initial conditions. Doubling t_w increased $[alk]_p$ to 45 μeq/L; decreasing t_w by 50% decreased $[alk]_p$ to 1 μeq/L. Model predictions thus are sensitive to t_w, and this has two important implications. First, it illustrates the need to know t_w accurately. This is a significant problem in seepage lakes, for which estimated t_w may have an uncertainty of ±50%. Second, because the outflow (hence t_w) of seepage lakes is highly dependent upon the balance between precipitation and evaporation, t_w may change in response to short-term (e.g., 5-year) climatic variations. This raises the possibility that temporal trends in alkalinity of seepage lakes over such time periods may reflect climatic changes rather than a long-term response to anthropogenic acidification.

Changing k_{SO_4} also has a significant effect on $[alk]_p$. A 50% decrease in k_{SO_4} (to 0.26 m/yr) decreased $[alk]_p$ to 2 μeq/L, and doubling k_{SO_4} (to 1.04 m/yr) increased $[alk]_p$ to 22 μeq/L. Model predictions are insensitive to changes in k_{NO_3} or K_{NH_4}. Doubling k_{NO_3} (to 2.6 yr⁻¹) increased $[alk]_p$ by <1 μeq/L, while halving k_{NO_3} decreased $[alk]p$ by 2 μeq/L (to 11 μeq/L). Doubling k_{NH_4} decreased $[alk]_p$ to 12 μeq/L, while halving k_{NH_4} increased $[alk]_p$ to 14 μeq/L. The insensitivity of model predictions to changes in values of k_{NO_3} and k_{NH_4} suggests that refinement of these coefficients by acquisition of new ion budget data is unlikely to alter predictions substantially.

APPLICATION

Effect of H⁺ Loading on Steady State Alkalinity

To show how $[alk]_p$ changes in response to acid inputs, the atmospheric acid inputs were changed by increasing or decreasing inputs of H_2SO_4 or HNO_3 to the lake described
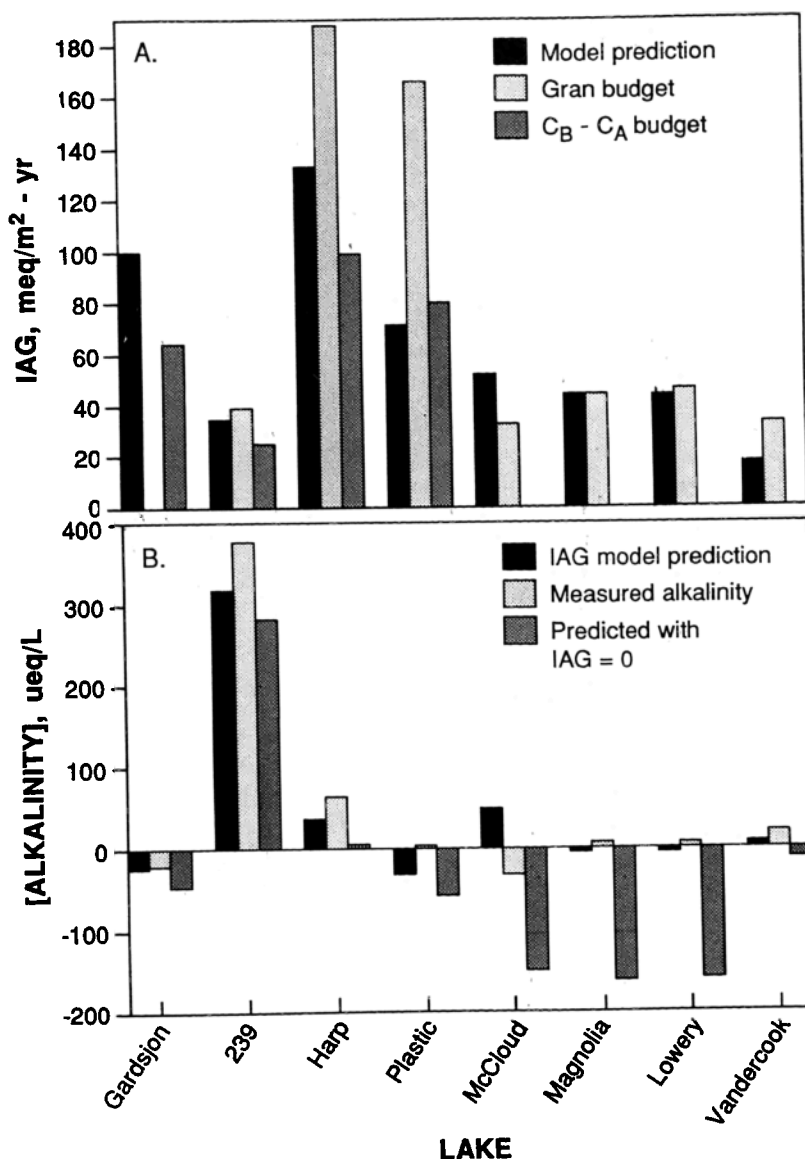
Fig. 4. (a) Predicted and measured IAG for eight study lakes. Model predictions are based on model using calibrated values of k_{SO_4}, k_{NO_3}, and k_{NH_4} and measured inputs of sulfate, nitrate, and ammonium. Measured alkalinity budgets are based on Gran titration budgets, when available, and $C_b - C_a$ budgets. (b) Predicted and measured lake water alkalinity. Predictions from model generally agree with measured lake water alkalinity. By contrast, predicted alkalinity in absence of IAG is much lower than measured or predicted values for lakes, particularly for lakes with long t_w.

above. For example, doubling the H$^+$ input with H$_2$SO$_4$ increased H$^+$ input from 8 to 16 meq/(m^2 yr) and SO$_4^{2-}$ input from 30 to 38 meq/(m^2 yr). For comparison, alkalinity response also was calculated for constant IAG (i.e., zero-order response) calculated from initial conditions and for IAG = 0 (i.e., no internal alkalinity generation).

If the H$^+$ input were decreased by 50% (H$_2$SO$_4$ input reduced by 4 meq/(m^2 yr)), lake water alkalinity would increase to 16 μeq/L, compared to 13 μeq/L at the current loading. If the H$^+$ input were increased by a factor of 4 with H$_2$SO$_4$, lake water alkalinity would decrease to −11 μeq/L (Figure 5). In contrast, if IAG is held constant (at 14.2 meq/(m^2 yr), the predicted IAG at current loadings), the change in alkalinity over this range of loadings is nearly twice as large (20 μeq/L at 50% of current H$^+$ loading and −36 μeq/L at 4 times current H$^+$ loading). Thus our IAG model predicts less change in [alk]$_p$ in response to changes in H$_2$SO$_4$ loading than does the zero-order IAG model.

The effect of changing HNO$_3$ inputs on lake water alkalinity is minimal. With a 50% reduction of H$^+$ input (HNO$_3$ input reduced by 4 meq/(m^2 yr)), predicted alkalinity increases by <1 μeq/L; conversely, [alk]$_p$ decreases by only 4 μeq/L (to 9 μeq/L) when H$^+$ inputs are quadrupled using HNO$_3$ (Figure 5). This prediction agrees with the conclusion of Schindler et al., [1985] that HNO$_3$ is an inefficient acidifying agent.

In the absence of IAG, lake water alkalinity would change from −8 μeq/L (at 50% of current H$^+$ loading) to −64 μeq/L (at four times H$^+$ loading) (Figure 5), and the response is the same with either H$_2$SO$_4$ or HNO$_3$. Comparison of this prediction with that of the IAG model clearly shows the importance of in-lake alkalinity regulation in lakes with long water residence times.

Although the above example assumes no groundwater input, there is undoubtedly some groundwater input to all seepage lakes. Since groundwater is generally well buffered, small inputs may contribute substantially to lake water alka-

TABLE 4.   Sensitivity Analysis for IAG Model

	t_w, years	k_{SO_4}, m/yr	k_{NO_3}, yr^{-1}	k_{NH_4}, yr^{-1}	[alk], μeq/L
Initial conditions	10	0.52	1.3	1.5	12.5
k_{SO_4} = 2 × calibration	10	1.04	1.3	1.5	22.4
k_{SO_4} = 0.5 × calibration	10	0.26	1.3	1.5	2.4
k_{NO_3} = 2 × calibration	10	0.52	2.6	1.5	13.4
k_{NO_3} = 0.5 × calibration	10	0.52	0.65	1.5	10.7
k_{NH_4} = 2 × calibration	10	0.52	1.3	3.0	11.6
k_{NH_4} = 0.5 × calibration	10	0.52	1.3	0.75	14.1
t_w = 0.5 × initial	5	0.52	1.3	1.5	1.2
t_w = 2 × initial	20	0.52	1.3	1.5	44.9

Initial conditions: z = 5 m, t_w = 10 years, L_{SO_4} = 30 meq/(m^2 yr), L_{NO_3} = 14 meq/(m^2 yr), L_{NH_4} = 15 meq/(m^2 yr), L_{H+} = 8 meq/(m^2 yr). Model constants equal calibrated values.

linity. To estimate the relative importance of groundwater inputs versus IAG on lake water alkalinity, we calculated the effect of groundwater inputs amounting to 1, 2.5, 5, and 10% of total water input to our seepage lake, assuming that the groundwater alkalinity is 400 μeq/L (based on the work by Lin et al. [1987] and our unpublished data for Little Rock Lake, Wisconsin) (Table 5). If groundwater input is 1% of total water input, IAG contributes 85% of the total alkalinity input, and [alk]$_p$ is 18 μeq/L (compared with 13 μeq/L for no groundwater input). With a groundwater input of 2.5%, IAG is 69% of alkalinity input, and [alk]$_p$ = 26 μeq/L. At 10% groundwater input, IAG contributes 36% of the total lake water alkalinity (now 65 μeq/L). These calculations show that for the given hydrologic conditions and atmospheric inputs, IAG is an important alkalinity input in seepage lakes receiving approximately 10% or less of their total water input from subsurface seepage.

Rate of Recovery

Recovery from decreased H$_2$SO$_4$ loading for the same lake was modeled using a nonsteady state solution (Figure 6). Recovery is 50% complete in 3.5 years and 90% complete in 12 years. In contrast, if sulfate were conservative and recovery occurred solely by replenishment of water, a 50% response
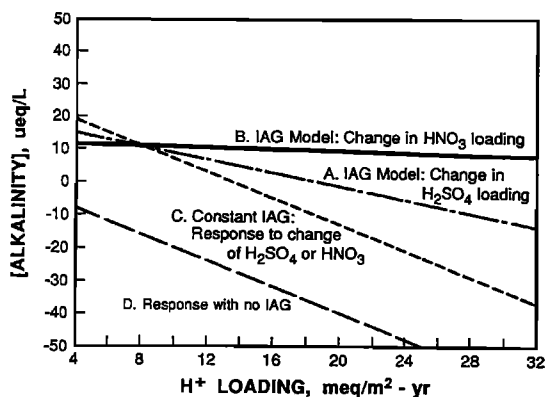

Fig. 6.   Predicted recovery from acid inputs in same lake as Figure 5. Recovery (%) = ([alk]$_{ss}$ − [alk]$_t$)100/([alk]$_{ss}$ − [alk]$_i$), where [alk]$_{ss}$ is postreduction steady state value, [alk]$_i$ is prereduction steady state value, and [alk]$_t$ is [alk] at time t. Curve A is the response to reduction in H$_2$SO$_4$ inputs, and curve B is the response to reduction in HNO$_3$ loading. Note that 50% recovery with reduced H$_2$SO$_4$ input occurs in 3.5 years; 50% recovery with reduced HNO$_3$ occurs in <0.5 years.

would take 7 years and a 90% response would occur in 23 years. Recovery from a decrease in HNO$_3$ inputs occurs much more rapidly: 50% recovery would occur in <0.5 years and 90% recovery would occur in <2 years. The rapid recovery from HNO$_3$ inputs again reflects the efficiency with which this nutrient is retained in oligotrophic systems.

DISCUSSION

The IAG model has been calibrated for three ions (sulfate, nitrate, and ammonium), but other internal processes also may generate alkalinity. In-lake production or consumption of cations also may be involved in alkalinity regulation, but this component of the model could not be calibrated, because there are few lakes with accurate cation budgets and there is little relationship between lake characteristics and cation production in those for which budgets are available.

Further development of a cation component would be facilitated by improved understanding of in-lake cation cycling. As noted above, mineral weathering of sediments may contribute cations to the overlying water, and budgets for lakes 223 and 239 show that in-lake cation sources may generate a small but significant portion of internally generated alkalinity [Cook et al., 1986; Schindler et al., 1986]. Enclosure studies also show that cation production is a significant component of alkalinity production in short-term experiments [Perry, 1987]. Conversely, some evidence suggests that seston deposition may result in in-lake sinks in some groundwater recharge lakes [Baker et al., 1987; LAB et al., 1987]. Available evidence suggests that the net source or sink of major cations (Ca^{2+}, Mg^{2+}, K$^+$, and Na$^+$) accounts for <25% of total IAG. However, neither process is understood well enough to allow more elaborate model development.

Allochthonous inputs of organic acids also may undergo in-lake reactions that generate alkalinity, but these reactions also are not included in this model. Two processes probably contribute to these sinks: (1) photodecomposition of organic acids and (2) chemical precipitation of humic acids. Both reactions produce alkalinity, but their quantitative significance has been determined for only a few systems. Nevertheless, we postulate that in-lake losses of organic acids contribute to alkalinity production in colored lakes.

Fig. 5.   Predicted alkalinity in lake with z = 5 m and t_w = 10 years. Initial loadings: L_{H+} = 8 meq/(m^2 yr); L_{SO_4} = 30 meq/(m^2 yr); L_{NO_3} = 14 meq/(m^2 yr); L_{NH_4} = 15 meq/(m^2 yr) (loadings are wet deposition from Marcell National Atmospheric Deposition Program site). Groundwater inputs were assumed negligible. H$^+$ loading was changed by adding or subtracting H$_2$SO$_4$ or HNO$_3$; sulfate and nitrate loadings were changed concomitantly. Line A is the response to changes in H$_2$SO$_4$ inputs; B, the response to changes in HNO$_3$ inputs; C, the response from holding IAG constant at predicted initial value (e.g., zero-order response); and D, the response if IAG = 0 (e.g., no internal alkalinity generation).
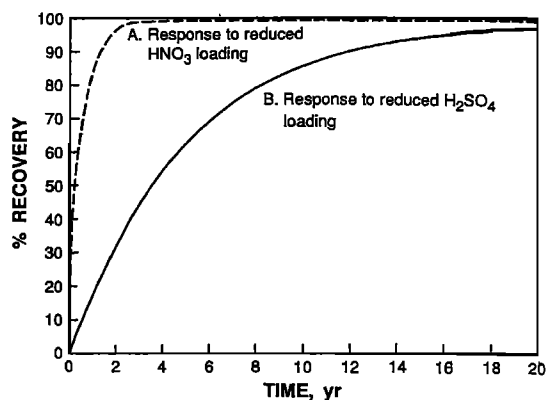
TABLE 5. Relative Contribution of Groundwater Inputs and IAG

Groundwater Input, %	Alkalinity Input, meq/(m² yr)				$[alk]_p$, $\mu eq/L$	Percent of Alkalinity From IAG
	Atmosphere	Groundwater	IAG	Total		
1	−8	2.6	14.4	17.0	18	85
2.5	−8	6.5	14.4	20.9	26	69
5	−8	13.0	14.4	17.4	39	53
10	−8	26.0	14.4	34.4	65	36

Calculations assume $z = 5$ m and $t_w = 10$ years; loadings as in Table 3. To calculate groundwater input, we assume precipitation is 65 cm/yr and groundwater [alk] = 400 $\mu eq/L$.

Finally, the IAG model predicts average lake water alkalinity and should not be used to estimate the effects of short-term acidification processes, such as runoff during snowmelt. Modeling at this level requires the use of more complicated models.

Despite these limitations the model presented here predicts the magnitude of IAG reasonably well, implying that it accounts for the majority of IAG processes. Further, it is encouraging that the model is robust with respect to modest changes in coefficients. Because it is simple in structure and has modest data requirements, the IAG model is well suited for regional application.

An important characteristic of this model is that it recognizes the homeostatic nature of IAG. Thus if inputs of H_2SO_4 increase, IAG increases because sulfate reduction increases. Conversely, if H_2SO_4 inputs decrease, IAG decreases. Changes in HNO_3 inputs are even better buffered, because NO_3^- is more efficiently retained in lakes than is SO_4^{2-}. As shown in the above example, lake water alkalinity changes far less when IAG reactions are modeled as first-order processes than when they are modeled as a zero-order process.

The model also shows that IAG becomes most important in lakes with long residence times (> 5 years) and that inclusion of IAG is essential to predict lake water alkalinity correctly in these lakes. For lakes with much shorter residence times (< 1 year), IAG has little effect on lake water alkalinity.

In order to make predictions with this model, knowledge of all inputs (atmospheric, groundwater, stream) to the lake is required. For calibration and testing we used lakes for which these inputs were known. However, for application the IAG model can be coupled with models that predict terrestrial alkalinity outputs. The merger of terrestrial and in-lake models will improve our ability to predict lake water alkalinity as a function of acid inputs for lakes of widely varying water residence times.

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L. A. Baker and P. L. Brezonik, Department of Civil and Mineral Engineering, University of Minnesota, 122 Civil and Mineral Engineering Building, 500 Pillsbury Drive, SE, Minneapolis, MN 55455.