LAKE ACIDIFICATION MODEL: PRACTICAL TOOL

By Wu-Seng Lung,[1] A. M. ASCE

ABSTRACT: A two-layer time-variable model is developed to quantify seasonal variations of pH and alkalinity levels in acidic lakes. The model incorporates the $CO_2/HCO_3^-/CO_3^-$ equilibria with internal sources and sinks of alkalinity and acidity in the water column. External alkalinity and CO_2 acidity loadings are also incorporated. The modeling framework is applied to the Bickford Reservoir in Massachusetts and to Woods Lake and Panther Lake in Adirondack Park, New York. In general, in-lake alkalinity generation by reduction processes in the Bickford Reservoir during the summer months is simulated by the model. The observed response to snowpack release in Woods Lake and Panther Lake during the spring months is also reproduced by the model. All three model applications are efficiently run on a personal computer system.

INTRODUCTION AND PURPOSE

Many lakes in northeastern North America, particularly in upstate New York, New England, and Canada, are reported to be experiencing acidification (Henriksen 1979; Kramer and Tessier 1981; Schofield 1979). One of the adverse impacts of acidification on lake water is the disappearance of fish (e.g., in Adirondack lakes of New York). In addition, a reduction of the pH of a water supply impoundment will increase the corrosivity of the water and will in turn increase the solubility of metals such as copper, iron, lead, and zinc, posing potential public health problems (Weber and Stumm 1963).

Extensive research on acid precipitation, including its effects on lakes and impoundments, has been underway for several years. In view of the potential effects, it is important to quantify lake acidification processes and to establish a cause-and-effect relationship between acid input and pH and alkalinity changes in the lakes.

The purpose of this paper is to present a relatively simple modeling framework. The modeling framework is based upon the well-known carbon dioxide-bicarbonate-carbonate equilibria in natural waters. In addition, production and consumption of alkalinity and acidity through biologically mediated processes are grouped as internal sources and sinks of alkalinity and acidity in the modeling framework. Further, mass transport including inflow, outflow, and vertical exchange in the water column is also incorporated. A unified procedure of analysis to apply the modeling framework to lakes and impoundment is presented. Finally, the results from model applications to three acidic lakes are summarized to demonstrate the validity of the modeling framework.

RATIONALE OF PROPOSED MODEL

A brief review of lake acidification models is presented to put the rationale of this model development into perspective. In general, lake aci-

dification models fall into two categories. First, simplified, empirical models have been developed using historical lake chemistry data. These models are often used to identify acidified lakes and to evaluate the extent of acidification. In a recent review of simplified lake acidification models, Lung (1984) summarized and reviewed a few of these empirical models. Although these simplified models are easy to use, they provide no analysis capability beyond the fact that many surface waters can be positioned on the same graph showing one water quality parameter versus another. Without additional water quality information, their predictive capability is highly limited (Lung 1984). If significant decisions are to be made as to the acidification control (e.g., seasonal liming), more quantitative analysis is required.

Second, quantitative models that incorporate interactions between the watershed and lake water have been developed. A recent modeling study sponsored by the Electric Power Research Institute (EPRI) has developed a comprehensive numerical model ILWAS (Gherini, et al. 1984) of this type. The ILWAS model includes and formulates a large number of factors such as rainwater composition, atmospheric concentrations of acidic and alkaline species, efficiency of hydrogen ion removal by specific vegetation types, soil and groundwater chemistry, weathering rates of rocks and minerals, buffering capacity of soils, size of drainage areas, volumes of water bodies, transport/mixing rates in the lake, and vertical diffusion of mass. A five-year data collection program was implemented at three lakes in New York's Adirondack Park to support the modeling effort. As a result, a very comprehensive data base is required to apply the ILWAS model, which simulates over 40 chemical constituents in a lake.

The simplified and comprehensive models are the extremes of complexity in modeling lake acidification. There is an urgent need for modeling frameworks in which degree of complexity in terms of prediction capacity, data requirement, model accuracy, and model limitations lies somewhere between those two extremes, i.e., a model capable of calculating lake pH and alkalinity with a modest data demand. Such a model may be used in assisting lake managers to develop a sound liming schedule for controlling acidification.

MODEL DEVELOPMENT

The model presented in this paper focuses on the lake water column. Input from the watershed is incorporated as input to the lake proper. Such an approach is not intended to discount the importance of the watershed. Rather, the simplification would reduce the number of model processes and parameters to be simulated to a manageable level. Therefore, the modeling framework may be applied to other lakes with a relatively small data base compared to the data base required by the ILWAS model.

Model Variables.—The primary model variables are alkalinity and carbon dioxide acidity. Alkalinity [or acid neutralizing capacity (ANC)] is selected because it is a conservative parameter and can therefore be used directly in mass balance equations. That is, when equal volumes of two waters are mixed, the resulting alkalinity is just the average of the alkalinities of the two waters (Gherini, et al. 1984). Carbon dioxide

(CO_2) acidity is also selected because, for most natural waters with low aluminum and organic acid levels, the pH values can be readily calculated from the $CO_2/HCO_3^-/CO_3^=$ equilibria without serious errors once the alkalinity and CO_2 acidity levels are quantified. In very low alkalinity or low pH (5.5) water, however, the concentration of other H^+-ion acceptors such as organic acid and monomeric aluminum becomes large relative to the total concentration of HCO_3^-, $CO_3^=$, and OH^- and may represent a significant portion of the total ANC (Gherini, et al. 1984). Additional equilibrium equations for organic acid and aluminum species are therefore required to calculate the pH levels. In this study, the organic acid and aluminum levels in the Bickford Reservoir in Massachusetts (Eshelman and Hemond 1985) and Panther Lake (Schofield 1984) in the Adirondacks of New York are reported insignificantly low compared with the total alkalinity levels. Thus, the $CO_2/HCO_3^-/CO_3^=$ equilibria may be employed to calculate reasonably accurate pH levels in these lakes (Small and Sutton 1986).

Model Segmentation.—The water column is sliced into two layers (referred to as the epilimnion and hypolimnion). Alkalinity stratification in the water column can be approximated by this two-layer structure. Horizontal segments may be included in the modeling framework if warranted by observed data.

Mass Transport.—External mass transport includes watershed input to the lake, which is represented by tributary input. Other external input includes acid deposition on the lake surface as well as snowpack releases during the spring months. Output through lake outlet(s) is also included and is only from the epilimnion. In many lakes, groundwater seepage or infiltration may be significant, and the model allows such external interchanges. Mass transport within the water column is characterized by advection and dispersion in the vertical direction. The two-layer transport pattern developed for lakes is shown in Fig. 1.
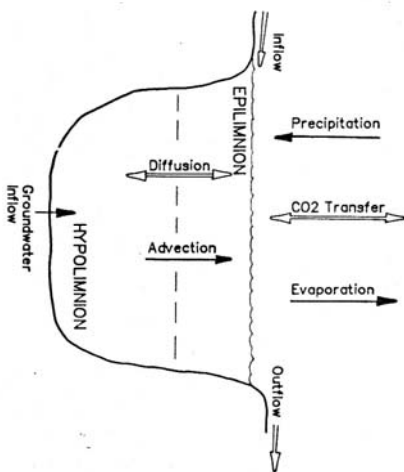

FIG. 1.—Two-Layer Lake Transport Pattern

Another mass transport process is CO_2 transfer across the air-water interface and can be formulated as follows:

$$CO_2 \text{ mass rate} = K_L([CO_{2(s)}] - [CO_2]_l)A \quad \ldots\ldots\ldots (1)$$

where K_L = CO_2 transfer coefficient, m/day or ft/day, $[CO_{2(s)}]$ = saturation concentration of dissolved CO_2 in natural water, $[CO_2]_l$ = average concentration of dissolved but unionized CO_2 in the epilimnion, and A = lake surface area

In Eq. 1, $[CO_2]_l$ may be approximated by $[CO_2\ Acy]_l - [H^+]_l$, according to Weber and Stumm (1963), where $[CO_2\ Acy]_l$ = concentration CO_2 acidity in the epilimnion and $[H^+]_l$ = hydrogen ion concentration in the epilimnion. K_L in Eq. 1 depends highly upon wind action on the lake surface. Numerous experimental investigations and analytical studies of K_L for dissolved oxygen have been reported (Holley 1977; Yu 1977). In this study, an empirical formula developed by Banks and Herrara (1977) for the dissolved oxygen transfer coefficient was used:

$$K_L(\text{m/day}) = 0.728W^{1/2} - 0.317W + 0.0371W^2 \quad \ldots\ldots\ldots (2)$$

where W = windspeed over the surface in m/s. The transfer coefficient for dissolved oxygen is then converted to the transfer coefficient for CO_2, using an expression by Shen (1982). K_L is dependent upon temperature in the following fashion:

$$K_L(\text{at temp } T) = K_L(\text{at } 20° \text{ C})\theta^{T-20} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where T = temperature (°C) and θ = 1.005–1.030 with a commonly used value of 1.024 (Holley 1977). The empirical formula proposed by Kelly, et al. (1974) is used in the model to determine the saturated CO_2 levels in the epilimnion:

$$[CO_{2(s)}] = 10^{[2,385.73/(T+273)-17.5184+0.015164(T+273)]} \quad \ldots\ldots\ldots\ldots (4)$$

where $[CO_{2(s)}]$ = saturated CO_2 concentration in mol/L. Eqs. 1–4 are incorporated into the model, and therefore the calculation of K_L (for CO_2) requires the windspeed and temperature data.

Processes Affecting Alkalinity and pH in Lakes.—$CO_2/HCO_3^-/CO_3^=$ is not the only chemical equilibria operative in many lakes or impoundments affecting the alkalinity and CO_2 acidity levels. Other processes, primarily of a biochemical nature, may also affect the lake alkalinity and CO_2 acidity levels. For example, hypolimnetic sulfate reduction during a period of anoxia tends to increase the alkalinity concentration by decreasing the total concentration of nonprotolytic anions (i.e., $SO_4^=$). Schindler (1980) reported that in Lake 223 of Experimental Lakes Area in Canada, over 60% of the acid neutralization was accounted for by sulfate reduction and denitrification. In some lakes, denitrification is a source of alkalinity because it generates N_2O and N_2, which are volatile gases and could be lost from the water system, thereby increasing alkalinity. In addition, ammonification (i.e., ammonium production by sediments) and nitrate uptake by algae generate alkalinity. On the other hand, sulfide oxidation, nitrification, and ammonia uptake by algae decrease alkalinity. Further, algal photosynthesis reduces CO_2 levels and increases pH levels while algal respiration increases CO_2 levels and de-

TABLE 1.—Kinetics Formulations in Lake Acidification Model

Model layer (1)	Alkalinity sink (mass/time) (2)	CO₂ acidity sink (mass/time) (3)	Alkalinity source (mass/time) (4)	CO₂ acidity source (mass/time) (5)
Epilimnion	Ammonia uptake/nitrification/sulfide oxidation $= \mu_2[Alk]_1V_1$	Photosynthesis $= \mu_2[CO_2\ Acy]_1V_1$	—	—
Hypolimnion	—	—	Ammonification/denitrification/sulfate reduction $= \mu_3[Alk]_2V_2$	Respiration $= \mu_4[CO_2\ Acy]_2V_2$

Note: μ_1, μ_2, μ_3, and μ_4 are first-order reaction coefficients. $[\ ]_1$ and $[\ ]_2$ are concentrations in the epilimnion and hypolimnion, respectively. V_1 and V_2 are volumes of the epilimnion and hypolimnion, respectively.

creases pH levels. Weber and Stumm (1963) summarized these biochemically mediated processes affecting pH and alkalinity levels in natural waters.

In many cases there is not sufficient data to allow the quantification of the kinetics of individual processes. In this modeling framework, an approximation is made to formulate these processes in lieu of specific quantification of individual processes. That is, they are grouped into sources and sinks of alkalinity and CO_2 acidity in the epilimnion and the hypolimnion, respectively. The formulations of these reactions using first-order kinetics is summarized in Table 1. Such an empirical approach has been reported for phosphorus components in lake eutrophication modeling studies (Lung and Canale 1977; Stumm and Leckie 1970). The kinetics structure of the modeling framework is presented in Fig. 2. Note that the kinetic structure is not intended to ignore epilimnitic alkalinity generation or hypolimnitic alkalinity consumption processes. Rather, the kinetics formulation quantifies the net sources and sinks of alkalinity and CO_2 acidity in the epilimnion and hypolimnion, respectively.

Model Equations.—The governing equations in the modeling framework designed to mimic the dynamics of alkalinity and CO_2 acidity in acidified lakes are presented in Appendix I.

Carbon Dioxide/Bicarbonate/Carbonate Equilibria.—Once the alkalinity and CO_2 acidity levels in each layer are calculated, the hydrogen ion concentration is then determined from the $CO_2/HCO_3^-/CO_3^=$ equilibria based on the following equations (Kemp 1971):

$$[H^+] = \frac{K_1\left([CO_2\ Acy] - K_2 - \frac{K_w}{K_1}\right)}{[Alk] + K_1} \quad \text{if} \quad [Alk] > 0 \ldots\ldots\ldots\ldots (5)$$

$$[H^+] = \frac{-K_1}{2} + 0.5(K_1^2 + 4K_w + 4K_1[CO_2\ Acy])^{1/2} \quad \text{if} \quad [Alk] = 0 \ldots (6)$$

$$[H'] = -[Alk] \quad \text{if} \quad [Alk] < 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where $[H'] =$ hydrogen ion concentration in mol/L, $[Alk] =$ total alkalinity concentration in mol/L, $[CO_2 \, Acy] = CO_2$ acidity concentration in mol/L, $K_1 =$ first dissociation constant of carbonate equilibrium (temperature dependent), $K_2 =$ second dissociation constant of carbonate equilibrium (temperature dependent), and $K_w =$ dissociation constant of water (temperature dependent).

Computational Scheme.—The lake acidification model is implemented using a very efficient computer code WASP (water quality analysis simulation program) available from the United States Environmental Protection Agency (EPA) (DiToro, et al. 1983). Designed to serve as a general purpose code, WASP is flexible enough to provide freedom of describing kinetic processes and geophysical morphology or setting that into the framework of the model. In this study, while the lake hydrological transport processes such as inflow, outflow, advective, and diffusion flows can be readily incorporated into WASP, a kinetic subroutine is required to implement the source and sink terms of alkalinity and CO_2 acidity (Table 1). The entire computation is performed on a microcomputer system. The total turnaround time for a typical run (3 system variables, 2 segments, and over 1,200 integration steps) is about 5 minutes (including result plotting by a HP personal computer plotter) with an 8087 math coprocessor.

PROCEDURE OF ANALYSIS

The general procedure to derive the model coefficients is relatively straightforward and is summarized in the following paragraphs, which

FIG. 2.—Principle Components of Lake Acidification Model

parallel the model development in the preceding section.

Lake Inflow and Outflow.—Tributary inflows, if any, to the lake may be available from the United States Geological Survey (USGS) records for the gaging stations in the stream tributary to the lake. If the stream is not gaged (e.g., headwater streams), estimates of inflow may be approximated based on watershed characteristics (Viessman, et al. 1977). Lake inflow may also include precipitation volume, which is particularly important if the lake surface area is relatively large compared with the watershed area. Precipitation data from available climatic records or from direct measurements may be used to quantify seasonal precipitation volume. Lake outflow may also be obtained from USGS records, if available, or from direct measurements. For lakes having large surface areas compared to the watershed areas, evaporation is also relatively important. The volumetric rate of evaporation may be measured directly or estimated indirectly from a flow budget for the lake when other flow quantities have been determined. In some lakes or impoundments, groundwater inflow may be important and direct measurements should be made to gather such information. Essentially, hydrologic budgets would be made for the lake (a balanced hydrologic budget) on a time-variable basis after all the flow estimates are complete.

Chloride Input.—Chloride input is needed to develop a mass balance of this conservation substance for the lake so that the mass transport pattern in the lake may be validated. Chloride is preferred over conductivity for such an exercise because many ions contributing to conductivity are not conserved in the lake under certain environmental conditions (e.g., $SO_4^=$ reduction under anaerobic conditions). The chloride data are usually available for tributary inflows, and precipitation as chloride is one of the commonly measured parameters. The chloride loading rates for tributary input and direct deposition can be readily calculated from flows and concentrations.

Alkalinity and Acidity Input.—The same procedure used to calculate the chloride loading rate can be employed to calculate the alkalinity and acidity loading rates. In many cases, CO_2 acidity is not measured and it may be derived by subtracting alkalinity from dissolved inorganic carbon (DIC) or computed from pH and alkalinity using the $CO_2/HCO_3^-/CO_3^=$ equilibria. The accuracy of indirect derivation is governed by the presence of noncarbonate ANC species such as organic acids and aluminum.

Mass Transport Coefficients.—They consist of advective transport and dispersive transport in the vertical direction. Advective transport expressed as a flow rate may be derived from flow balances for the epilimnion and the hypolimnion, respectively. Vertical dispersive transport is calculated as the product of the vertical diffusion coefficient and the interfacial area between the epilimnion and the hypolimnion divided by the average depth of the two layers (see Appendix I). The vertical diffusion coefficient may be calculated using the flux-gradient method following the methodology developed by Jassby and Powell (1975) and Lung and Canale (1977). The flux-gradient method calculates the vertical diffusion coefficient based on the concept of heat budget using temperature profiles in the lake. Therefore, vertical measurements of the temperature over an annual cycle or over a seasonal period are required for the calculation of vertical diffusion coefficients. Usually, measurements are re-
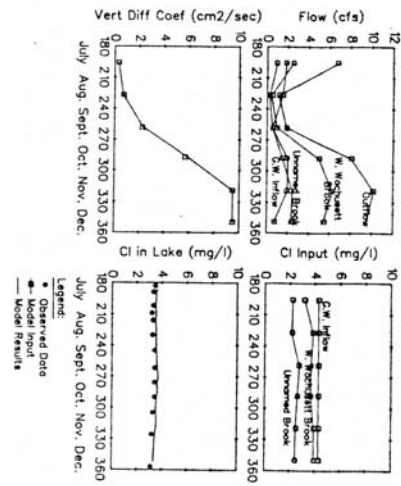
FIG. 4.—Calibration of Two-Layer Mass Transport in Bickford Reservoir

no data of CO_2 acidity are available, the model calculations for CO_2 are presented in Fig. 5 and subsequent figures for the sake of completeness.) The model calculations (i.e., for alkalinity) were found most sensitive to the variations of the kinetic coefficient μ_3 characterizing the generation of alkalinity due to reduction processes (see Fig. 5). Changes in μ_1, μ_2, and μ_4 have minimal effect on the model results. Component analyses also show that in-lake generation of alkalinity characterized by μ_3 (see Fig. 6) is responsible for the sharp rise of alkalinity levels in the hypolimnion during the summer months.

Panther Lake and Woods Lake.—The modeling framework was applied to two lakes in Adirondack Park of New York to analyze the snow-
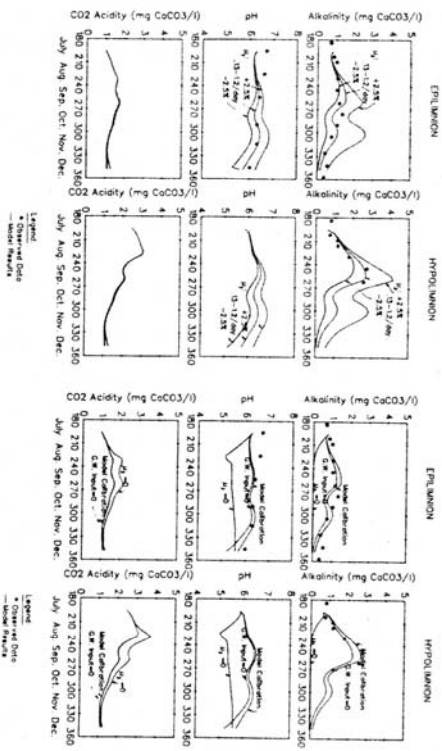
FIG. 5.—Model Calibration/Sensitivity Analysis for Bickford Reservoir
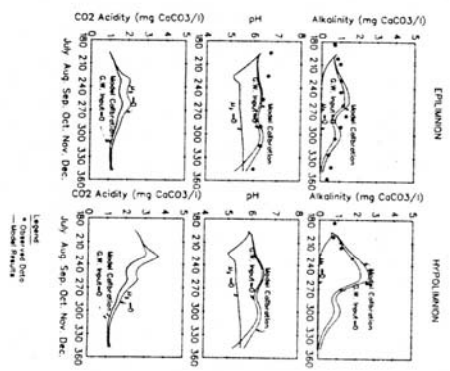
FIG. 6.—Model Component Analysis for Bickford Reservoir
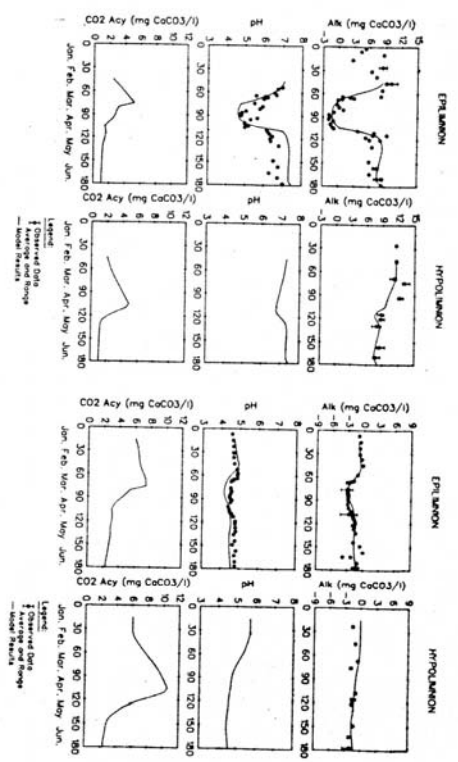
FIG. 7.—Model Calibration of Panther Lake Data, 1979
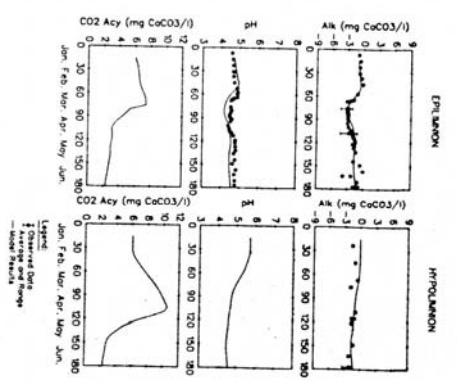
FIG. 8.—Model Calibration of Woods Lake Data, 1979

melt impact on the lake pH and alkalinity levels during the winter and spring months of 1979. The physical parameters for Panther Lake and Woods Lake are summarized in Table 2. The lakes are located only 19 miles apart and receive almost identical acid input. The data from the ILWAS study (Gherini, et al. 1984; Schofield 1984) were used to derive the model coefficient values following the procedure outlined in the preceding section. In addition, the snowmelt runoff rate was determined from the changes in the snow storage volume during February, March, and April using the data from Johannes, et al. (1981). Independent measurements of flow rates at the lake outlets supported the snowmelt period (Tetra Tech, Inc. 1983). The quantity of snowmelt runoff was significant for both lakes during this period, although the groundwater contribution was more important to Panther Lake than Woods Lake. The acid loading rates (in negative alkalinity loads) were derived from the actual loss of major ions $SO_4^=$ and NO_3^- in the snow storage (Johannes, et al. 1981). In this analysis, the snowpack release (in terms of runoff and alkalinity loading rate) was routed to the epilimnion of both lakes during the snowmelt and release period (February, March, and April). When the lakes were under ice and snow cover from December to April, no CO_2 exchange across the lake surface was allowed in the model (simply by setting K_L in Eq. 1 equal to zero). A more detailed derivation of the model parameter and coefficient values can be found in another document (Yamartino, et al. 1983).

The results of model applications to Panther Lake are summarized in Fig. 7. The model calculations match the measured alkalinity and pH levels reasonably well. During the period of ice and snow cover, biological activities affecting the change in alkalinity are probably at a minimal level, making alkalinity a more or less "conservative" tracer with

respect to the lake system (all the kinetics coefficients = 0). That is, the alkalinity dynamics in the lake simply become an input-output balance for this parameter. The lake can be viewed as a system receiving shock acid (negative alkalinity) loads during the snowmelt period followed by a recovery due to dilution from less acid water. As a matter of fact, due to small temporal and spatial variations of chloride, alkalinity is used as a tracer to calibrate the mass transport pattern.

When applying the model to Woods Lake (pH below 5), one may be concerned with the validity of calculating pH based on the $CO_2/HCO_3^-/CO_3^=$ equilibria alone without considering the alkalinity (ANC) contribution from aluminum species. A further examination of the water quality data from Woods Lake indicated that aluminum species contribute about 10% of the total alkalinity (Schofield 1984). A 10% difference in alkalinity does not always reflect the same numerical percentage difference in pH due to the nonlinear nature of the $CO_2/HCO_3^-/CO_3^=$ equilibria. The model results presented in Fig. 8 show a good-to-fair match between the model calculations and measured data for Woods Lake.

The responses of both lakes to snowmelt are somewhat different in that the changes in alkalinity and pH levels are more pronounced in Panther Lake (Fig. 7) than Woods Lake (Fig. 8). The EPRI study has attributed the different responses to the different buffering capacity provided by the watersheds (Gherini, et al. 1984). In both cases, the lake acidification modeling framework was able to simulate the trends in alkalinity and pH in the water system during the snowmelt period.

SUMMARY AND CONCLUSIONS

A modeling framework for lake acidification assessment has been developed to simulate alkalinity, CO_2 acidity, and pH levels in lakes and impoundments in a two-layer fashion. Mass transport and kinetic processes affecting the fate of acid input in the lake are incorporated. The $CO_2/HCO_3^-/CO_3^=$ equilibria are employed to calculate pH levels once the alkalinity and CO_2 acidity levels are calculated. A unified procedure of analysis was developed to derive the model parameter and coefficient values.

The modeling framework has been applied to three acidified lakes in Massachusetts and New York to test its general validity. The model results indicate that in-lake generation of alkalinity in the hypolimnion caused the increase of alkalinity levels in the Bickford Reservoir. Alkalinity increase in the hypolimnion was possibly due to ammonium production and, to a lesser degree, sulfate reduction during the summer months (Eshelman 1982). Model applications to Panther Lake and Woods Lake show that the trends in alkalinity and pH during the snowmelt period can be simulated by the model. The lakes are viewed as a water system receiving shock acid (negative alkalinity) loads that are followed by dilution from less acidic water in spring. By focusing on the lake system, the models are able to simulate seasonal dynamics of the lake chemistry in the water column with given watershed input. Thus, this modeling framework can be used together with a watershed model.

The assumption of using the $CO_2/HCO_3^-/CO_3^=$ alone to calculate pH from alkalinity and CO_2 acidity in the model limits the application of the

modeling framework to lakes with small contributions of ANC from organic acid and aluminum species. However, it is this assumption that decouples the linkage between the carbonate ANC and the noncarbonate in calculating the pH levels and renders the modeling framework concise and computationally efficient. Such an advantage can usually be translated, in practical terms, into not-too-demanding data requirements to use the modeling framework.

One of the practical applications of the modeling framework may be the development of liming schedules in terms of quantifying the amount of lime required and deriving a timetable for seasonal application of lime to maintain pH levels. Thus, lake managers may use the model as a tool to understand the seasonal dynamics of the lake chemistry and to develop strategies for controlling lake acidification.

APPENDIX I.—MODEL EQUATIONS

Total Alkalinity in Epilimnion

$$V_1 \frac{d[Alk]_1}{dt} = \frac{\xi A_{1,2}}{L_{1,2}} ([Alk]_2 - [Alk]_1) - \mu_1[Alk]_1 V_1 + D_{Alk}$$

$\qquad\qquad\qquad$ eddy diffusion $\qquad$ reaction $\qquad$ loading

$$- Q_{out}[Alk]_1 + Q_{1,2}(\alpha[Alk]_1 + \beta[Alk]_2) \quad \dots\dots\dots \quad (8)$$

$\qquad$ outflow $\qquad$ vertical advection

CO_2 Acidity in Epilimnion

$$V_1 \frac{d[CO_2\,Acy]_1}{dt} = \frac{\xi A_{1,2}}{L_{1,2}} ([CO_2\,Acy]_2 - [CO_2\,Acy]_1)$$

$\qquad\qquad\qquad\qquad$ eddy diffusion

$$+ K_L A([CO_2_{(s)}] - [CO_2] + [H^+]_1)$$

$\qquad$ CO_2 exchange of air-water exchange

$$- \mu_2[CO_2\,Acy]_1 V_1 + D_{CO_2} - Q_{out}[CO_2\,Acy]_1$$

$\qquad$ reaction $\qquad$ loading $\qquad$ outflow

$$+ Q_{1,2}(\alpha[CO_2\,Acy]_1 + \beta[CO_2\,Acy]_2) \quad \dots\dots\dots \quad (9)$$

$\qquad$ vertical advection

Total Alkalinity in Hypolimnion

$$V_2 \frac{d[Alk]_2}{dt} = \frac{\xi A_{1,2}}{L_{1,2}} ([Alk]_1 - [Alk]_2) + \mu_3[Alk]_2 V_2$$

$\qquad\qquad\qquad$ eddy diffusion $\qquad$ reaction

$$- Q_{1,2}(\alpha[Alk]_1 + \beta[Alk]_2) + W_{Alk} \quad \dots\dots\dots\dots\dots \quad (10)$$

$\qquad$ vertical advection $\qquad$ groundwater input

CO₂ Acidity in Hypolimnion

$$V_2 \frac{d[CO_2 \, Acy]_2}{dt} = \frac{\xi A_{1,2}}{L_{1,2}} ([CO_2 \, Acy]_1 - [CO_2 \, Acy]_2) + \mu_4[CO_2 \, Acy]_2 V_2$$

<div align="center">eddy diffusion   reaction</div>

$$- Q_{1,2}(\alpha[CO_2 \, Acy]_1 + \beta[CO_2 \, Acy]_2) + W_{CO_2} \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

<div align="center">vertical advection   groundwater input</div>

APPENDIX II.—REFERENCES

Banks, R. B., and Herrera, F. F. (1977). "Effect of wind and rain on surface reaeration." *J. Envir. Engrg.*, ASCE, 103(3), Jun., 489–504.

Chadderton, R. A., and Shane, R. M. (1978). "A model of the behavior of pH determining parameters in impoundments." *Water Resour. Bull.*, 14(6), Dec., 1357–1373.

DiToro, D. M. (1976). "Combining chemical equilibrium and phytoplankton models—A general methodology." *Modeling biochemical processes in ecosystems*, R.P. Canale, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 233–255.

DiToro, D. M., Fitzpatrick, J. J., and Thomann, R. V. (1983). "Water quality analysis simulation program (WASP) and model verification program (MVP) documentation." *Report submitted by Hydroscience, Inc. to U.S. EPA Environmental Research Laboratory*, Duluth, Minn.

Eshleman, K. (1982). "A biogeochemical mass balance approach to reservoir acidification by atmospheric deposition," thesis presented to M.I.T. Dept. of Civ. Eng., Cambridge, Mass., in partial fulfillment of the requirements for the degree of Master of Science.

Eshleman, K. N., and Hemond, H. F. (1985). "The role of organic acids in the acid-base status of surface waters at Bickford Watershed, Massachusetts." *Water Resour. Res.*, 21(10), Oct., 1503–1510.

Gherini, S. A., et al. (1984). "The ILWAS model: Formulation and application." *The integrated lake-watershed acidification study vol. 4: Summary of major results*, Electric Power Research Institute Report EA-3221, Palo Alto, Calif.

Henriksen, A. (1979). "Acidification of freshwaters: A simple approach for identification and quantification." *Nat.*, 278, 542–545.

Henriksen, A. (1980). "Acidification of freshwaters—A large scale titration." *Ecological impact of acid precipitation. Proceedings of an international Conference*, Sandefjord, Norway, Mar. 11–18, 1980, 68–74.

Holley, E. R. (1977). "Oxygen transfer at the air-water interface." *Transport processes in lakes and oceans*, R. J. Gibbs, Ed., Plenum Press, New York, N.Y.

Jassby, A., and Powell, T. (1975). "Vertical patterns of eddy diffusion during stratification in Castle Lake, California." *Limnology and Ocean.*, 20(3), May, 530–543.

Johannes, A. H., Galloway, J. N., and Troutman, D. E. (1981). "Snow pack storage and ion release." *The Integrated lake-watershed acidification study (ILWAS)*, Electric Power Res. Inst. Report EA-1825, Palo Alto, Calif.

Kelly, M. G., Church, M. R., and Hornberger, G. M. (1974). "A solution of the inorganic carbon mass balance equation and its relation to algal growth rates." *Water Resour. Res.*, 10(3), Jun. 493–497.

Kemp, P. H. (1971). "Chemistry of natural waters—I. Fundamental relationships." *Water Res.*, 5(2), Feb., 297–311.

Kramer, J., and Tessier, A. (1981). "Acidification of aquatic systems: A critique of chemical approaches." *Envir. Sci. & Tech.*, 16(11), Nov., 606A–615A.

Lung, W. S. (1984). "Understanding simplified lake acidification models." *J. Envir. Engrg.*, ASCE, 110(5), Oct., 997–1002.

Lung, W. S., and Canale, R. P. (1977). "Projections of phosphorus levels in White Lake." *J. Envir. Engrg. Div.*, ASCE, 103(4), Aug., 663–670.

Schindler, D. W., et al. (1980). "Experimental acidification of Lake 223, experimental lake area: Background data and first three years of acidification." *Canadian J. Fishery and Aquatic Sci.*, 37(3), Mar., 342–354.

Schofield, C. L. (1979). "Effects of acid rain on lakes." *Acid rain*, C. G. Gunnerson and B. E. Willard, Eds., ASCE, New York, N.Y., 55–69.

Schofield, C. L. (1984). "Surface water chemistry in the ILWAS basins." *The integrated lake-watershed acidification study vol. 4: Summary of major results*, Electric Power Res. Inst. Report EA-3221, Palo Alto, Calif.

Shen, T. T. (1982). "Hazardous air emissions from industrial waste treatment facilities." *Proceedings of 14th Mid-Atlantic Industrial Waste Conference*, College Park, Md., Jun. 27–29, 1–6.

Small, M. J., and Sutton, M. C. (1986). "A regional pH-alkalinity relationship." *Water Res.*, 20(3), Mar., 335–343.

Stumm, W., and Leckie, J. O. (1970). "Phosphate exchange with sediments; Its role in the productivity of surface waters." *Paper presented at the 5th Int. Water Pollution Res. Conf.*, Jul.–Aug.

Tetra Tech, Inc. (1983). "Workshop notes: ILWAS aquatic system workshop." Lafayette, Calif., Jan. 14 and 17.

Viessman, W., et al. (1977). *Introduction to hydrology*. Harper & Row, New York, N.Y.

Weber, W. J., Jr., and Stumm, W. (1963). "Mechanisms of hydrogen ion buffering in natural waters." *J. Amer. Water Works Assoc.*, 55(12), Dec., 1553–1578.

Yamartino, R. J., Pleim, J. E., and Lung, W. S. (1983). "Development of an acid rain impact assessment model." *Report submitted by ERT, Inc. to Empire State Electric Energy Research Corporation*, Jul. 1983.

Yeasted, J. C., and Shane, R. (1976). "pH profiles in a River system with multiple acid loads." *J. Water Pollution Control Federation*, 48(1), Jan., 91–106.

Yu, S. L. (1977). "Atmospheric reaeration in a lake." *Report*, Rutgers Univ., New Brunswick, N.J., 50 pp.

APPENDIX III.—NOTATION

The following symbols are used in this paper:

A = lake surface area;

$A_{1,2}$ = interfacial area between epilimnion and hypolimnion;

$[Alk]_1, [Alk]_2$ = alkalinity concentrations in epilimnion and hypolimnion, respectively;

$[CO_2 \, Acy]_1, [CO_2 \, Acy]_2$ = CO_2 acidity concentrations in epilimnion and hypolimnion, respectively;

$[CO_{2(s)}]$ = CO_2 concentration in epilimnion and hypolimnion, respectively;

$[CO_2]_e$ = saturated concentration of CO_2;

D_{Alk}, D_{CO_2} = CO_2 concentration in epilimnion from direct deposition and tributary input to epilimnion;

$[H^+]$ = concentration of hydronium ion;

K_1, K_2 = first and second dissociation constants of carbonate equilibria;

K_w = dissociation constant of water;

$K_L(CO_2)$ = reaeration coefficient for CO_2;

$K_L(O_2)$ = reaeration coefficient for O_2;

L_e = average depth of epilimnion;

L_h = average depth of hypolimnion;

$L_{1,2}$ = average of epilimnion depth and hypolimnion depth;

$Q_{1,2}$ = advective flow between epilimnion and hypolimnion;

Q_{out} = outflow from epilimnion;

T = temperature;

V_1, V_2 = volumes of epilimnion and hypolimnion; respectively;

W = windspeed;

W_{Alk}, W_{CO_2} = groundwater input of alkalinity and CO_2 acidity, respectively;

θ = temperature correction constant for reaeration coefficient;

$\mu_1, \mu_2, \mu_3, \mu_4$ = first-order kinetic coefficients for alkalinity and CO_2 acidity in the epilimnion and hypolimnion, respectively;

α, β = weighting factors to determine concentrations at epilimnion-hypolimnion interface; and

ξ = vertical diffusion coefficient in water column.