

MODELING SULFATE RETENTION IN A LAKE RECEIVING ACID MINE DRAINAGE¹

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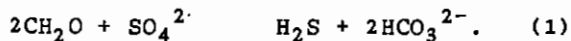
Abstract. -- Bacterial sulfate reduction in the sediments of Lake Anna, VA combined with geochemical processes in the water column remove half the SO_4^{2-} entering the lake in acid mine drainage (AMD) from Contrary Creek. In addition to SO_4^{2-} removal, the pH of the water is increased from about 3.5 to 6.0 within the boundaries of the contaminated arm. A simple water quality model was constructed to predict the spatial and temporal distribution of SO_4^{2-} in the lake water and to help identify the important processes controlling the distribution of the pollution in the lake. The model successfully predicted distribution of SO_4^{2-} in most locations, except for those closest to the mouth of the AMD stream. The model demonstrated that chemical stratification of the lake water was more important than thermal stratification near the mouth of the acid mine stream and that a strong chemical gradient there inhibits vertical mixing. Maintenance of the AMD plume near the sediment surface where the biological activity occurs likely enhances SO_4^{2-} removal. The proportion of SO_4^{2-} retained in the Contrary Creek arm (SO_4^{2-} retained / SO_4^{2-} influx) was 0.48, consistent with other lakes which actively retain sulfur in the sediments. The comparatively short residence time of this arm of Lake Anna (ca. 100 days) yields an SO_4^{2-} -removal coefficient of 12 to 14, which is over an order of magnitude higher than reported for lakes acidified experimentally or by precipitation. In those lakes diffusion is assumed to be the major mechanism of SO_4^{2-} transport to the sediments where most SR occurs. In Lake Anna, the model results demonstrated that some other mechanism plays an important role in transporting the AMD constituents from the lake water to the sediments. The amount of AMD neutralized by the biogeochemical processes in this lake suggests that some impoundments might be appropriate for the renovation of AMD-contaminated waters.

Proceedings America Society of Mining and Reclamation, 1987 pp 261-268
DOI: 10.21000/JASMR88010261

<http://doi.org/10.21000/JASMR88010261>

In Lake Anna, VA, successful neutralization of AMD from a series of abandoned pyrite mines occurs within one arm of the lake within 2 km of the point where Contrary Creek enters the lake. Contrary Creek has an annual average pH about equal to 3.2, SO_4^{2-} about equal to 1 to 20 $\mu\text{mol/L}$, and total iron about equal to 10 to 50 mg/L. On average, 48 % of the SO_4^{2-} that enters the lake from Contrary Creek is removed in the first two kilometers of the lake (Herlihy et al., 1987). Concomitantly, the pH rises to approximately 6 and the iron levels drop to levels similar to uncontaminated arms of the lake. This homeostatic renovation of the water has been attributed to anaerobic bacterial activities, specifically sulfate reduction (SR) in the sediments underlying the contaminated arm of the lake (Mills 1985, Mills and Herlihy 1985, Herlihy and Mills 1985, Herlihy et al. 1987; Mills et al. in press).

The establishment of anaerobic conditions, SR, and the resultant precipitation of metal sulfides are significant in increasing the pH and reducing the AMD-derived iron and SO_4^{2-} concentrations in the lake water. Alkalinity generation from SR occurs according to the equation:



Evaluation of the relative amount of neutralization that SR can provide is related to the amount of SO_4^{2-} removed from the water. Although SR plus dilution provides a thorough cleansing of water in the Contrary Creek Arm of Lake Anna, prediction of the efficiency of this homeostatic process in other systems must rely on an adequate quantitative model to test other systems prior to construction of new impoundments or contamination of pre-existing waters. The present study applied a modified version of the WASP model (Water Quality Analysis Simulation Program) to simulate the conditions in Lake Anna, with the intent of applying the model to other acidified impoundments in the future.

¹ Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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Model Description

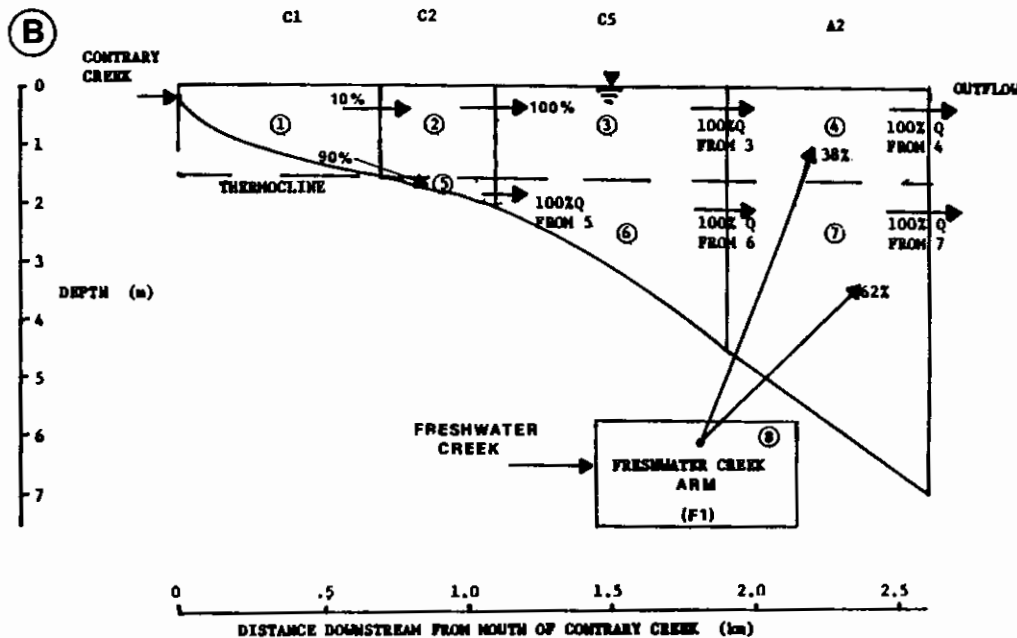
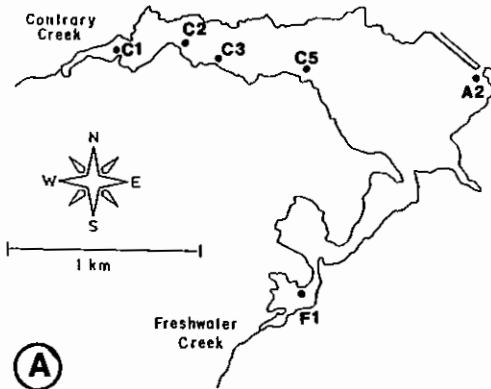
WASP is a general model capable of handling one, two, or three dimensional time-variable calculations (DiToro et al. 1983). The water body to be modeled is divided into segments and mass balance equations for each segment are constructed for the constituent of interest. The mass balance equations are solved using a finite difference technique with a backwards-difference approximation in the spatial plane and a forward-difference approximation in the temporal plane. The finite difference equations are integrated using a second-order Runge-Kutta method. WASP has been used successfully in modeling lake acidification in Bickford Reservoir, and Woods and Panther Lakes (Lung, 1987).

Application of WASP to Lake Anna

Only the area of the lake between the mouths of Freshwater and Contrary Creeks and the Route 652 bridge near station A2 was included in the model (fig. 1). To implement WASP in the Contrary Creek arm of Lake Anna, this part of the lake was divided into eight segments (fig. 1). Epilimnion and hypolimnion segments were included for areas of the lake around stations C2, C5, and A2. The Freshwater Creek section of the lake was treated as one segment as was the small segment of lake near the mouth of Contrary Creek around station C1. Sulfate concentration was the only constituent modeled, as SO_4^{2-} retention approximates the neutralization process for the lake.

The flows into each segment of the model are shown diagrammatically in figure 1, and the mass balance and discharge and loading equations are given in table 1. Sulfate from Contrary Creek enters into segment 1, and 90% flows into segment 5 (hypolimnion of station C2) with the remainder flowing into segment 2 (epilimnion of station C2). Water from segment 2 flows into segment 3, and then segment 4 along the surface of the lake (epilimnion segments of stations C5 and A2) before exiting out the outflow. Water in segment 5 flows into segment 6 and then segment 7 along the bottom of the lake (hypolimnion segments of stations C5 and A2) before exiting out the outflow. Sulfate is mixed between the epilimnion and hypolimnion of each station (segments 2 and 5, 3 and 6, and 4 and 7) by vertical eddy diffusion. Flow percentages were calculated from lake cross sectional areas and current velocity observations. Water and SO_4^{2-} from Freshwater Creek enter into segment 8, and then 38% flows into segment 4 and the remaining 62% into segment 7. Each surface segment (1,2,3,4 and 8) received SO_4^{2-} and water from

Figure 1. -- A. Map of the Contrary Creek arm of Lake Anna. Water flows in an easterly direction. The area shown represents about 13% of the total surface area of the impoundment which lies to the northeast and southeast of the arm shown. B. Schematic diagram of flow routing and segment location for the model applied to the Contrary Creek arm of Lake Anna.



precipitation and direct input (overland flow and ephemeral streams) and lost water due to evaporation. Sulfate is removed from the segments overlying sediments (1,5,6,7 and 8) by SR minus sulfide oxidation (Herlihy et al. 1987).

The data needed by WASP to run the model (described later) included the volume and initial SO_4^{2-} concentration of each segment, the waterflows between each segment, the eddy diffusion between segments, and the external SO_4^{2-} load into each segment of the model. The kinetic term for SR and the associated coefficients were also input. Finally boundary conditions indicated the sulfate concentration of the outflow from segments 4 and 7.

Flow, Load and Concentration Data

The model was calibrated using data collected during the 1984 water year (October 1, 1983 to September 30, 1984) and verified using data collected during the 1983 water year. Discharges and loads were input into the model at 5-day intervals using the mean value of the five daily discharges and loads. Discharge and load data were taken from the measured sulfate budget for the lake (Herlihy et al. 1987), recalculated for each segment. Initial conditions and boundary conditions were taken from the observed lake water sulfate concentrations. Segment volumes and surface areas were obtained from Bruckner (1986).

Table 1. -- Mass balance and loading and discharge equations used in the application of the modified WASP model to Lake Anna.

MODEL MASS BALANCE EQUATIONS

$$V_1 dC_1/dt = W_1 - Q_{12}C_1 - Q_{15}C_1 - k_{sulf}C_1A_1$$

$$V_2 dC_2/dt = W_2 + Q_{12}C_1 - Q_{23}C_2 + K_z A_{25}/L_{25}(C_5 - C_2)$$

$$V_3 dC_3/dt = W_3 + Q_{23}C_2 - Q_{34}C_3 + K_z A_{36}/L_{36}(C_6 - C_3)$$

$$V_4 dC_4/dt = W_4 + Q_{34}C_3 + Q_{84}C_8 - Q_{40}C_4 + K_z A_{47}/L_{47}(C_7 - C_4)$$

$$V_5 dC_5/dt = Q_{15}C_1 - Q_{56}C_5 + K_z A_{25}/L_{25}(C_2 - C_5) - k_{sulf}C_5A_{25}$$

$$V_6 dC_6/dt = Q_{56}C_5 - Q_{67}C_6 + K_z A_{36}/L_{36}(C_3 - C_6) - k_{sulf}C_6A_{36}$$

$$V_7 dC_7/dt = Q_{67}C_6 + Q_{87}C_8 - Q_{70}C_7 + K_z A_{47}/L_{47}(C_4 - C_7) - k_{sulf}C_7A_{47}$$

$$V_8 dC_8/dt = W_8 - Q_{84}C_8 - Q_{87}C_8 - k_{sulf}C_8A_8$$

V_i = Volume of segment i (m^3).
 C_i = Concentration of sulfate in segment i (mol/m).
 Q_{ij} = discharge from segment i to segment j (m^3/day).
 W_i^j = external sulfate loading into segment i (mol/day).
 K_z = vertical eddy diffusion coefficient (m^2/day).
 A_z = surface area between segments i and j (m^2).
 A_i^j = surface area of segment i (m^2).
 L_{ij} = sum of the depths of segments i and j (m).
 k_{sulf} = sulfate removal coefficient (m/day).

$$Q_{66} = Q_{15}$$

$$Q_{67} = Q_{56}$$

$$Q_{08} = Q_{fc} + S_8 Q_{fc} + A_8 Q_{prec} - A_8 Q_{evap} - A_8 Q_{store}$$

$$Q_{84} = 0.38 * Q_{08}$$

$$Q_{87} = 0.62 * Q_{08}$$

$$Q_{40} = Q_{34} + Q_{84} + Q_{04}$$

$$Q_{70} = Q_{67} + Q_{87}$$

Note that segment 0 represents external boundary condition.

Q_{ij} = discharge from segment i to segment j.
 Q_{cc} = discharge from Contrary Creek.
 Q_{fc} = discharge from Freshwater Creek.
 Q_{prec} = water input from precipitation.
 Q_{evap} = water loss due to evaporation.
 Q_{store} = discharge due to change in lake storage volume.
 S_i = ratio of direct input watershed area in segment i to the Freshwater Creek watershed area.
 A_i = ratio of lake surface area in segment i to total lake surface area.

DISCHARGE EQUATIONS

$$Q_{01} = Q_{cc} + S_1 Q_{fc} + A_1 Q_{prec} - A_1 Q_{evap} - A_1 Q_{store}$$

$$Q_{02} = S_2 Q_{fc} + A_2 Q_{prec} - A_2 Q_{evap} - A_2 Q_{store}$$

$$Q_{03} = S_3 Q_{fc} + A_3 Q_{prec} - A_3 Q_{evap} - A_3 Q_{store}$$

$$Q_{04} = S_4 Q_{fc} + A_4 Q_{prec} - A_4 Q_{evap} - A_4 Q_{store}$$

$$Q_{12} = 0.02 * Q_{01}$$

$$Q_{23} = Q_{12} + Q_{02}$$

$$Q_{34} = Q_{23} + Q_{03}$$

$$Q_{15} = 0.98 * Q_{01}$$

LOADING EQUATIONS

$$W_1 = W_{cc} + A_1 W_{prec} + S_1 W_{fc}$$

$$W_2 = A_2 W_{prec} + S_2 W_{fc}$$

$$W_3 = A_3 W_{prec} + S_3 W_{fc}$$

$$W_4 = A_4 W_{prec} + S_4 W_{fc}$$

$$W_8 = W_{fc} + A_8 W_{prec} + S_8 W_{fc}$$

W_i = external sulfate loading into segment i.
 W_{cc} = sulfate loading from Contrary Creek.
 W_{fc} = sulfate loading from Freshwater Creek.
 W_{prec} = sulfate loading from precipitation.

Vertical Eddy Diffusion Coefficients

Sulfate transport via vertical eddy diffusion was calculated as the product of the vertical diffusion coefficient (K_z) and the interfacial area between the epilimnion and hypolimnion divided by the average depth of the two layers. There are no data about the magnitude of the vertical eddy diffusion coefficient in Lake Anna, so a value of 0.05 cm^2/sec was chosen as a first approximation of K_z , based on a range of literature values for a number of similar and dissimilar lakes.

Sulfate Removal Kinetics

Sulfate removal was modeled by the equation

$$V_i * dC_i/dt = k_{sulf} * C_i * A_i \quad (2)$$

where C_i is the SO_4^{2-} concentration in segment i (mols/ m^3), A_i is the surface area of segment i (m^2), V_i is the volume of segment i (m^3) and k_{sulf} is the sulfate removal coefficient (m/yr). Sulfate removal only takes place in segments overlying sediments. As modeled here, k_{sulf} describes the net reaction of sulfate reduction minus sulfide oxidation. The coefficient can be thought of as a piston velocity relating how many meters of water per year must be processed by the sediments to account for the observed sulfate removal.

Baker et al. (1986) presented an equation for calculating k_{sulf} based on the mean depth, water residence time, and sulfate retention of a lake:

$$k_{sulf} = R * z / (t_w * (100-R)). \quad (3)$$

In this equation, R is the retention of SO_4^{2-} as percentage of input, t_w is the water residence time (yr.), and z is the mean depth (m). Values of k_{sulf} in the present study were then calculated using the budget data from Herlihy et al. (1987). The average depth was calculated by dividing the Contrary Creek arm lake volume by its surface area ($4.4 \times 10^6 \text{ m}^3 / 1.1 \times 10^6 \text{ m}^2 = 4 \text{ m}$). Calculated values of k_{sulf} were 12.7 m/year in the 1983 water year and 14.1 m/year for the 1984 water year. These coefficients were used in the model in the kinetic expression for sulfate removal as shown in equation 2.

RESULTS

Model Calibration

Average epilimnetic and hypolimnetic sulfate concentrations predicted by the model for the 1984 water year were in good agreement with observed data. However, the model predicted little chemical stratification between epilimnion and hypolimnion using a K_z of $0.05 \text{ cm}^2/\text{sec}$. The observed SO_4^{2-} data showed a strong stratification at station C2 during most of the year and at station A2 in the winter. Therefore the model was rerun after changing the spatial and temporal values of K_z so that a reasonable fit to the data set was obtained. The K_z values for stations C5 and A2 were lowered to $0.01 \text{ cm}^2/\text{sec}$. In order to obtain a good fit to the observed station C2 data, the K_z had to be lowered even more to $0.002 \text{ cm}^2/\text{sec}$. It was also necessary to change the flow routing so that 98% of the water from Contrary Creek coming from segment 1 went into segment 5 (C2 hypolimnion). In order to fit the observed winter sulfate distribution at station A2, it was necessary to decrease all three K_z s to $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ from December 25 to February 15 to reflect the reduction in vertical diffusion due to ice cover on the lake. The ice cover would lower K_z by stopping any wind mixing.

To make the model more realistic, k_{sulf} was set to 0 during the months of January and February to reflect the cessation of sulfate removal as observed previously (Herlihy, 1987). During October, November, and December, k_{sulf} was decreased linearly with time from the maximum summer value to zero. Similarly during March, April, and May, k_{sulf} was increased linearly with time from zero to the maximum summer value. The maximum summer k_{sulf} (in effect from June through September) was calculated so that the value calculated in equation 3 was the annual average k_{sulf} .

After these calculations, the predicted SO_4^{2-} concentrations in both epilimnion and hypolimnion at station C2

were in fairly good agreement with the observed data (fig. 2). The model failed to predict the low hypolimnetic SO_4^{2-} concentrations in June and July. The model also underestimated SO_4^{2-} concentration in the epilimnion from October to April and overestimated it from July to September.

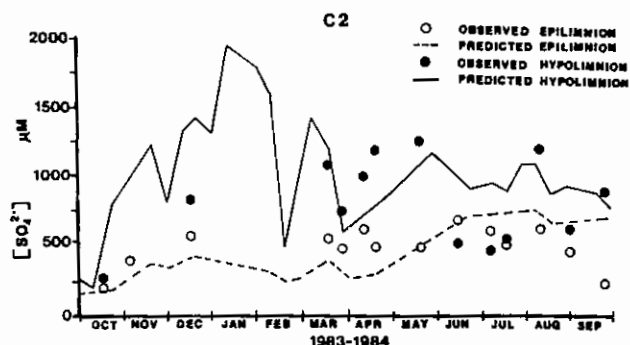


Figure 2. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station C2 (segments 2 and 5) during the 1984 water year.

The model predicted SO_4^{2-} concentrations at station C5 (fig. 3) better than it did at station C2. Most of the observed SO_4^{2-} concentrations were within 10-20% of the predicted concentrations. At station A2 the model predicted the observed SO_4^{2-} stratification in January and February (fig. 4). From June through September, the predicted SO_4^{2-} concentrations in the hypolimnion were about 50% lower than the observed concentrations.

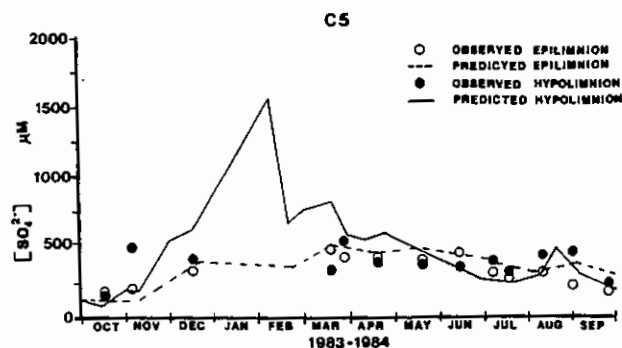


Figure 3. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station C5 (segments 3 and 6) during the 1984 water year.

Sensitivity Analysis

To understand the sensitivity of the model to k_{sulf} and K_z a sensitivity analysis of these parameters was

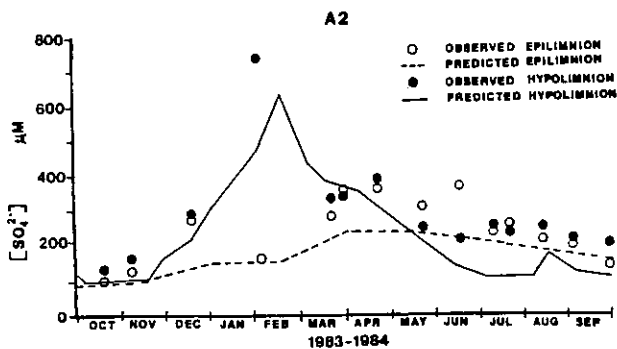


Figure 4. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station A2 (segments 4 and 7) during the 1984 water year.

performed. The predicted sulfate concentration in the hypolimnion at station A2 was very sensitive to small changes in k_{sulf} (fig. 5). The solid line in the middle of figure 5 was the 1984 value of k_{sulf} calculated from equation 3 (14.1 m/yr). The line predicting higher SO_4^{2-} concentrations represents an annual k_{sulf} of 1.85 m/yr and the lower SO_4^{2-} concentration line had a value of 70.0 m/yr. All of the k_{sulf} values in this exercise were set to 0 during the winter months and varied with time as described above. The sensitivity analysis shows that the range of acceptable values of k_{sulf} is small, about 5-20 m/yr.

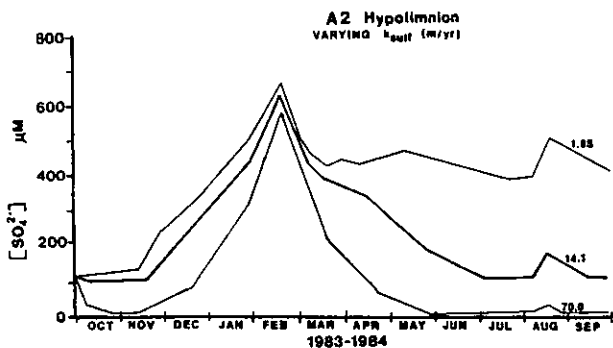


Figure 5. -- Model-predicted sulfate concentrations in the hypolimnion of station A2 (segment 7) at varying values (m/yr) of the sulfate removal coefficient (k_{sulf}).

The sensitivity analysis for K_z showed that large (order of magnitude) changes made small, but significant changes in the predicted epilimnetic SO_4^{2-} concentration at station C2 (fig. 6). With a K_z of $1 \times 10^{-4} \text{ cm}^2/\text{sec}$ there was little or no mixing between epilimnion and hypolimnion. Thus, predicted SO_4^{2-} concentrations were low and remained fairly constant with time

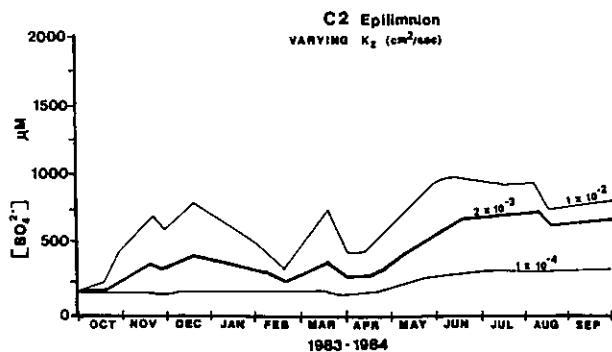


Figure 6. -- Model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion of station C2 (segment 2) at varying values (cm^2/sec) of the vertical eddy diffusion coefficient (K_z).

because waterflow through the epilimnion was low (only 2% of Contrary Creek inflow), and there was little SO_4^{2-} influx from direct input and precipitation. There was more SO_4^{2-} transfer between hypolimnion and epilimnion when K_z was $1 \times 10^{-2} \text{ cm}^2/\text{sec}$. The effects of different K_z values on the predicted hypolimnetic SO_4^{2-} concentrations at station C2 were less than 10% (data not shown).

Model Verification

The model was verified using data collected during the 1983 water year and the same values of K_z used in the calibration. The value of k_{sulf} used in the verification was 12.7 m/yr, and it was varied temporally as described above. The predicted SO_4^{2-} concentrations in the hypolimnion at station C2 were higher than the observed concentrations but the trends were similar (fig. 7). Observed epilimnetic SO_4^{2-} concentrations were scattered around the predicted concentration line.

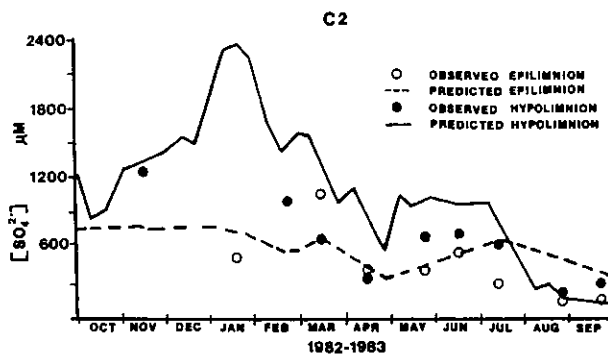


Figure 7. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station C2 (segments 2 and 5) during the 1983 water year.

Except for the late winter and early spring months, the observed and predicted SO_4^{2-} concentrations at station C5 were in good agreement (fig. 8). The high SO_4^{2-} concentrations predicted in the hypolimnion in the winter were not seen in the observed February and March data. The predicted and observed SO_4^{2-} concentrations at station A2 were also similar except for the predicted hypolimnetic sulfate peak in February and March that was not present in the observed data (fig. 9). Model efficiency was calculated using the verification data (predicted and observed) from March through September 1983. F values (sum of the squares of the observed data about the mean divided by the sum of the squares of the predicted data-observed data) were very low (ranging from 0.19 in the A2 hypolimnion to 2.03 in the A2 epilimnion); there was as much variance in the model prediction about the observed data as in the observed data about the mean.

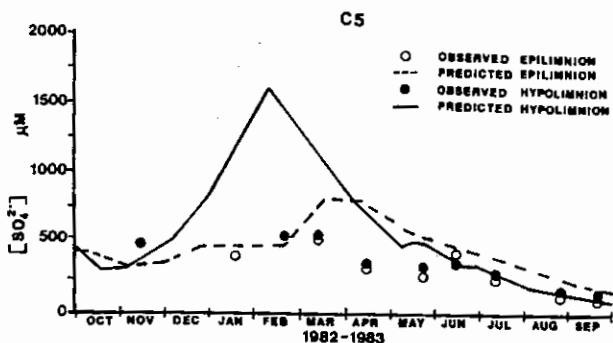


Figure 8. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station C5 (segments 3 and 6) during the 1983 water year.

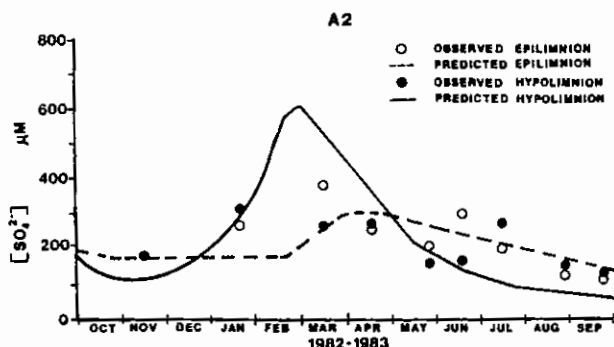


Figure 9. -- Observed and model-predicted sulfate concentrations ($\mu\text{mol/L}$) in the epilimnion and hypolimnion at station A2 (segments 4 and 7) during the 1983 water year.

In order to fit the model to the observed data, it was necessary to assume that 98% of the AMD inflow went into the hypolimnion of C2 and that K_z at station C2 was lower than the other stations. At C2 the more AMD impacted water in the hypolimnion has a higher density than the epilimnetic water so there is a barrier to mixing that would cause a lower K_z . At stations C5 and A2 the chemical gradient has been reduced by SO_4^{2-} and metal removal, dilution, and mixing so that the chemical barrier to mixing is reduced and a higher K_z would be expected. At certain times in the year, especially at station C2, the observed and predicted SO_4^{2-} concentrations were not very close. It is likely that the actual K_z varies more temporally than the K_z used in the model. Factors such as storm events, and large changes in air temperature, and wind direction could cause large changes in K_z for short periods of time. A storm event would carry in a large amount of dilute water destroying a chemical stratification and perhaps causing turbulent mixing. Similarly, the SO_4^{2-} maximum predicted by the model in January and February 1983 was not seen in the observed data. The ice cover in 1983 was much less than it was in 1984. If ice cover was the factor reducing K_z in the winter of 1984, it is likely that the K_z in the winter of 1983 should not have been as low as it was modeled. Actual measurements of K_z with time and the percent of AMD inflow entering the hypolimnion would enhance the predictive ability of the model.

Baker et al. (1986) reported a mean k_{sulf} of $0.46 (\pm 0.30)$ m/yr for 14 softwater lakes. They found that k_{sulf} was inversely related to the lake's residence time. Lakes with a long residence time allow more time for SO_4^{2-} to remove SO_4^{2-} yielding a higher SO_4^{2-} retention. Lakes with a short residence time, like Lake Anna, had a low SO_4^{2-} retention (<10% of input) since the SO_4^{2-} is rapidly flushed out of the lake. The values of k_{sulf} in Lake Anna (12-14 m/yr) were almost two orders of magnitude greater than the values reported by Baker et al. (1986). The implications of this drastic difference could be attributed to different SO_4^{2-} removal mechanisms. The lakes sampled by Baker et al. were all affected by acid precipitation, not AMD, and diffusion was said to be the major mechanism for SO_4^{2-} transport into the sediments. In Lake Anna, diffusion could account for no more than 5% of the observed SO_4^{2-} removal from the lake (Herlihy et al. 1987). A mechanism with a more rapid SO_4^{2-} transport rate could account for the higher k_{sulf} observed in Lake Anna. It has been hypothesized that SO_4^{2-} is transported to the sediment via adsorption onto settling solid particles or iron floc (Mills et al. in press).

Therefore the higher iron concentrations in Lake Anna could account for the higher k_{sulf} . The value of k_{sulf} in Lake Anna needed to make the model results match the observed results supports the hypothesis that some mechanism operating much more rapidly than diffusion is working to transport SO_4^{2-} to the sediments.

Another possible improvement to the model would be to adjust the SO_4^{2-} removal coefficient to account for the iron concentration. If iron flocculation is the major SO_4^{2-} transport mechanism then it is important to account for this process in the model. It is likely that SO_4^{2-} removal is most rapid near the mouth of Contrary Creek where the majority of the iron precipitates.

CONCLUSIONS

In order to accurately model the observed sulfate distribution in Lake Anna it was necessary to reduce both the vertical diffusion coefficient and the amount of Contrary Creek water flowing into the epilimnion. The steep chemical gradient near the mouth of Contrary Creek effectively inhibits vertical mixing. The observed data showed a great deal of fluctuation at station C2 indicating that the actual pattern of creek inflow and vertical diffusion has a great deal of temporal variability.

The predicted SO_4^{2-} concentration in Lake Anna was very sensitive to the SO_4^{2-} removal coefficient. The model results showed that the SO_4^{2-} removal coefficient could be calculated successfully using equation 3. The removal coefficient in Lake Anna was more than an order of magnitude higher than observed in lakes where diffusion is the major mechanism of SO_4^{2-} transport to the sediments. Thus some other transport mechanism plays an important role in removing SO_4^{2-} from Lake Anna.

LITERATURE CITED

Baker, L.A., P.L. Brezonik, and C.D. Pollman. 1986. Model of internal alkalinity generation: sulfate retention component. *Water Air Soil Pollut.* 31:89-94.

Bruckner, A. E. 1986. Groundwater lake interactions in fractured rock terrane. M.S. thesis, Dept. of Environ. Sci., Univ. of Va., Charlottesville. 88 pp.

DiToro, D.M., J.J. Fitzpatrick, and R.V. Thomann. 1983. Water quality analysis simulation program (WASP) and model verification program (MVP) documentation. Report submitted by Hydroscience, Inc. to the U.S. EPA environmental research laboratory, Duluth, MN.

Herlihy, A.T. 1987. Sulfur dynamics in an impoundment receiving acid mine drainage. Ph.D. Dissertation. Dept. of Environ. Sci., University of Virginia, Charlottesville. 214 pp.

Herlihy, A.T. and A.L. Mills. 1985. Sulfate reduction in freshwater sediments receiving acid mine drainage. *Appl. Environ. Microbiol.* 49:179-186.

Herlihy, A.T. and A.L. Mills. 1986. The pH regime of sediments underlying acidified waters. *Biogeochemistry* 2:95-99.

<http://dx.doi.org/10.1007/BF02186967>

Herlihy, A.T., A.L. Mills, G.M. Hornberger, and A.E. Bruckner. 1987. The importance of sediment sulfate reduction to the sulfate budget of an impoundment receiving acid mine drainage. *Water Resour. Res.* 23:287-292.

Lung, W.S. 1987. A lake acidification model: a practical tool. *J. Environ. Eng. In Press.*

Mills, A.L. 1985. Acid mine waste drainage: microbial impact on the recovery of soil and water ecosystems. pp. 35-81. In D. Klein and R.L. Tate (eds.), *Soil reclamation processes*, Marcel Dekker Inc., New York.

Mills, A.L., and A.T. Herlihy. 1985. Microbial ecology and acidic pollution of impoundments, pp. 169-189. In D. Gunnison (ed.), *Microbial processes in reservoirs*. Dr W. Junk Publ., Dordrecht.

Mills, A.L., P.E. Bell, and A.T. Herlihy. In press. Microbes, sediments and acidified waters: The importance of biological buffering. In S.S. Rao (ed.) *Microbial Interactions in Acid Stressed Aquatic Ecosystems*. CRC Press, Inc., Boca Raton, FL.

<http://dx.doi.org/10.1007/BF00630822>