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The Potential of Organic Matter Additions for Neutralizing Surface Mine Lakes

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ABSTRACT

The potential of anaerobic bacterial metabolism to raise the pH of acid lakes was tested by adding 9.1 metric tons of fresh cow manure to a 2.1 ha, 6 m deep, pH 2.9 coal mine lake near DeSoto, Illinois. This additive was expected to provide a substrate for sulfate- and iron-reducing bacteria that generate alkalinity. Lake water chemistry was monitored for 2.5 years in the treated lake and in a nearby untreated lake. The main effects of this cow manure addition were a rise in pH, iron, and sulfide and a decrease in oxygen, acidity, and aluminum in deep water of the treated lake during summer stratification. Surface water chemistry remained unchanged except for a decline in oxygen concentrations. During fall turnover, the chemistry of the entire lake returned to its pre-treatment condition. The results of this investigation indicate that anaerobic bacterial decay of organic matter can raise the pH of acid mine water. In our experiment low hydraulic retention time probably prevented a permanent increase in alkalinity and pH in the entire treated lake.

INTRODUCTION

Acid Surface Mine Lakes in Illinois

Lakes are common on lands surface mined for coal in Southern Illinois and adjacent states. These lakes form as groundwater seepage and runoff fill terminal box-cuts of land that have been strip-mined for coal (Grim and Hill 1974; Smith and Frey 1971). Many mine lakes are acid as a result of weathering of pyrite and marcasite in their watersheds (Stumm and Morgan 1970; Miller et al.1996). About 6 percent of the coal surface mine lakes in Illinois are acid (pH<5.0)(Haynes and Klimstra 1975). These lakes provide ideal locations to examine neutralization processes in sulfuric acid-contaminated lakes. They allow us to test the hypothesis that increased organic loading will enhance sulfate reduction which will raise lake pH.

pH Rises in Acid Lakes Caused by Internal Alkalinity Generation

Internal alkalinity generation, mostly by dissimilatory sulfate reduction (equation a), has been demonstrated in a variety of waters, including acid strip-mine lakes (e.g. Campbell and Lind 1969, King et al. 1974, Brugam and Lusk 1986, Brugam et al. 1990a,b, Fryson et al. 1998, Kleeburg 1998; Castro et al. 1999), constructed wetlands receiving acid mine drainage (Vile and Wieder 1993, Wieder 1993), in acid seeps from underground coal mines (Dvorak et al. 1991), and soft-water lakes vulnerable to acid rain (Anderson and Schiff 1987). The sulfate-reducing bacteria that are active in these waters require anaerobic conditions and an adequate supply of dissolved sulfate and organic matter (Baas-Becking et al.1960). Brugam et al. (1995) isolated anaerobic sulfate-reducing bacteria from an organically loaded enclosure in a strip-mine lake on the Will Scarlett Mine in Southern Illinois.

Acid mine waters typically have high sulfate concentrations, so it is more likely that organic matter might limit the rate of sulfate reduction in them than in low sulfate soft-water lakes. Additions of organic matter seem to be a promising treatment for acid mine waters (Castro et al. 1999).

Various kinds of organic matter have been added to mine water contaminated systems. Wieder (1993) tested five combinations of additives in constructed wetlands, including *Sphagnum* peat with limestone and fertilizer, *Sphagnum* peat alone, sawdust, straw/manure, and mushroom compost. The last two were most effective in generating alkalinity, but after two years their effectiveness diminished. Brugam et al. (1990a,b) added straw to enclosures in an acid mine lake, and did obtain alkalinity generation, but the pH change was not permanent. Davison (1986) added activated sludge and hydrated lime to an acidic sand pit, and obtained a rise in pH and internal alkalinity generation for about two years, but after that alkalinity and pH began to decrease.

Wieder (1993) has pointed out that treatment effectiveness of constructed wetlands continues to be both variable and rather unpredictable. More investigation is needed to determine the sources of this variability and unpredictability. For a permanent rise in pH it is necessary to prevent the reversal of the alkalinity-generating reactions and to keep alkalinity-generating reactions proceeding at a rate sufficient to remove incoming acid (Wieder 1993).

The reversal of alkalinity-generating reactions can be prevented by the escape of H_2S gas (King et al. 1974; equation a); by the formation of organic sulfur compounds (Anderson and Schiff 1987; reaction b); or by the formation and burial of FeS (Schindler et al. 1980; reaction c). Fe^{++} must be available for FeS precipitation and burial to proceed. Fe^{++} is produced by heterotrophic bacterial activity that also creates alkalinity (reaction d). The precipitation of FeS consumes alkalinity (reaction c).

a) $2CH_2O + SO_4^- + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$
b) $2C_{12}H_{22}O_{11} + 3C_{12}H_{26} + 7H_2S \rightarrow 4C_6H_8S + 3C_{12}H_{20}S + 22H_2O$
c) $Fe^{++} + H_2S \rightarrow FeS + 2H^+$
d) $CH_2O + 4FeOOH + 8H^+ \rightarrow CO2 + 4Fe^{++} + 7H_2O$

We wanted to test if organic matter (such as cow manure) added to a seasonally stratified high-sulfate coal mine lake could increase the rate and amount of internal alkalinity generated in the hypolimnion to permanently raise the pH of the lake.

METHODS

Study Lakes

Two acid lakes on the Burning Star #1 mine site near DeSoto, Illinois, were used for this study (Table 1). The site was surface mined before 1968. The lakes were chosen because of their small size and relatively large depth. Pit Y was the untreated lake; Pit C was the treated lake which received repeated additions of cow manure starting on Oct. 19, 1991 (Figure 1).

The hydrology of the lakes differed. The untreated lake had no inlet or outlet, but was separated from a very acidic lake (pH=2.5) by an approximately 15 m wide road. A small pile of exposed mine spoil was evident on the southeast shore of the untreated lake. We hypothesize that the acid contamination of the untreated lake occurs by seepage through the fill which supports the road.

The treated lake has a small inlet and outlet which run only in late fall to late spring. At other times the lake is fed by groundwater. Input of acid water to the treated lake is probably by surface run-off because it is surrounded by many large, groundwater-fed lakes with pH>7.0 suggesting that the groundwater itself is not acid. The lake has a number of large piles of unvegetated surface mine spoil on its shore.

Organic Additions

Cow manure used in dosing the treated lake was scraped directly from the feed lot floor at the Southern Illinois University at Carbondale Dairy Barns. Additions were carried out at irregular intervals over a period of about a year and a half (Figure 1). The largest amounts of cow manure were added in May 1992 and September 1992.

The phosphorus and nitrogen concentrations of the cow manure were measured by Alvey Laboratories, Belleville, IL.

Field Sampling

Both lakes were sampled at approximately two week intervals from 18 July, 1991, to 28 October, 1993. Water level was measured from an arbitrary fixed reference point with a board calibrated in centimeters. Secchi disc readings were taken, and water was sampled at the deepest location at one meter intervals with a Kemmerer sampler. Each water sample was divided into three containers; a 250-ml acid-washed and distilled-water-rinsed polyethylene bottle and two 300-ml glass BOD bottles. Temperature was measured immediately, and pH within one hour, in the polyethylene bottle. One of the BOD bottles had 1 ml of 1N zinc acetate solution for sulfide measurements, the other was treated with Winkler reagents for oxygen measurements.

Laboratory Methods

All procedures were taken from Standard Methods (American Public Health Association 1985). Acidity was measured within 6 hrs by boiling with H_2O_2 and titrating potentiometrically with 0.02 N NaOH to pH 8.3. Alkalinity was also measured within 6 hrs by titrating with 0.02 H_2SO_4 to pH 4.4. Alkalinity measurements were made only if the starting pH of the water was >4.4. Total phosphorus was measured by the phosphomolybdate-blue method on unfiltered samples digested with persulfate. Ascorbic acid was used as the reducing agent.

Oxygen was measured by iodometric titration of the Winkler samples with 0.025 N $Na_2S_2O_3$ within six hours of collection. Total sulfide was measured by titration of the zinc-acetate dosed BOD bottles with 0.025 N $Na_2S_2O_3$ within 24 hours of collection.

One hundred ml subsamples were taken from the plastic bottle, acidified with HNO_3 and stored at 4^o C for analysis of sulfate, aluminum, and iron. Sulfate was determined turbidimetrically using barium chloride. Aluminum was measured with the Eriochrome Cyanine method. Iron was determined by atomic absorption using a Varian model A10 atomic absorption spectrophotometer.

RESULTS

Water Level

Water level changes in both lakes were nearly synchronous (Figure 2). Levels rose in November 1991 and remained high until June 1992. The lowest levels occurred in autumn 1992. In late November levels again rose and remained high until the end of the study in September 1993. Both sites were flooded through 1993. That year was extremely wet, causing floods throughout the Midwestern U.S.

Water levels were somewhat correlated with rainfall as measured at Carbondale, Illinois, approximately 15 km away.

Changes in Lake Water Chemistry

All results of chemical analysis of lake water are presented as isopleth diagrams (Figures 3 to 12). These diagrams show amounts of the various chemical and physical parameters as contours. The x axes of the graphs are dates and the y axes are depth below the water surface. Isopleth graphs summarize complex lake data in a concise form (Wetzel 1983).

Temperature and Oxygen

The temperature isopleth diagram shows that both lakes were thermally stratified from June through October of 1991, 1992 and 1993 (Figure 3). Oxygen levels in the hypolimnion of the treated lake were low in 1992, but lower still in 1993 (Figure 4). In 1992 the 5 mg/L isopleth reached 5m depth, but after most manure additions in 1993 that isopleth reached the lake surface. In contrast, hypolimnetic oxygen levels remained relatively high in the untreated lake. During late summer 1992 the untreated lake had a metalimnetic oxygen maximum (Wetzel 1983) that was greater than 15 mg/L (indicated by arrows in Figure 4).

pH, Acidity and Alkalinity

Most of the water column of both lakes had a pH near 3.0 (Figure 5). The exception occurred during summer stratification when pH rose in both lakes. The highest pH (6.0) was measured at the very bottom of the treated lake during the summer of 1993. During fall 1991 the whole water column of the untreated lake reached a pH of 4.0.

Acidity of both lakes remained between 100 and 200 mg/L $CaCO_3$ during most of the study (Figure 6). Alkalinity could only be measured in the hypolimnion of the treated lake during the summer of 1993 after all manure had been added (Figure 7).

Sulfate and Sulfide

During 1992 the sulfide concentration of the treated lake hypolimnion reached 0.2 mg/L but during 1993 it reached 0.4 mg/L(Fig. 8). Sulfide was undetectable in the untreated lake during the summer. Low levels of sulfide were distributed throughout the water column during fall 1991. Sulfate concentrations were similar in both lakes (about 800 mg/L)(Figure 9).

Aluminum and Iron

Aluminum concentrations were nearly constant throughout the water columns of both lakes during this study. Although it is not evident from Figure 10, aluminum concentrations declined to values less than 1 mg/L at 6 m depth in the treated lake from mid-June to September 1993. Overall aluminum concentrations were lower in the untreated lake during the whole study, but they never declined below 1 mg/L.

Measurable dissolved iron appeared in the hypolimnia of both lakes during the summer (Figure 11). The iron concentration was, however, greatest (75 mg/L) at 6 m in the treated lake during 1993.

Total Phosphorus

Total phosphorus concentrations were mostly unchanged in both lakes except for the hypolimnion of the treated lake during the summer of 1993 (Figure 12). At that time total phosphorus concentrations reached 2,000 μg/L - a level seen in the hypolimnia of only the most highly eutrophic lakes (Wetzel 1998; Brady 1999).

Transparency

In spite of the additions of nutrient-rich cow manure, water clarity did not vary much during this study (Figure13). What variation did occur was not related to the timing of the cow manure additions.

Summary of Physical and Chemical Changes in Both Lakes

The largest changes in physical and chemical variables were seen in the treated lake during the summer of 1993 after all cow manure had been added. Oxygen levels were low throughout the water column. Alkalinity, pH, dissolved iron, total phosphorus and sulfide reached their highest levels in the lake hypolimnion. Aluminum declined. Acidity and sulfate were unchanged. Similar changes did not occur in the untreated lake.

DISCUSSION

The changes in the hypolimnion of the treated lake occurred in a sequence consistent with the Anderson and Schiff (1987) lake neutralization model and were similar to changes observed by Sigg et al. (1991) in the Greifensee, a eutrophic Swiss lake of moderate pH.

Oxygen disappeared, pH, sulfide, phosphorus, and iron increased in late spring or summer each year, as aluminum decreased. These changes were more pronounced in the summer of 1993, and indeed only then was alkalinity detectable. Presumably, the additional time allowed more decomposition of the cow manure.

The addition of nutrient-rich organic matter did not seem to change the trophic status of the treated lake. While it is true that deep water total phosphorus levels increased when the cow manure was added, there was no decrease in lake transparency due to the organic matter additions (Figure 13).

Alkalinity Production by Added Organic Matter

Although the pH of the deep water of the treated lake did begin to rise after organic matter was added, there was insufficient alkalinity to raise the pH of the whole lake. It is clear that each mole of organic carbon consumed in sulfate reduction should produce at maximum 2 equivalents of acid neutralizing capacity assuming that all of the organic matter added could be metabolized by the bacteria present. If this is true, then the amount of organic matter added to the lake (1970 kg) should have reduced the acidity of the lake by 2.6 milliequivalents per liter (130 mg $CaCO_3$/l). While that addition might not have entirely removed all acidity from the lake, it should have caused a greater reduction in acidity than we saw.

The production rate of Acid Neutralizing Capacity (ANC) by the treated lake sediment can be estimated from the changes in alkalinity and acidity in the hypolimnion. We estimate net ANC by subtracting our measured acidity from alkalinity. From March to August 1993 net ANC increased in a linear fashion (Figure 14) at a rate of 0.033 meq/l/day. Assuming a 1 m thick hypolimnion, the rate of ANC generation by the sediment was 330 meq/m^2/day. A similar calculation made with Sigg et al.'s (1991) data from the Greifensee yields a rate of 136 meq/m^2/day. This rate of ANC generation is much higher than that inferred by Brugam et al. (1988), Giblin et al. (1990), and Norton et al.(1988) using the accumulation rates of reduced sulfur compounds in the lake sediment.

Our calculated rate of ANC generation also explains why the pH of the whole lake was not raised by our cow manure addition. The area of the lake at 6 m depth was 1200 m^2. In total the hypolimnetic sediment produced 396 eq of ANC per day (1200 m^2 x 330 meq ANC/m^2/day = 396 eq ANC/day). Although the generation rate of ANC was higher in the treated lake than in other lakes reported in the literature (Brugam et al. 1988; Giblin et al. 1990; Norton et al. 1988), the total amount of acidity in the lake was higher still ($2x10^6$ eq). The rate of ANC generation was far too slow to remove all of the acidity in the treated lake over any reasonable time period although it did increase pH and alkalinity in the hypolimnion for a time. We hypothesize that the thermal stratification of the lake prevented the circulation of acidic water into the hypolimnion of the treated lake during the summer of 1993 allowing ANC to build up.

Although the rate of ANC generation was high in the treated lake, a number of factors could have reduced the efficiency with which anaerobic processing occurred in this lake. The low pH of the lake water itself might have reduced the rate of sulfate reduction in the treated lake. Gyure et al. (1990) found that sulfate reducing bacteria from a pH 3.8 coal mine lake had an optimal pH for sulfate reduction of 5.0.

Vastly increased organic matter loading might have allowed us to keep the deep waters of the lake at a sufficiently low redox potential to cause neutralization. Such additions might have caused the whole lake to become anaerobic resulting in a pollution problem different from acid mine drainage. Kleeburg (1998) has suggested that the addition of organic matter to acid surface mine lakes would eventually sequester iron as FeS, liberating phosphate from the lake sediment causing a massive eutrophication problem. During the summer of 1993 it appears that this process had begun in the hypolimnion of the treated lake.

A factor that influences the effectiveness of bacterial iron and sulfate reduction in removing sulfuric acid from water is the sensitivity of the process to changes in temperature. Gyure et al. (1990) found that bacterial sulfate reduction is highly temperature sensitive proceeding most rapidly at 37° C -- an unlikely temperature in Midwestern U.S. lakes. Cooler temperatures cause proportionate reductions in metabolic rates. Herlihy and Mills (1985) in a study of Lake Anna, Virginia, found that sulfate reduction rates were lowest in winter and highest in summer. In our study, this temperature sensitivity of bacterial sulfate reduction means that alkalinity generation would be most vigorous in summer.

It is probable that the location of most sulfate reduction is the sediment. Anderson and Schiff (1987) point out the ubiquity of sulfate reduction within a few centimeters of the sediment/water interface in lakes. If the major effect of cow manure addition in the treated lake was to increase sulfate reduction in the sediment, then alkalinity generation would have been limited by the diffusion of sulfate into the sediment and alkalinity out of the sediment. Schiff and Anderson (1986) analyzed pore water from epilimnetic sediments in eight lakes and found that the zone of sulfate consumption was deepest in the two most acid lakes and that the alkalinity flux from the sediments was least in those lakes.

It may be that cow manure additions did not raise the pH in the whole water column of the treated lake because the input of acid from surrounding spoil banks overwhelmed alkalinity production from the sediment. The treated lake is small and receives a heavy input of acid water from an adjacent lake during rainy periods. The hydraulic retention time of the treated lake is also probably too short in relation to the rate of ANC generation to allow the accumulation of significant alkalinity in the water column. It is likely that rates of water flow through the treated lake varied from season to season. Baker et al. (1986) emphasize the importance of long hydraulic residence times in the removal of sulfuric acid contamination in lakes by sulfate reduction. Our pH rises occurred in the summer, when thermal stratification and low water levels extended hydraulic retention times.

Finally, one might argue that the cow manure itself may have kept the lake acid. Nitrification (the oxidation of ammonium to nitrate) releases 2 equivalents of acid per mole of ammonium (Baker et al. 1985). Raw cow manure contains large amounts of reduced nitrogen compounds (Table 1). If all of the nitrogen added to the treated lake were oxidized to nitrate only 0.27 meq/L of acid would be produced. Thus, oxidation of reduced nitrogen compounds in the cow manure is unlikely to have confounded the neutralization effects we expected.

Our field experiment can be compared with work by Davison (1986) who added hydrated lime and a slurry of human sewage to a pond in an acid sand quarry in England. His pond was similar in volume to our treated lake and his addition rates of organic matter were similar to ours. His work was different from ours because he added calcium hydroxide with the organic matter. Davison's additions caused rapid neutralization, but it is difficult to differentiate the effect of the hydrated lime from that of the organic matter in his experiment. It may be that additions of chemical neutralizing agents might enhance the effect of added organic matter.

CONCLUSIONS

Our results show that bacterial sulfate and iron reduction can raise the pH of waters contaminated by sulfuric acid. However, the simple addition of moderate amounts of organic substrate to waters contaminated with sulfuric acid may not be adequate to remove acidity in the whole lake because bacterial activity is limited by a number of chemical and physical processes including low temperature and low pH. Furthermore, lakes with short hydraulic retention times receiving much additional acidity from surface and subsurface inputs will require much larger amounts of organic matter additive than lakes in which water is retained for a long time. The potential to exchange one form of pollution (organic matter) for another (sulfuric acid) suggests that organic matter additions be done carefully.

ACKNOWLEDGMENTS

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Table 1. Comparisons of the treated and untreated lakes.

	Treated Lake Pit C	Untreated Lake Pit Y
Maximum Depth (m)	6	11
Surface Area (ha)	2.1	1.4
Volume (m^3)	50,000	100,000
pH	3.1	3.8
Acidity (meq/l)	4.0	2.0
Location (Latitude)	47°50'30"N	47°50'00"N
(Longitude)	89°14'30"W	89°15'30"W
ADDITIVES		
Total cow manure added (kg)	9,092	0
Total organic matter added(kg)	1,970	0
Total P added in cow manure (kg)	28	0
Total Kjehldahl N added in cow manure (kg)	94	0
LOADING RATES		
cow manure g/m^2	408	0
organic matter g/m^2	94	0
Total P g/m^2	1	0
Total Kjehldahl N g/m^2	2	0

Figure 1. Dates and amounts of cow manure additions to the Treated Lake.

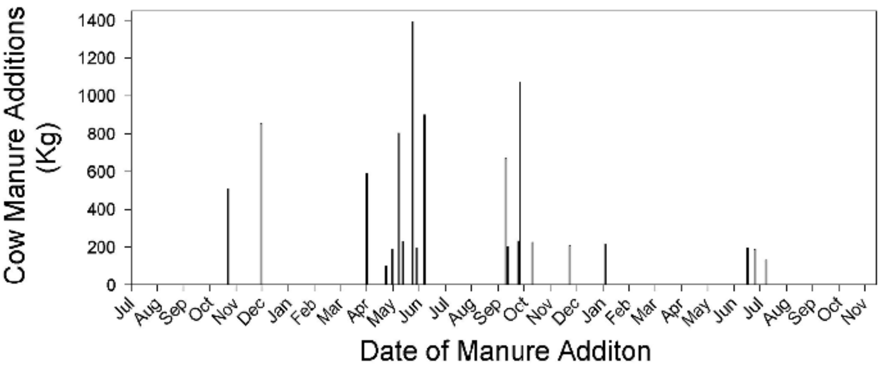

Figure 2. Variations in water level in the study lakes.

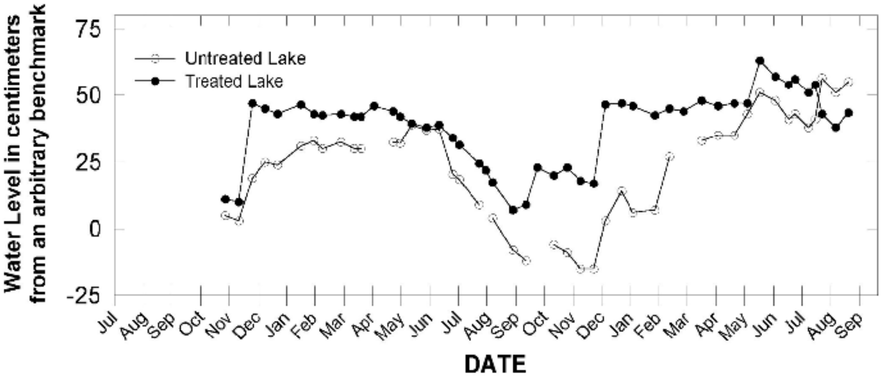

Figure 3. Lake temperature. Contour interval = 10ºC.

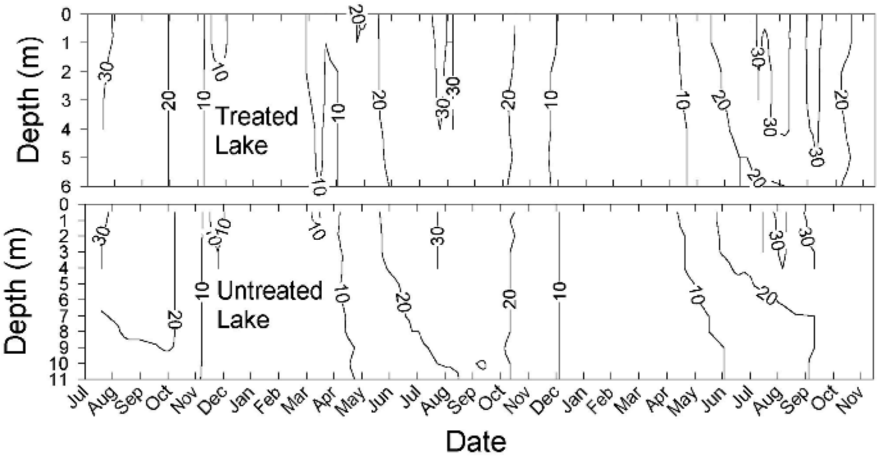

Figure 4. Lake oxygen concentrations. Contour interval=5 mg/L.

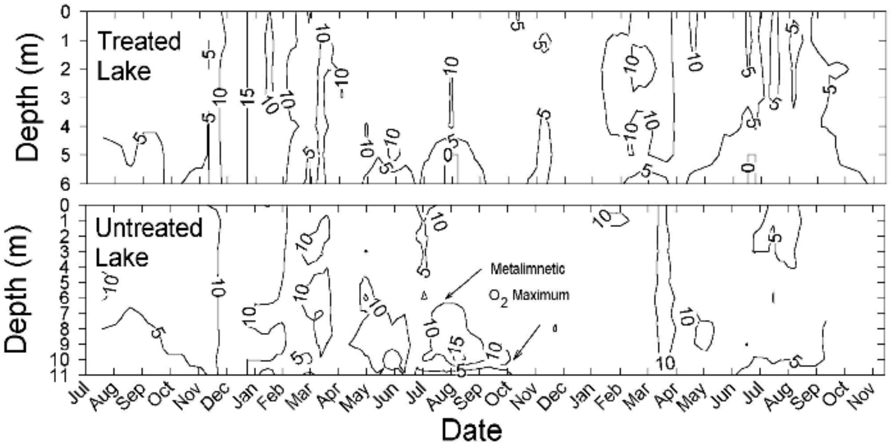

Figure 5. Lake pH. Contour interval= 2 pH units.

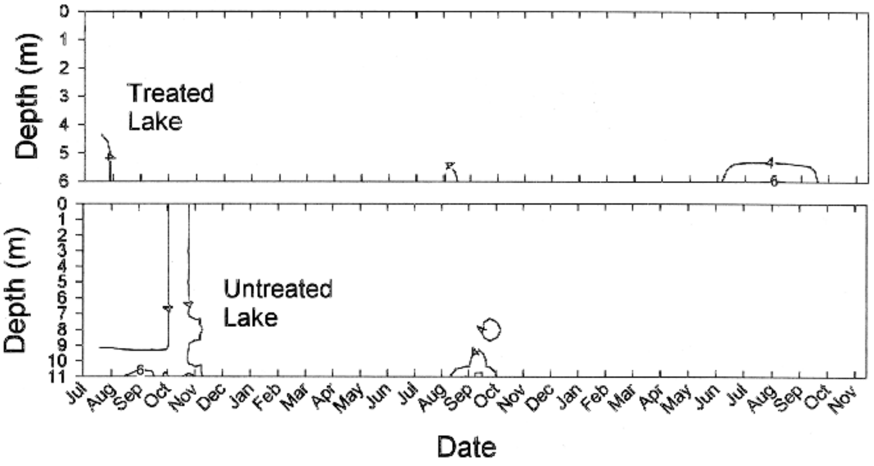

Figure 6. Lake acidity. Contour interval=100 mg/L $CaCO_3$.

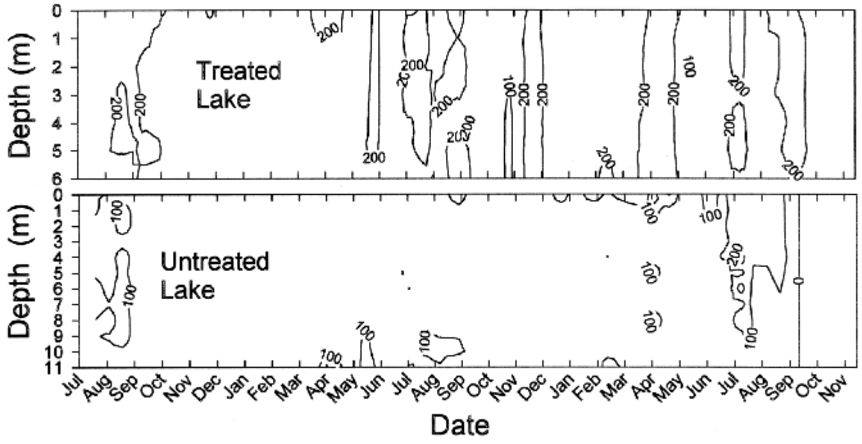

Figure 7. Lake alkalinity. Contour interval=24 mg/L $CaCO_3$.

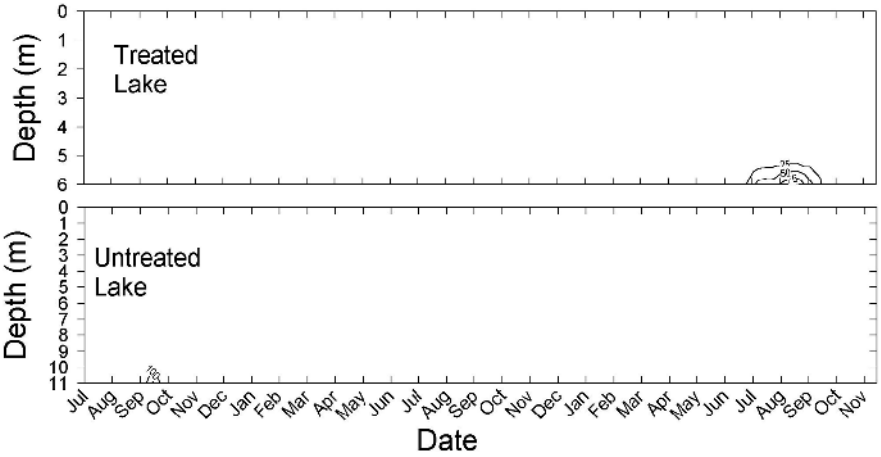

Figure 8. Lake sulfide concentrations. Contour intervals as indicated.

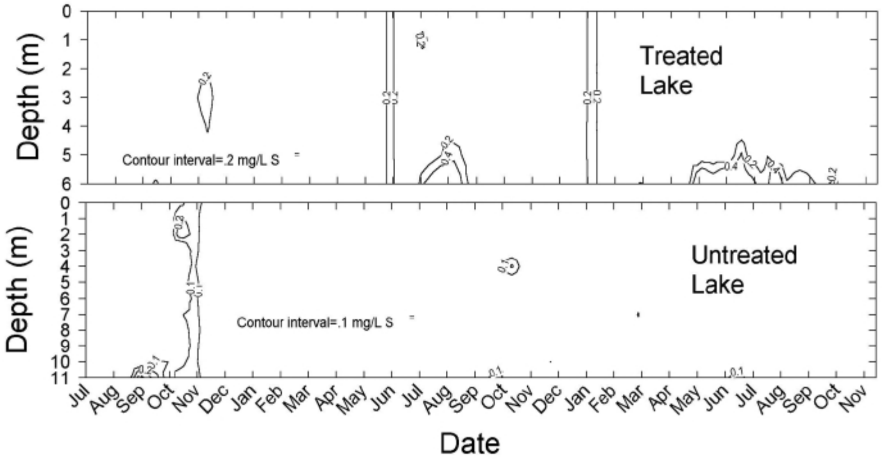

Figure 9. Lake sulfate concentrations. Contour interval=400 mg/L.

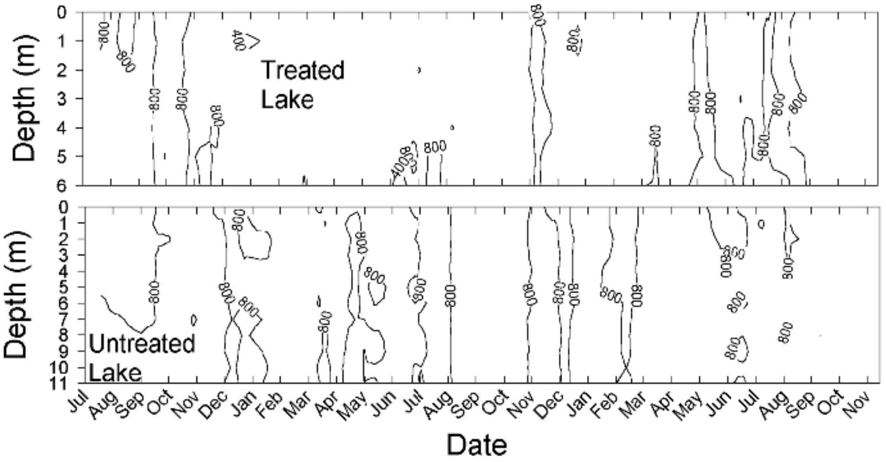

Figure10. Lake aluminum concentrations. Contour intervals as indicated.

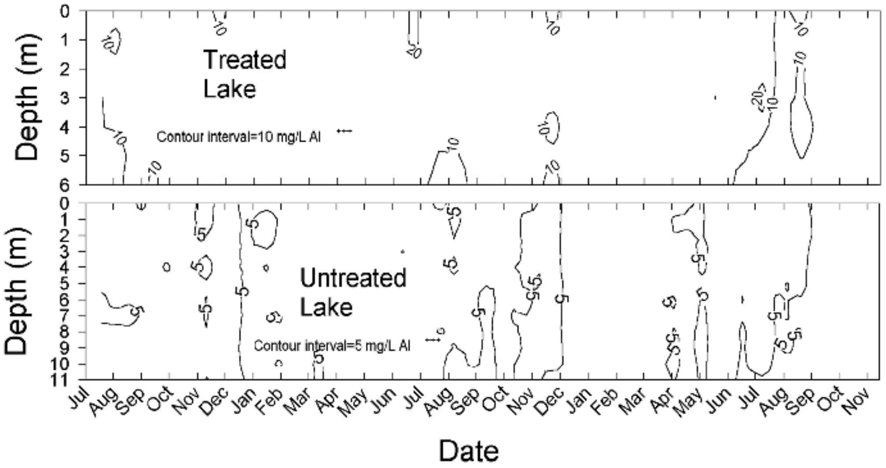

Figure11. Lake iron concentrations. Contour interval=25 mg/L.

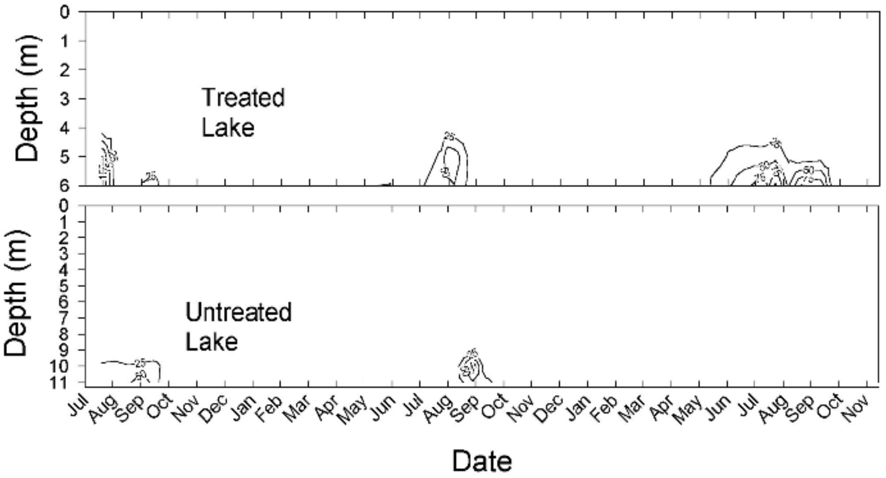

Figure12. Lake total phosphorus concentrations. Contour intervals as indicated.

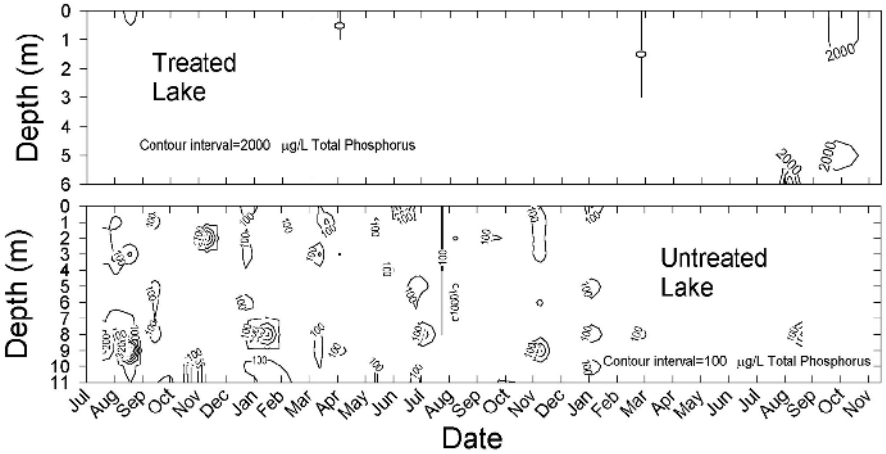

Figure13. Secchi disc transparency in meters.

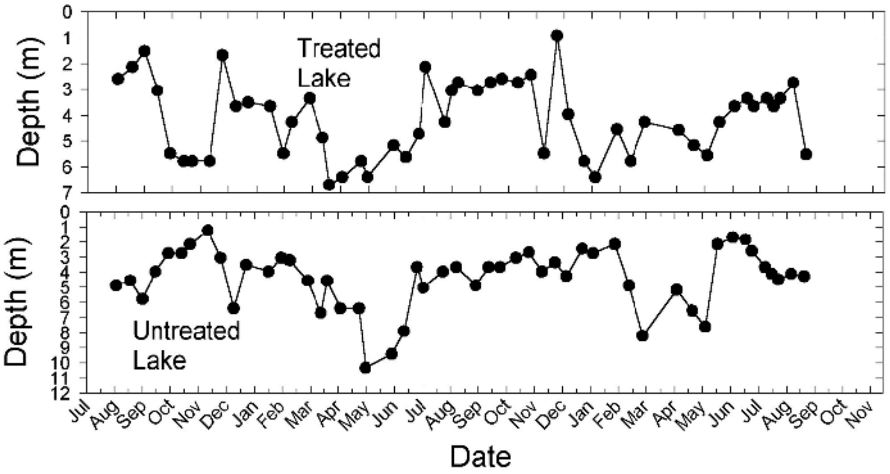

Figure14. Variations in acid neutralizing capacity (ANC) in the hypolimnion of the treated lake from March to August of 1993. ANC cannot be calculated for the untreated lake.