MODELING FATE AND TRANSPORT OF SULFATE AND ALKALINITY IN AN ACIDIFIED LAKE

WU-SENG LUNG[1], AARON L. MILLS[2], LISE A. MOVALL[1],
and ALAN T. HERLIHY[2]

Abstract. Acid mine drainage from Contrary Creek flows into an entire arm of Lake Anna. Much of the acid inflow is neutralized by bacterial sulfate reduction in the lake sediments. We developed a simple model to track the seasonal fate and mass transport of sulfate and alkalinity along the acidified arm. The loss of sulfate from the water column was characterized by a first-order decay reaction. A gain in alkalinity due to sulfate removal was also incorporated in the model. In addition, CO_2 acidity and pH in the water column were calculated. The model was calibrated with data collected in 1983 and 1984. Model sensitivity runs were conducted to demonstrate the importance of sulfate reduction in the system.

1. Introduction

It has been clearly established in a number of studies that microbial processes in anaerobic waters and sediments can supply substantial amounts of alkalinity to acidified waters. Such alkalinity can develop in water bodies acidified to a moderate degree, as by acid precipitation (Kelly *et al.,* 1982; Schindler *et al.,* 1980; Schindler, 1985; Cook *et al.,* 1986), and it can also develop in strongly acidified waters, such as those acidified by acid mine drainage (Tuttle *et al.,* 1969a, b; Mills, 1985; Herlihy and Mills, 1985, 1986; Mills and Herlihy, 1985; Herlihy *eta/.,* 1987). The studies of internal buffering have concentrated largely on sulfate reduction **(SR)** as the prime mechanism of alkalinity production, although several groups have recognized the potential importance of similar processes such as denitrification and iron reduction (Hemond and Eshleman, 1984; Bell *et al.,* 1987).

In studies of the impact of anaerobic microbial processes on the acid pollution in Lake Anna, Virginia (Figure 1), we have concentrated mainly on SR in sediments. Given the high concentration of SO; in the water column there (1 to 20 mM), the relative magnitude of other alkalinity generating reactions appears minimal. A mass balance budget indicated that 48% of the annual SO; input was retained in the contaminated arm of the lake, and the SR measurements showed that the process accounted for the SO; retention measured in the budget study (Herlihy *et al.,* 1987). Furthermore, based on the SO; retention figures, alkalinity generation was more than adequate to account for the increase in pH observed between the mouth of the acid mine stream and the arm's outflow, 2 km down the lake.

In order to apply the information gained in the above studies to more general situations, modeling exercises have been undertaken. A model describing sulfate

[1] Dept. of Civil Eng., Univ. of Virginia, Charlottesville, VA 22901, U.S.A.
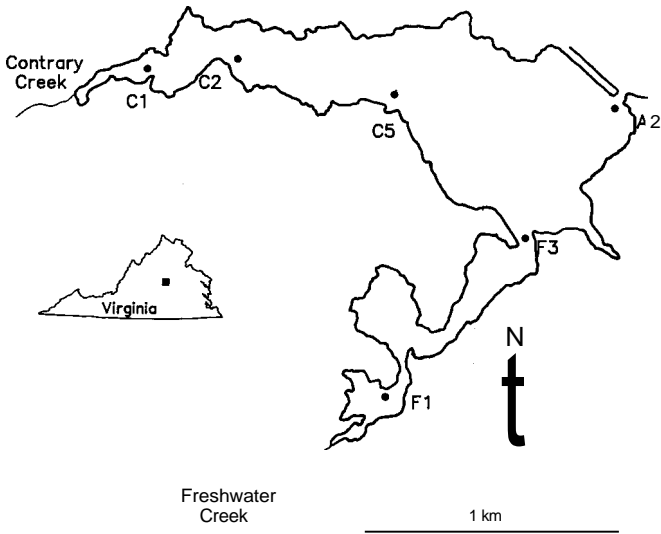[2] Dept. of Environmental Sciences, Univ. of Virginia, Charlottesville, VA 22901, U.S.A.

Fig. 1.   Stu y area at Lake Anna, Virginia.

removal has been proposed by Baker *et al.* (1986). Kelly *et al.* (1987) proposed a mathematically similar model and obtained results and conclusions consistent with those of Baker *et al.* (1986). A portion of the model was based on observations of the sulfate retention in a variety of northern temperate lakes subjected to moderate acidification by precipitation or experimental manipulation. The sulfate removal models utilize a first order loss term that is later used in more general models of internal alkalinity generation. In these studies, the authors determined an average loss coefficient of about 0.46 (although the range of all lakes used for the modeling was from 0.11 to 1.28). The constancy of the first order loss term across lakes was taken by Baker *et al.* to imply that the movement of sulfate from the water column to the sediments is driven by diffusion gradients.

The model proposed by Baker *et al.* (1986) is likely not appropriate for heavily acidified impoundments such as Lake Anna. Given the short retention time of the arm of the lake receiving the **AMD,** ca. 100 days (Herlihy *et al.,* 1987), the coefficients used in the Baker *et al.* (1986) model fail to predict the observed sulfate retention. A coefficient calculated on the basis of the actual sulfate retention in Lake Anna is 10.11. Furthermore, horizontal dynamics of any reservoir require that a different approach to the model formulation must be used. It is not adequate to simply divide the water into 'epilimnetic' and 'hypolimnetic' zones, nor is it appropriate to consider the water as being well mixed horizontally, an assumption implicit in the formulations used by Baker *et al.* (1986) and Kelly *et al.* (1987).

The purpose of the work described here was to develop a water quality model to accomplish such a task and to track the seasonal trends in sulfate concentration and other key water quality constituents along the arm. The model formulations are based

on the principle of mass balance. The key kinetic process incorporated in the model is the loss of sulfate in the water column as a result of sulfate reduction minus sulfide oxidation. Further, a gain in alkalinity in the system resulting from the loss of sulfate (Schindler *et al.,* 1980) is incorporated. Also included are calculations of alkalinity, CO_2 acidity, and pH levels in the acidified arm. To aid the investigation, field data necessary for calibrating the model were collected.

The field program and sample analyses are first summarized. Then model development and calibration analyses utilizing the results of the field program are presented. Subsequent model sensitivity runs show the importance of sulfate removal in quantifying the fate and transport of sulfate and alkalinity in the system.

2. Study Area

A portion of Lake Anna (Figure 1) receives acid mine drainage from Contrary Creek which drains an 1820 ha watershed with abandoned pyrite mines, and provides 35% of the water entering that part of the lake (Bruckner, 1986). Contrary Creek has very acidic water (pH 2.5 to 3.9) and large concentrations of sulfate (1 to 20 mM) and Fe (150 to 450 µM) (Herlihy *et al.,* 1987). Lake Anna also receives drainage from Freshwater Creek (Figure 1) with a 2288 ha watershed, but non-acidic water. Average pH at the outlet of the arm is about 5, almost 2 units higher than the acidic inflow from Contrary Creek.

3. Data Collection and Sample Analyses

Limited water quality data for the acidified arm were collected prior to 1984. To aid model development and model calibration, a field sampling program was conducted in 1984 to gather in-lake data on alkalinity, acidity, pH, and sulfate. The monitoring program was designed to better understand the seasonal trends of alkalinity and sulfate in Lake Anna.

Lake Anna was sampled at approximately 2-week intervals from April 1984 through August 1984, the period when bacterial sulfate reduction is greatest (Herlihy and Mills, 1985). Sampling stations were selected to generate a longitudinal profile of acidification, neutralization, and dilution along the arm. Station Fl was 30 m from a non-acidic inflow (Freshwater Creek) to Lake Anna (Figure 1). Station Cl was located 300 m from Contrary Creek's mouth and had a depth of 1.5 m. Located progressively further from the inflow of Contrary Creek were Station C2 (2 m deep), Station C5 (3 m), and Station A2 (7 m).

Samples of surface and bottom waters were collected using a peristaltic pump. Specific conductance and water temperature were measured at 0.5 m intervals with a LabLine probe and specific conductance/temperature meter.

Alkalinity and acidity were determined using Gran's (1952) potentiometric titrations. The pH meter was calibrated with pH 8 and 4 buffers prior to alkalinity titration, and with pH 8 and 10 buffers prior to acidity measurements. pH was measured poten-

tiometrically with a Sensorex combination electrode and a Corning pH meter. Sulfate
was determined by ion chromatography (Moses *et al.,* 1984). A more detailed descrip-
tion of laboratory procedures is given in Movall (1986).

4. Model Design

Model Segmentation and Mass Transport- The study area was divided into 4 longitudinal
segments (Figure 2a) to account for the horizontal dynamics of the reservoir. Segment 1
received acidic inflow from Contrary Creek while Freshwater Creek entered the last
longitudinal segment. All segments except the first (because of its shallow depth) were
also partitioned into 2 vertical layers to account for concentration gradients in the
vertical direction. Altogether, seven segments were used in the system, and each segment
was considered completely mixed. Figure 2b also shows such a two-layer mass transport
pattern in the system, including longitudinal advection, vertical advection, and vertical
dispersion.

a. Horizontal Segmentation
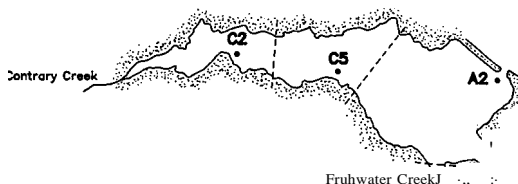
b. Vertical Segmentation and Mass Transport
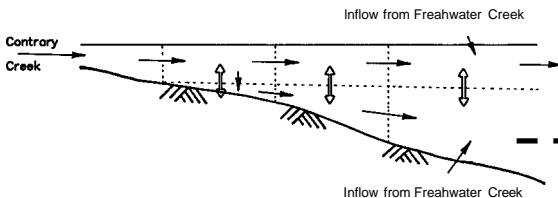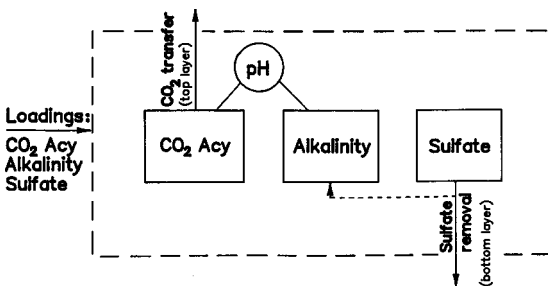
c. Major Processes

Fig. 2. Lake Anna acidification model.

Sulfate Removal Kinetics - Sulfate removal from the bottom layer was formulated in the model to account for the net loss of sulfate and to estimate alkalinity generation since sulfate removal accounts for alkalinity generation by sulfate reduction minus the consumption of alkalinity by sulfide oxidation (Schindler, *et al.,* 1980; Herlihy *et al.,* 1987). In this study, first-order kinetics were used to formulate the rate of sulfate removal as a function of sulfate concentration in the bottom layer of the water column and of a reaction rate constant (day-^{1}). Such a formulation was used by Balcer *et al.* (1986), Kelly *et al.* (1987), and Lung (1987) in quantifying the internal generation of alkalinity in acidic lalces.

Alkalinity Generation - In-lalce alkalinity generation associated with sulfate removal was also included. The rate of alkalinity generation was quantified based on stoichiometric relationships. That is, the loss of $1 \, eq \, L^{-1}$ of sulfate per day would contribute to a gain of $1 \, eq \, L^{-1}$ alkalinity per day in the system (Bemer *et al.,* 1970).

CO_2 *Acidity and pH* - In addition to tracking sulfate and alkalinity concentrations in the water column, CO_2 acidity was also included as a model variable. Once alkalinity and CO_2 acidity were calculated, pH can be readily calculated from the $CO_2/HCO_3/CO_3$= equilibria for waters such as Lalce Anna with low Al and organic acid concentrations (Lung, 1987).

CO_2 *Transfer* - Mass transfer of CO_2 across the air-water interface can be formulated as follows:

$$CO_2 \text{ mass rate} = K_L([CO_{2(s)}] - [CO_2]_1)A , \tag{1}$$

where

$$K_L = CO_2 \text{ transfer coefficient (m day-}^1),$$

$$[CO_{2(s)}]1 = \text{saturation concentration of dissolved } CO_2 \text{ in the top layer},$$

$$[CO_2]_1 = \text{average concentration of dissolved but unionized } CO_2 \text{ in the top layer,}$$

$$A = \text{lalce surface area.}$$

Equation (1) implies that when sufficient acidic input to the system yields water oversaturated with respect to CO_2, CO_2 would escape from the water to the atmosphere. The process is formulated in a way that the direction of such an exchange could be reversed when the water is under-saturated with respect to CO_2. In Equation (1), $[CO_2]_1$ maybe approximated by $[CO_2Acy]_1 - [H+]_1$ according to Weber and Stumm (1963), where $[CO_2Acy]_1$ is the concentration of CO_2 acidity in the top layer and $[H_+]_1$ is the H_+ concentration in the top layer. Through this approximation, the CO_2 process is coupled with other system variables (e.g., CO_2 Acy and pH). Derivation of K_L for lakes and saturated CO_2 concentrations is presented in another section of this paper.

5. $CO_2/HCO_3/CO_3$ Equilibria

After the alkalinity and CO_2 acidity concentrations in each segment were calculated, the H_+ concentration was then determined from the $CO_2/HCO_3/CO_3-$ equilibria, based on the following equations (Kemp, 1971):

(a) $[H+] = \dfrac{K_1([CO_2 Acy-]\ K_2\ Kw/K_1)}{[Alk] + K_1}$ if $[Alk] > O$,

(b) $[H+] = -Ki/2 + 0.5(Kf + 4Kw + 4K_1[CO_2Acy])^{112}$ if $[Alk] = 0$,

(c) $[H+] = -[Alk]$ if $[Alk] < 0$

where

     $[H+] = H+$ concentration in mol Ł$^{-1}$,

     $[Alk]$ = total alkalinity concentration in mol Ł$^{-1}$,

     $[CO_2 Acy]$ = CO_2 acidity concentration in mol Ł$^{-1}$,

     K_1 = first dissociation constant of carbonate equilibrium,

     K_2 = second dissociation constant of carbonate equilibrium,

     Kw = dissociation constant of water.

6. Derivation of Model Parameters

Hydrologic Budget - Time-variable hydrologic budgets were developed from Bruckner (1986). Major surface inflows to the acidified arm are from Contrary Creek and Freshwater Creek. Groundwater inflow was less than 1% of the total inflow (Bruckner, 1986) and was omitted from the budget. Monthly inflows from April to September in 1983 and 1984 are summarized in Table I.

     Sulfate/Alkalinity/CO2 Acidity Input- These were calculated from the measured flow and concentrations of the water quality constituents at the mouths of Contrary Creek and Freshwater Creek (Herlihy *et al.,* 1987). It should be pointed out that CO_2 acidity concentration was not measured. Instead, they were calculated from measured alkalinity and pH. The monthly inputs of alkalinity, CO_2 acidity, and sulfate are shown in Table I.

     Mass Transport Patterns - Precise routing of the flows from Contrary Creek and Freshwater Creek through the acidified arm was difficult to achieve due to lack of data. However, a mass transport pattern was approximated by allowing most (about 90%) of the Contrary Creek inflow going through the bottom segments. Such an assumption is justified because the Contrary Creek inflow is high in total dissolved solids that lead to greater density for the Contrary Creek water than the rest of the inflows to the acidified arm. Such a pattern has been observed in a West Virginia impoundment receiving acid mine drainage (Koryak *et al.,* 1979) and in Lake Anna (Herlihy and Mills,

TABLE I

Monthly inflow, alkalinity, CO_2 acidity, and sulfate input to the Contrary Creek arm of Laka Anna

	April	May	June	July	August	September
	1983					
Inflow (m^3)	1.32×10^6	0.37×10^6	0.15×10^6	0.6×10^5	0.8×10^4	0.9×10^4
Alkalinity (eq)	-0.37×10^6	-0.85×10^5	-0.87×10^5	-0.81×10^5	-0.28×10^5	-0.28×10^5
CO_2 acidity (eq)	0.85×10^6	0.28×10^6	0.16×10^6	0.13×10^6	0.4×10^5	0.6×10^5
Sulfate (mo!)	1.29×10^6	0.70×10^6	0.43×10^6	0.24×10^6	0.7×10^5	0.76×10^5
	1984					
Inflow (m^3)	1.55×10^6	0.47×10^6	0.14×10^6	0.14×10^6	0.68×10^6	0.82×10^5
Alkalinity (eq)	-0.45×10^6	-0.95×10^5	-0.11×10^6	-0.17×10^6	-0.4×10^5	-0.4×10^4
CO_2 acidity (eq)	0.98×10^6	0.35×10^6	0.18×10^6	0.16×10^6	0.94×10^6	0.13×10^6
Sulfate (mo!)	1.47×10^6	0.82×10^6	0.41×10^6	0.43×10^6	0.80×10^6	0.31×10^6

1985). Rastetter *et al.* (1984) indicated that the density differences in Lake Anna resulted in such an advective transport pattern, particularly when wind action caused little mixing in the water column during summer months.

Another important transport mechanism is vertical diffusion which characterized concentration gradients between the upper layer and lower layer. There are various ways of determining the vertical diffusion coefficient for mass transport in lakes. In this study, the vertical diffusion coefficients were computed by the flux-gradient method (Lung *et al.,* 1976) using temperature data. Basically, the vertical diffusion coefficients were obtained by fitting the following equation with temperature data:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(D\ \frac{\partial T}{\partial z}\right),$$

where T = temperature, t = time, and D = vertical diffusion coefficients. Layer-averaged diffusion coefficients were then obtained from the calculated discrete values of D and used in the model.

The CO_2 exchange mechanism across the air-water interface depends on the mass transfer coefficient and the saturation concentration of CO_2 in the upper layer (see Equation (1)). In this study, an empirical formula developed by Banks and Herrera (1977) for the dissolved oxygen transfer coefficient was used:

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

where W = windspeed over the surface in m-s^{-1}. The transfer coefficient for dissolved oxygen is then converted to the transfer coefficient for CO_2 according to the ratio of molecular weights. K_L is also dependent upon temperature in the water column. An empirical formula proposed by Kelly *et al.* (1974) was used in the model to determine the CO_2 saturation concentration (in mol Ł$^{-1}$) as a function of temperature:

$$[CO_{2(s)}] = 1O^{[2385.73/(T+\ 273)-\ 17.5184\ +\ 0.015164(T+\ 273)]}. \qquad (3)$$

where *T* is temperature in °C. Based on the above discussions, the calculation of K_L (for CO_2) require windspeed and temperature data. Windspeed data were obtained from the Virginia Power Company and temperatures were measured in the field.

Sulfate Removal Rates - Herlihy *et al.* (1987) presented sulfate budgets for the acidified arm based on data collected in 1983 and 1984. Sulfate input to and output from the arm were derived from the data and used to determine the mass rate of sulfate loss (removal), which was then divided by the water volume and sulfate concentration to yield the first-order reaction rate constant for sulfate removal, μ (day^{-1}), according to the following equation:

$$\text{Sulfate removal [mass/time]} = \mu \ [1/\text{day}] * \text{Sulfate conc. [mass/vol]} * \text{Vol.}$$

It should be stressed that the sulfate removal rates so determined were based on budgets for the entire acidified arm. They were considered as first approximations to the sulfate removal rates used in the bottom segments of the model. Subsequent model calibration analyses eventually fine tuned the rates in the model.

7. Model Calibration Analysis

Calibration Procedure - The first step in model calibration was to assign appropriate values of transport and kinetic coefficients to the model. These coefficients may be determined from a fundamental analysis relating to the specific process, as may be accomplished in the case of the hydrologic or hydrodynamic terms. Thus, the vertical diffusion coefficient between the two layers was derived analytically from heat budget principles as described in an earlier section. Other model coefficients may be reported in the literature. In any case, assuming a range of these kinetic coefficient values (e.g., sulfate removal rate) was known or indirectly derived, a best estimate was made of each, the model was run and the output was compared to the data. Invariably, successive adjustements were required to obtain a 'reasonable fit' of the model and data (O'Connor *et al.,* 1975). It should be pointed out that model calculations were not intended to 'curve fit' the data. That is, the calibrated sulfate removal rate was obtained through a series of model sensitivity runs with a reasonable range of removal rates based on the seasonal sulfate budgets for the acidic arm. The modeling framework was designed to mimic the seasonal trends of sulfate, alkalinity, and **pH** along the arm and is shown to accomplish the task in the following sections. Although the model has many coefficients and rate constants, the degree of freedom to calibrate it was rather limited. In fact, the model system variables such as sulfate, alkalinity, CO_2 acidity, and pH are interrelated so that adjustments to improve the calibration of a particular water quality constituent would often result in an adverse outcome for calibrating other constituent(s).

Model Calibration of 1984 Data - Figure 3 shows the comparison between model results and measured alkalinity, pH, CO_2 acidity, and sulfate for the top layer and bottom layer of the acidified arm at three locations: C2, CS, and A2. Simultaneous displays of the results in such a multi-panel fashion describe the temporal and spatial trends of the water quality conditions in the system. Figure 3 shows that the modeling
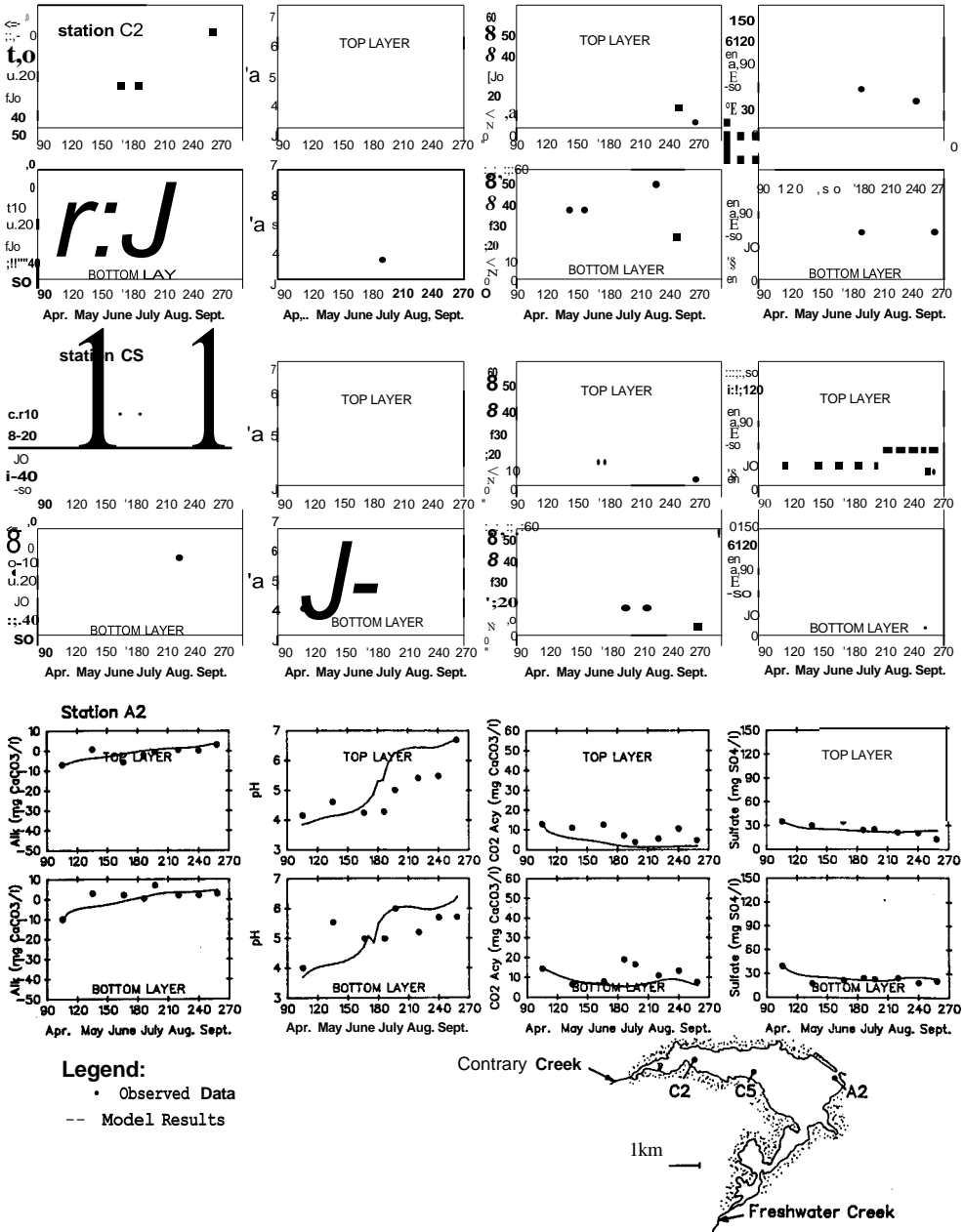
Fig. 3. Model calibration of Lake Anna data - 1984.

framework has accomplished such a task. While alkalinity and pH levels increased through the summer months in the arm, observed CO_2 acidity and sulfate depletion were reproduced by the model. More specifically, during the summer months, sulfate removal

caused an increase of alkalinity which was followed by an increase in pH (from 4 to 7). Examining the results along the arm from Station C2 to Station A2, one sees a progressive increase in alkalinity and pH in the downstream direction concurrent with a decreasing trend of CO_2 acidity and sulfate.
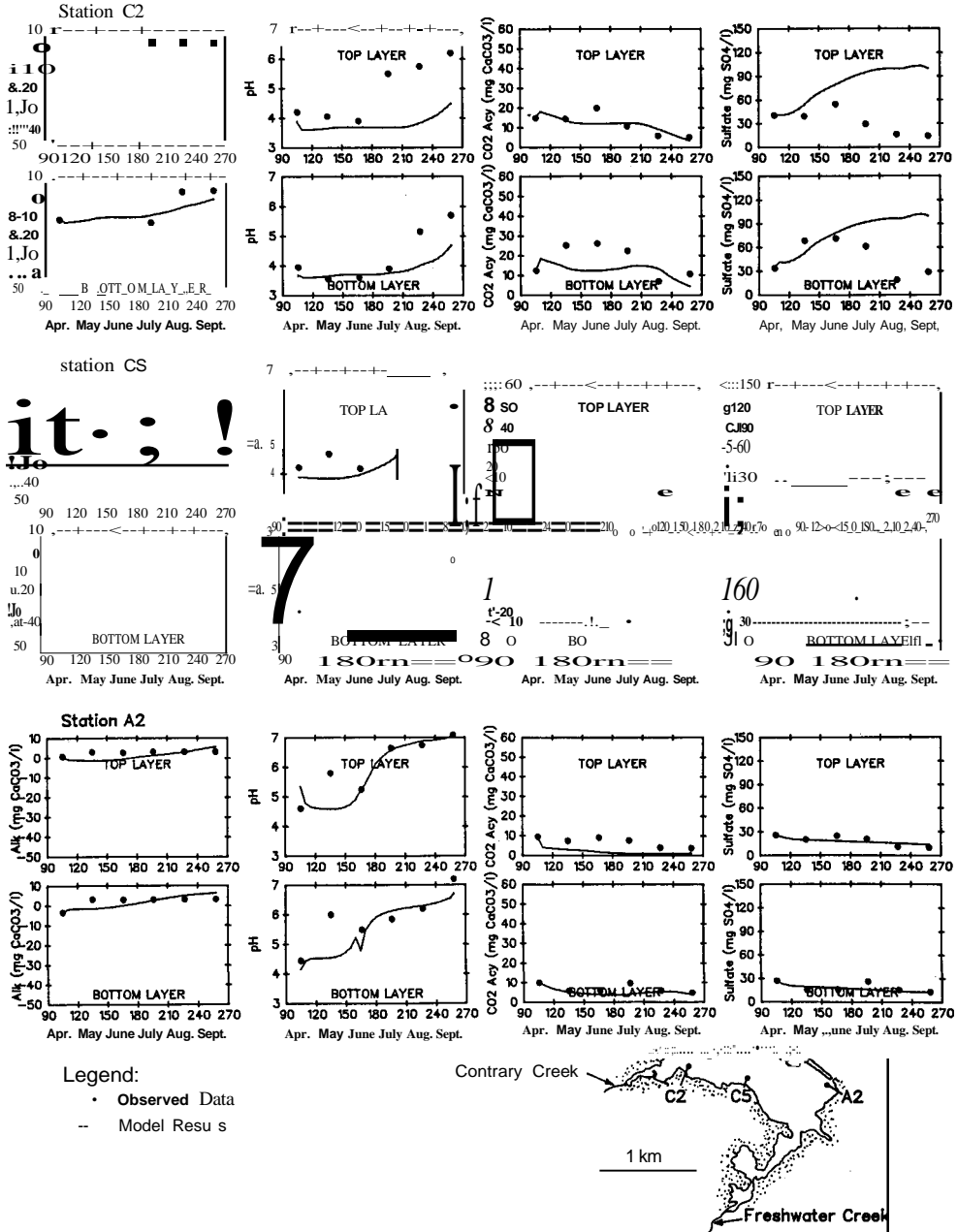

Fig. 4.   Model calibration of Lake Anna data - 1983.

Model Calibration of 1983 Data - The model was subsequently tested to see how its predictions fit the 1983 data collected in a previous study (Herlihy and **Mills,** 1985). Associated 1983 hydrology, mass transport, and sulfate loading were incorporated into the model. Model results (Figure 4) showed similar seasonal trends for alkalinity, **pH,** CO_2 acidity, and sulfate to those in 1983. Again, sulfate removal from the water column was accompanied by increases in alkalinity and pH over the summer period. That is, the acidified arm recovered at A2 as **pH** reached 7 by the end of summer. Differences between the model results and observed data (e.g., **pH** and sulfate) at Station C2 are probably due to additional precipitation and sedimentation of sulfate in relatively shallow water. Such additional removal of sulfate from the water column would be particularly pronounced in a dry season (summer 1983) when flows from Contrary Creek and Freshwater Creek are very small. In fact, the data in Table I show that the total inflows to the system in July, August, and September 1983 were much smaller than those during the same period of 1984. This observation implies that spatially variable rates of sulfate removal are needed to account for the significant removal at Station C2. Although such a feature could be easily incorporated into the model, such was not done due to lack of data to support the derivation of spatially variable removal rates. Nevertheless, application of this modeling framework to the 1983 data has uncovered this important aspect of the sulfate removal process which warrants further studies. This is one of the benefits resulting from a modeling analysis of this sort.

Importance of Sulfate Reduction - As pointed out earlier, preliminary sulfate removal rates were derived from sulfate budgets for summer periods of 1983 and 1984. Subsequent model calibration analyses (see the results in Figures 3 and 4) finalized the first-order kinetic coefficients (day-^{1}) characterizing the sulfate removal process. Table II shows the finalized kinetic coefficients on a seasonal time-variable basis. It is seen that during the months of June, July, and August, the sulfate removal coefficients were high. To evaluate the significance of the sulfate removal process, a model sensitivity analysis was made by setting the sulfate removal rates equal to zero. The results of such a run are presented in Figure 5 using the 1984 data. Figure 5 shows that sulfate removal

TABLE II

Kinetic coefficient rate constant (I/day) for net sulfate removal in Lake Anna

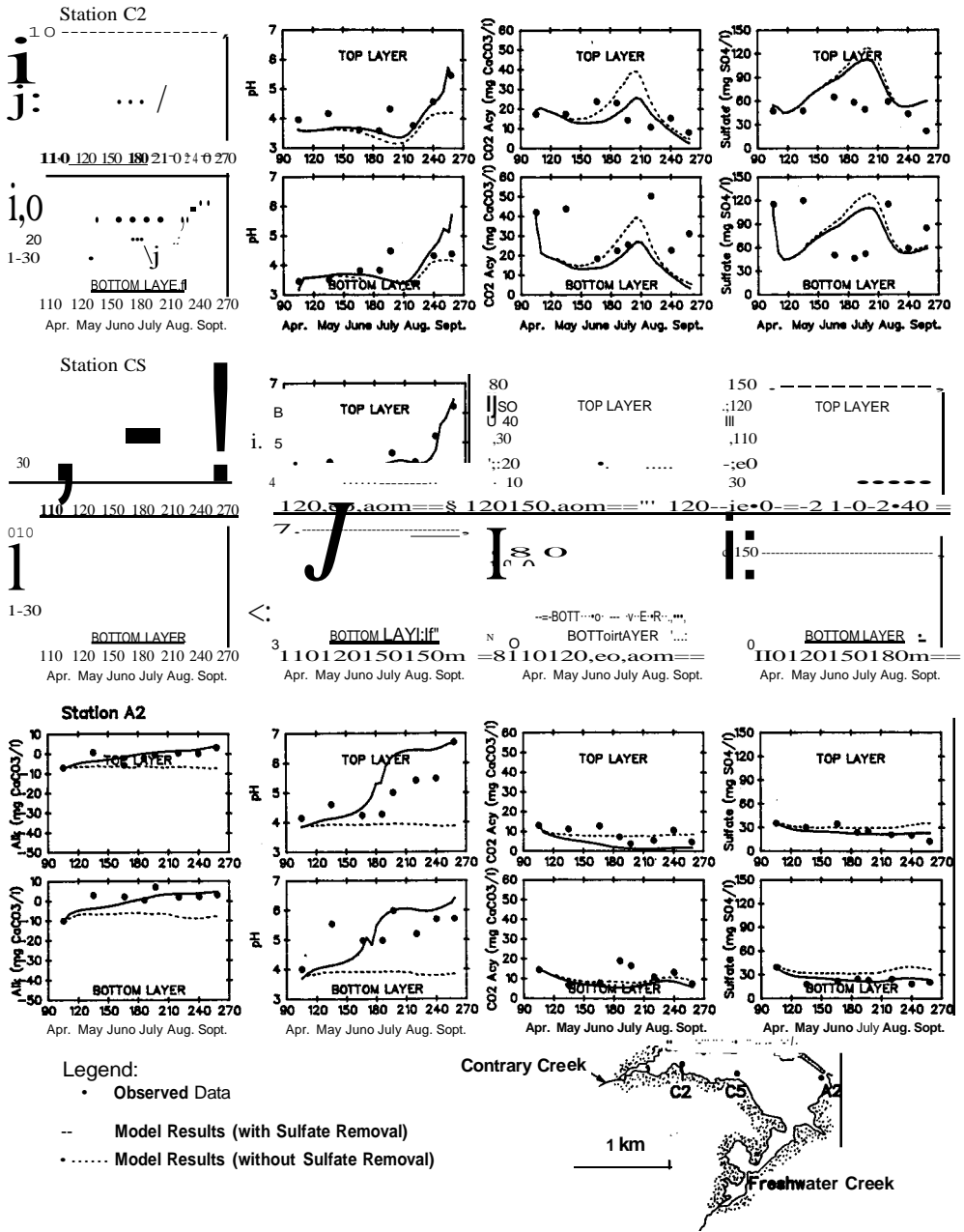| Month	Approximation from sulfare budgets		Calibrated values
	1984	1983	
April	0.013	0.018	0.010
May	0.022	0.0023	0.004
June	0.017	0.0156	0.008
July	0.014	0.0085	0.008
August	0.023	0.0027	0.008
September	0.012	0.0023	0.006

Fig. 5.   Significance of sulfate removal in Lake Anna (1984).

is primarily responsible for the decrease in sulfate levels and the sharp rise in pH levels in the acidified arm during the summer period in 1984. During 1983 and 1984, about 48% of the sulfate entering the acidified arm was removed from the water column by

these processes (Herlihy *et al.,* 1987). The modeling analysis reported in this paper provides additional quantitative support to their conclusion.

8. Summary and Conclusions

A mathematical model was developed to examine the fate of sulfate from acid mine drainage to one arm of Lake Anna. First, field measurements of sulfate, alkalinity, and pH were used to estimate the acid loads and degree of acidification in the receiving water. These data were then used to construct the model for sulfate, alkalinity, and CO_2 acidity. In addition, pH levels were also computed in the model based on calculated alkalinity and CO_2 acidity levels.

The acidified arm was divided into 2 layers to account for vertical concentration gradients. Key processes incorporated in the model include sulfate removal in the bottom layer and CO_2 exchange across the air-water interface. Sulfate is removed from the water column as a net result of sulfate reduction in the sediments and sulfide reoxidation, particularly during summer months. The process is formulated using first-order kinetics relating the mass rate of removal to the concentration of sulfate in the water column and a first-order reaction rate. Carbon dioxide exchange across the air-water interface depends on the mass transfer coefficient for CO_2 and the saturated CO_2 concentration in the water column.

The modeling framework was calibrated with data in 1983 and 1984, two years with very different summer hydrologic conditions. The model results mimicked the seasonal and spatial trends of alkalinity, pH, CO_2 acidity, and sulfate in the system for 1984. The model results for 1983 suggest that spatially variable sulfate removal rates be quantified to account for significant sulfate removal rate near the entrance of Contrary Creek, particularly during low flow periods. Further model sensitivity analysis demonstrate the significance of sulfate removal in contributing to increases in alkalinity and pH over the summer period.

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