

Microbial ecology and acidic pollution of impoundments

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Abstract. Many impoundments are becoming acidified by acid precipitation (AP) and acid mine drainage (AMD). Because of its more dilute constitution, AP is not expected to significantly affect microbial processes in mesotrophic or eutrophic impoundments, although some reduction in heterotrophic activity might be expected in oligotrophic situations. AMD can cause extensive alteration of the microbial community and associated functions. The input of sulfate in the pollution tends to enhance bacterial sulfate reduction in the anaerobic waters and sediments of the impoundment. Sulfate reduction generates carbonate alkalinity which can effectively neutralize the acid pollution if the alkalinity is not consumed by CO₂ fixation during reoxidation of the reduced sulfur species. Presence of reduced iron precipitates the sulfides preventing diffusion into the oxic zones. Bacterial sulfate reduction represents an important homeostatic mechanism in acidified impoundments, and should be explored as a possible management tool for impoundments acidified by AP or AMD.

Introduction

Acid pollution of surface waters comes largely from two sources, acid precipitation and acid mine drainage. While the qualitative constituencies of these contaminants is similar, quantitative differences and input differences dictate dissimilar effects on the receiving waters. Furthermore, major differences between lakes and reservoirs may generate dissimilarities in effect within each pollutant type. This chapter will examine problems of acidification of surface waters with special attention paid to reservoirs in light of their many differences from lakes. The effects of acidification on the microbial processes and the concomitant effect on overall water quality will be discussed, and details of the microbial effect on the acid pollutants will be presented. Because of a lack of direct information on acid pollutants and microorganisms in impound-

ments, it will be necessary to draw on knowledge of other systems, and to extrapolate to impoundments using knowledge of the similarities and differences between those systems.

Effects of any environmental perturbation on microbes may be expressed through an alteration of the structure of the community, a qualitative or quantitative alteration in the ecosystem functions carried out by the community, or a combination of structure/function changes. Community structure encompasses the identity of the organisms present and the distribution of individuals among the various guilds or taxonomic groups (Mills & Wassel, 1980). While changes in community structure may be of interest to the academic ecologist, such alterations are of importance to the ecosystem only if they are associated with changes in the functional status of the community. Thus, studies which merely list species present before and after acid-

ification or in acidified vs non-acidified waters are irrelevant from a system viewpoint and will be largely ignored in this discussion. Instead, acidification effects will be approached from a functional viewpoint, i.e. how do acid precipitation and acid mine drainage affect the ability of the microbial community to carry out essential ecosystem functions such as primary productivity, organic matter decomposition, nutrient cycling, and pollutant diminution.

Magnitude of the problem

Acid rain

The most important acidic pollutants affecting streams, lakes, and impoundments are acid precipitation and acid mine drainage. Acid rain (defined as having a pH less than 5.0) is generated by the dissolution in the atmosphere of emissions from the burning of fossil fuels. Of primary importance are the oxides of sulfur and nitrogen, which, when dissolved, form sulfuric and nitric acid, respectively. Acid precipitation was described in England in 1955 (Gorham, 1955), and the Scandinavians first recognized the problem as regional in the late 1960's (Haines, 1981). In the United States, the most seriously affected region is the northeast where typical pH values for precipitation have been below

5 for many years. Acidity of the rainfall is still increasing, and the area impacted by acid rain continues to increase as well (Fig. 1). In addition to acidity, much of the precipitation that falls from air parcels contaminated with industrial emissions also may contain many metals (Table 1).

Acid precipitation must be considered as a non-point source pollutant, and the extent of alteration of the lake or impoundment by acid precipitation is dependent not only on the precipitation composition, but also on the geologic and hydrologic characteristics of the entire watershed feeding the reservoir. Except for that portion of the rain that falls directly on the lake, the composition of the water actually entering the water body will depend on the ability of the watershed to neutralize the acidity, and remove the trace element pollutants. As seen in Table 1, stream water entering lakes is generally higher in pH than the incoming precipitation. However, the stream chemistry is altered by the precipitation, usually including a reduction in pH, so that some portion of the acidity of the precipitation is transferred to the reservoir. The watershed serves as a buffer, and in many cases, the buffer capacity is quite weak. In such areas, lakes and reservoirs may lose alkalinity and suffer declining pH. The most notable changes have been reported for lakes in Scandinavia, Nova Scotia, Ontario, Quebec, Maine, New Hampshire, New York, New Jersey, North Carolina, and Florida (Haines, 1981).

Table 1. Constituents in acid mine waters, acid precipitation, and precipitation affected streams from several geographical locations and mineral sources. Units of concentration are $\mu\text{M/l}$.

	Balaklala CA Metal	Weil CA Metal	Mammoth CA Metal	Argo CO Metal	Contrary VA Sulfur	Karvatn ^a Precip	Denmark Stream	Birkenes ^b Denmark Precip
pH	2.75	1.61	2.83	2.60	2.85	4.90	5.95	—
Sulfate	7450	120000	10400	23700	3000–20000	34	24	5.1
Fe ²⁺	68	13000	32	100	35	—	—	—
Fe ³⁺	1840	35000	2970	3090	2010	—	—	—
Cu	255	4890	330	109	46	—	—	—
Al	626	5000	447	663	1073	9.0	—	—
Cd	—	15.0	2.7	1.0	—	0.002	—	0.0004
Zn	274	4800	449	675	172	0.274	—	0.046
Pb	—	3.4	—	—	—	0.052	—	0.007

^a Norwegian State Pollution Control Authority, 1983, and Hannsen *et al.*, 1980

^b Hannsen *et al.*, 1980

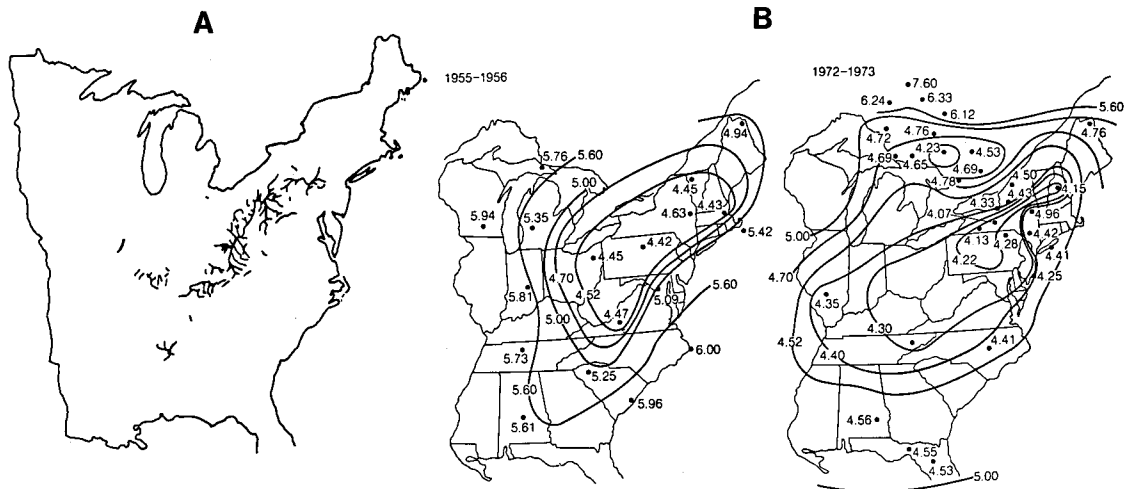
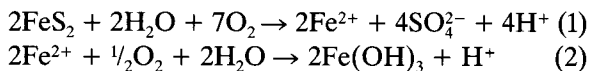


Fig. 1. Major areas of the United States affected by acid mine drainage (A) and acid precipitation (B). Data taken from Council on Environmental Quality (1982).

The degree which bodies of water are affected by acidic inputs is greatly dependent on the amount of bicarbonate present. Lakes with high alkalinities are not greatly influenced by acid rain. Goto *et al.* (1978) found that the pH of Lake Toya did not decrease appreciably despite the addition of acid mine drainage until the lake's alkalinity was depleted. The major factors effecting the vulnerability of a lake to acid rain are the watershed bedrock geology, soil cation exchange capacity, and permeability. Weathering reactions consume protons so that a watershed composed of an easily weatherable bedrock can buffer acidic inputs. Watersheds made up of resistant rocks such as granite or shale do not buffer acidity well and are susceptible to acid rain (Hendrey *et al.*, 1980; Root *et al.*, 1980; Galloway & Cowling, 1978). Watersheds that have soils with a high cation exchange capacity are also more resistant to acid rain since the protons can be trapped in the soil layer (McFee *et al.*, 1977). Galloway *et al.* (1983) found that two lakes with similar bedrock geology had different pHs due to different soil permeabilities. The watershed with the low permeability effectively funneled the acid precipitation into the low pH lake while the lake with the higher permeability allowed more rain water to infiltrate so that cation exchange and weathering reactions could buffer the acidity before it reached the lake.

Acid mine drainage

Acid mine drainage (AMD) is the effluent formed by the oxidation of reduced iron and sulfur to generate ferric iron, SO_4^{2-} and acidity.



Recent reports (Council on Environmental Quality, 1981) estimate that over 17,000 km of major streams in the United States are contaminated with AMD (Fig. 1). Many of those streams have been dammed for one reason or another, and the AMD contamination then becomes important to the impoundment as well as the stream. As seen in Fig. 1, the most serious AMD problem (on a regional basis) occur in the eastern portion of the United States, in an area that is also receiving acid precipitation. Thus, reservoirs in the eastern US are receiving acid pollutants both from the atmosphere and from mining activities. Acid mine drainage is also a serious problem on a local scale in other parts of the country where mining activity is intense. Examples include the iron-rich region near Redding, California and the metal-rich region west of Denver, Colorado. For example, drainage from mines in the former area (See Table 1) enters Lake Shasta via Squaw Creek.

Acid mine streams are very different from those

polluted by acid rain. Stream pH values are often below 2, and the concentration of dissolved solids, including metals, is very high (Table 1). In addition to the obvious chemical and biological effects, the acid mine streams may also have altered physical properties. The density contributed to the stream-water by the dissolved solids causes the water to behave like much colder water or like weakly saline water. The result is an immediate plunge of the inflow stream to a level of neutral buoyancy. In some cases, that level may be near the thermocline (Koryak *et al.*, 1979), while in shallow, unstratified impoundments, the flow may be along the sediment surface (Rastetter *et al.*, 1984, Herlihy & Mills, 1985). This behavior is important in terms of the microbial response to the acid inflow and will be discussed in detail later.

Microbiological effects

As pointed out by Wright *et al.* (1976), the decline in fish populations is well documented, but the effects of acidification on other aquatic life is poorly studied. Surveys suggest that reducing the ambient pH will tend to inhibit the decomposition of allochthonous organic matter, and decrease the number of species of phytoplankton, zooplankton and benthic invertebrate while encouraging the growth of benthic mosses.

The recovery of a community or ecosystem from any perturbation may be depicted as in Fig. 2. The horizontal axis may represent units of time if the environment is static or if the perturbation ceases. A lake-watershed complex acidified by acid precipitation might recover from the insult if the pollution is halted. In dynamic systems, such as streams or impoundments, the horizontal axis might represent distance from the pollution source. Herein lies a set of differences for both lakes vs. reservoirs and for acid precipitation vs. AMD. Reservoirs frequently function more like streams than lakes. Furthermore, point source pollutants (e.g. AMD) behave differently than non-point source contamination (e.g. acid precipitation).

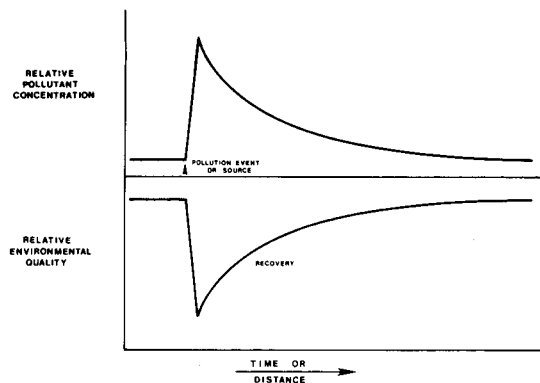


Fig. 2. General model of the abatement of pollution and the recovery of an ecosystem along a gradient of either time or space. Lakes would be expected to recover from a non-point source pollutant with time, while a reservoir receiving a point source discharge would demonstrate the response with distance from the insult.

Primary productivity

The effects of acidification on primary productivity by phytoplankton are not well studied. The most abundant evidence for an effect is in terms of a change in the number and type of species present. In fact, this may be the major effect. The number of species of phytoplankton in acidified lakes decreases as the pH declines (Almer *et al.*, 1974, 1978; Hendrey *et al.*, 1976; Kwiatkowski & Roff, 1976; Leivestad *et al.*, 1976; Yan & Stokes, 1978; Yan 1979), and the number of acidophilic species increases as the acidification proceeds (Leivestad *et al.*, 1976). Diatom diversity and the number of desmid species present in acidified Dutch moorland pools decreased over time as compared with unacidified pools (Van Dam *et al.*, 1980; Coesel *et al.*, 1978). Almer *et al.* (1974, 1978) reported that in Swedish lakes with pH above 6, the algal groups studied were about equally represented. As the pH declined, a reduction was observed for the Chrysophyta, Chlorophyta, and Cyanobacteria, and at pH 4 the Pyrrophyta became dominant. A similar pattern was obtained in several Ontario lakes (Yan & Stokes, 1976, 1978; Yan, 1979), however in other Ontario lakes, the Cyanobacteria became dominant as the pH decreased (Kwiatkowski & Roff, 1976). In the experimental acidification of Lake 223 in the Experimental Lakes Area, no change was

observed in the community structure of the phytoplankton (Schindler *et al.*, 1980). The acidification of that lake only changed the pH from 6.6. to 5.6.

A great many species of acid tolerant algae exist, and Rodhe (1981) suggested that species such as those found in some naturally acidic volcanic lakes in Japan be inoculated into culturally acidified lakes elsewhere to serve as a biological buffer against the acidification process. On the basis of observations of several Japanese lakes of different pH, Watanabe & Yasuda (1982) suggested that differences in the dominant diatoms in lakes of different pH values could be used for an acidity index.

The assumption is made that it is important to maintain the level of primary productivity in order to provide energy to higher trophic levels. There is little evidence to suggest that total phytoplankton production decreases with acidification of the lake or reservoir. Even in cases of extreme acidification, as by acid mine drainage, the acidophilic species take over and frequently generate extreme blooms. Chlorophytes such as *Ulothrix* are commonly found attached to rocks in acid mine streams with pH values from 2 to 3.

In cases where acidified lakes have been experimentally neutralized, the treatment initially decreased the standing crop of phytoplankton, and also zooplankton and benthic invertebrates (Schneider & Dillon, 1976). Within a year, the biomass of the phytoplankton was at the level observed prior to treatment, and species composition had begun to resemble that of unacidified lakes of the area. Similar effects have been observed in laboratory simulations (Yan & Stokes, 1978).

Measurements of primary productivity and production in acidified lakes are sparse, but those few studies suggest that acidification seems to have little effect on the biomass and productivity of phytoplankton as long as an adequate supply of phosphorus is maintained (Hendrey *et al.*, 1976; Almer *et al.*, 1978; Yan & Stokes, 1978; Dillon *et al.*, 1979; Yan, 1979; Raddum *et al.*, 1980; Wilcox & DeCosta, 1982). Experimental acidification of Lake 223 did not change the biomass or productivity of the phytoplankton (Schindler *et al.*, 1980). In several studies, growth of phytoplankton in lakes acidified

by acid precipitation or acid mine drainage was stimulated by the addition of phosphorus (Dillon *et al.* 1979; Wilcox & DeCosta, 1982). In experimentally neutralized lakes, the biomass of the phytoplankton is increased above that of pre-neutralization only by the addition of phosphate (Dillon *et al.*, 1979).

In summary, if acidification is to significantly impact the phytoplankton productivity of a reservoir, the mechanism is most likely to be alteration of the nutrient status as opposed to a direct pH effect on the algae.

Microbial heterotrophy

Similar to the studies on phytoplankton, much of the literature on bacterial and fungal effects of acidification consists of lists of organisms recovered from the polluted environment by various culture techniques (e.g. Weaver & Nash, 1968; Guthrie *et al.*, 1978). For the purposes of the present discussion, emphasis will be placed on those studies which provide information of relevance to ecosystem function.

Many heterotrophic microorganisms are inhibited at pH values below 5 or above 9 (Alexander, 1977). Concomitantly, any associated activities of those organisms also should be reduced in magnitude. In addition to the simple pH effects, other constituents of the pollutants may affect microbial activity. Such effects are most likely to be seen in the case of pollution by acid mine drainage where the concentrations of the compounds are much higher (See Table 1). Metals such as Cu, Cd, Pb, and Zn inhibit the functions of many microbes in polluted environments (Bhuiya & Cornfield, 1974; Mikkelsen, 1974; Babich & Stotzky, 1977; Jensen, 1977; Lawrey, 1977 a, b; Mills & Colwell, 1977; Bitton & Freihofer, 1978; Gadd & Griffiths, 1978; Bollag & Barabasz, 1979; Sunda & Gillespie, 1979; Zevenhuisen *et al.*, 1979; Sterritt & Lester, 1980).

In a comprehensive study of the combined effects of iron (the dominant metal in acid mine waters), H^+ , and SO_4^{2-} on bacterial growth, acidity was determined to be the most significant factor, with some concern for the amount of SO_4^{2-} present (McCoy & Dugan, 1968). Using test organisms

(strains of *Pseudomonas*, *Bacillus*, *Flavobacterium*) isolated from an unpolluted stream, it was concluded that the bacteria should grow if the pH were above 5.3, the iron concentration between 1 and 100 mg/l, and the SO_4^{2-} concentration between 5 and 500 mg/l. Growth of the organisms increased with increasing iron concentrations up to 100 mg/l at pH values greater than 5. The authors inferred that iron would not inhibit heterotrophic growth and activity unless the concentrations greatly exceeded 100 mg/l. The iron concentration in acid mine water may range as high as 10000 mg/l (see Table 1), so that the parameters applied by McCoy and Dugan would not be appropriate until the pH had increased to above 5 and the iron level had dropped to around 100 mg/l. In that state, the system might still be considered polluted, but certainly not so severely so as the majority of AMD contaminated waters.

In lakes acidified by acid precipitation, the action of the precipitation on the minerals in the watershed often leads to elevated levels of aluminum in the lake itself. The presence of the aluminum at levels in excess of 200 $\mu\text{g/l}$ (7.4 μM) in combination with low pH is toxic to fish (Grahn, 1980). The effect of elevated aluminum in acidified waters on the heterotrophic microbes has not been studied. Elevated aluminum in waters acidified by AMD is of little concern because of the comparatively greater effect of other dissolved metals and acidity (refer to table 1). Physiological data collected in laboratory experiments demonstrates that aluminum has variable effects on microbes; in some cases it is stimulatory, in others inhibitory, and in still others, no effect can be observed. For example, *Aspergillus niger* was stimulated by the addition of aluminum at concentrations of 0.19 to 3.7 μM (Bertrand, 1963), but aluminum was inhibitory to bacterial growth at all concentrations between 1850 and 14800 μM (Sulochana, 1952). Obviously, the great difference in concentration of the added aluminum precludes any conclusions drawn on the basis of comparisons of the two studies. The form in which the aluminum is added to the culture also influences the effect. Levels of aluminum above 370 μM added as an EDTA chelate were toxic to *Torula* and *Acetobacter* and similar ad-

ditions at concentrations of 926 – 1850 μM aluminum were toxic to *Saccharomyces* and *Pseudomonas* (Matsuda & Nagata, 1958). When aluminum oxide (Al_2O_3) was the amendment, *Staphylococcus aureus* was not inhibited at levels of 0.4% but was inhibited at 6 and 10% (Bunemann *et al.*, 1963). *Escherichia coli* was unaffected at all amendment levels. The variable results with aluminum additions suggest that in an acidified lake, the low levels of aluminum (as compared with those used in most of the cultural studies) might have an inhibitory effect on some specific member of the community, but that a more resistant strain might be expected to replace the functions vacated by the susceptible organism.

Although heterotrophic bacteria exist that are capable of growth in acid mine streams (Wichlach & Unz, 1981), the bacteria appear to be specialized organisms that have adapted to the extreme environment. Almost nothing is known of their activity, of their role in the ecosystem, or of their contribution, if any, to the rehabilitation of the polluted water. Some heterotrophs are capable of recovering and regrowing after exposure to concentrated AMD (Hackney & Bissonnette, 1978). In cases where heterotrophs are cultured from AMD, they are frequently considered to be transients that have entered the system from other aquatic or terrestrial sources (Wassel & Mills, 1983); Tuttle *et al.*, 1968).

The small amount of information available on the recovery of aquatic microbial communities from the effects of AMD and similar pollutants suggests that a successional pattern of increased heterotrophic biomass is observed along with a concomitant increase in the total activity of that community. Heterotrophs are known to be able to survive immersion in AMD. Although Carpenter & Herndon (1933) reported that wastewater was sterilized by exposure to AMD, all later work has demonstrated that viable heterotrophs can be recovered from mixtures of wastewater and AMD (Joseph & Shay, 1952; Hackney & Bissonnette, 1978). While many of the populations survive the exposure, most are injured or debilitated by the contact, such that attempts at isolation on selective media are often unsuccessful (Hackney & Bisson-

nette, 1978). Use of a less selective medium (Roth & Keenan, 1971; Hackney & Bissonnette, 1978) allows the organisms to recover from the effects of the AMD and to regain their former activity.

Natural situations in which heterotrophs encounter AMD undoubtedly work in the same way. Assuming the contact with the AMD is sufficiently brief, dilution of the pollutant by additional waters or removal of the toxicants by other means, allows the populations to gradually resume their normal role in that environment. Hackney & Bissonnette (1978) were able to recover significant numbers of a variety of indicator bacteria from membrane diffusion chambers submerged in an acid mine stream for up to 24 h. Survival of cells at levels below the limit of detectability of that study could provide a sufficient inoculum for recovery of the population upon lessening of the pollution stress. Such survival and gradual recovery is consistent with the suggestion that the low levels of heterotrophic activity observed in slightly diluted acid mine streams is due to the presence of transient populations that may be injured but survive the exposure (Tuttle *et al.*, 1969a; Wassel & Mills, 1983).

Given a source of inoculum, viz. injured or transient heterotrophs, the general homeostatic model (Fig. 2) will apply for microbial communities, either in time, as in small lakes with no additional input of AMD, or with distance from the pollution source, as in streams or impoundments with a reasonable current. The work of Tuttle *et al.* (1968) demonstrated that fact for streams using cultural counts as the quantitative method, but the only comprehensive study of the behavior of aquatic microbial communities affected by acid mine drainage is that of the Lake Anna-Contrary Creek system, which will be used as the primary example of acidification effects in an impoundment.

Lake Anna is an impoundment in east-central Virginia (Fig. 3). It was flooded in 1971 to provide cooling water for the North Anna Power Station. Contrary Creek, which flows into the arm used as the study site, drains an area that was extensively mined for pyrite for the 70 years prior to 1920. Although the mining operations have ceased, the flow of acid mine drainage has continued to the present. The primary objectives of the study, which

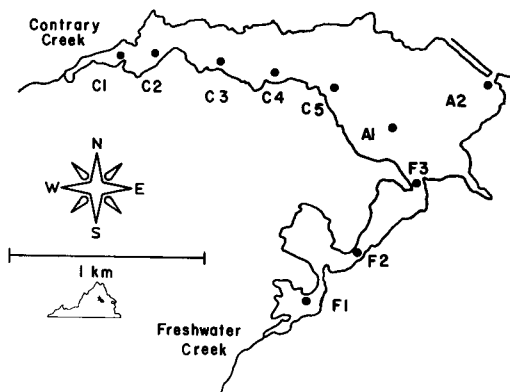


Fig. 3. Contrary Creek and the study sites in Lake Anna.

is still ongoing, were to determine the extent and types of alteration of the microbial communities of the lake due to inputs of acid mine drainage from Contrary Creek, and to determine the fate of the pollutant constituents once in the reservoir.

Another stream, Freshwater Creek, also flows into the arm, but contains no acid mine drainage. This stream and the area into which it flows served as control sites for the study. The mean discharge for Contrary Creek for the 1979 water year was $7.02 \text{ ft}^3 \text{ sec}^{-1}$, with a maximum flow rate of $259 \text{ ft}^3 \text{ sec}^{-1}$ and a minimum of $0.45 \text{ ft}^3 \text{ sec}^{-1}$ (USGS/Va. State Water Control Board, 1979). Discharge measurements have not been made in Freshwater Creek, but the watershed areas drained by the two streams provide a crude basis for comparing the relative contribution of water from the two streams to the lake. The area drained by the unpolluted stream comprises 2288 ha as opposed to 1820 ha for the Contrary Creek drainage basin. These values represent 44 percent and 35 percent of the total watershed areas which empty out through the causeway at station A2 (See fig. 3) for Freshwater and Contrary Creek, respectively.

A series of stations was established in the Contrary and Creek Freshwater Creek areas of the arm. The major physical parameters associated with some of the stations are presented in Table 2. Data are reported as the annual averages for the three year period from June 1978 to May 1981. An obvious gradient of pH and conductivity exists in the Contrary Creek arm with the pH increasing and the conductivity decreasing with increasing dis-

tance from the mouth of the stream. In the Freshwater Creek area, the trend is reversed, although the gradient there is not as steep as in the Contrary Creek arm.

When heterotrophs are recovered from contaminated waters, the abundance and diversity are observed to decrease with decreasing pH. Guthrie *et al.* (1978), observed a 44 percent reduction in total culturable bacteria as the pH was lowered from 6.8 to 5.4 by fly ash contamination of a stream, and a concomitant reduction in diversity (number of colony types) of 30 percent. Furthermore, a shift in the prevalent organisms inhabiting the system was observed. In order of quantitative importance, *Bacillus*, *Sarcina*, *Achromobacter*, *Flavobacterium*, and *Pseudomonas* were dominant at the higher pH, and *Pseudomonas*, *Flavobac-*

terium, *Chromobacterium*, *Bacillus*, and *Brevibacterium* were dominant at the lower pH. A noticeable increase in the number of pigmented forms accompanied the reduction in pH. Similar data were obtained in Lake Anna by Wassel and Mills (1983). The planktonic bacterial community was smaller and less diverse in the mouth of Contrary Creek (pH 3.2) than at the mouth of Freshwater Creek (pH 6.2).

The densities of bacterial communities were determined using both plate count techniques and acridine orange direct counts (AODC). In the 12 month period from June 1978 to May 1979 the sizes of the communities at C1, A2, and F1 (Fig. 3) as measured by AODC were not significantly different. Results using the plate count method revealed significant differences among the stations,

Table 2. Values of pH, conductivity, and temperature for selected stations in Contrary Creek and Freshwater Creek. Data are presented as annual averages and standard deviations for each of three years. Stations designated as T and B refer to surface and bottom water conditions respectively. Reproduced by permission from Mills (1985).

Station depth (m)	C1	C4T	C4B	A2T	A2B	F1	
0.5	3.0			7.0	1.5		
<i>pH</i>							
78-79	\bar{x}	3.5	5.0	4.1	5.9	5.3	6.4
	s.d.	.29	1.1	.29	.99	1.0	.60
79-80	\bar{x}	3.4	5.1	5.4	5.9	5.5	6.3
	s.d.	.43	.74	1.0	.97	.78	.41
80-81	\bar{x}	3.3	5.5	5.2	6.5*	6.1	6.3*
	s.d.	.26	.93	1.9	1.0	.83	.78
<i>Conductivity</i>							
78-79	\bar{x}	337.4	117.8	124.0	74.0	83.7	55.4
	s.d.	87.9	19.9	45.8	10.9	36.2	20.8
79-80	\bar{x}	259.3	116.7	77.6	59.4	71.5	52.2
	s.d.	100.8	130.6	22.8	10.9	22.4	23.9
80-81	\bar{x}	252.2	98.5	90.5	81.3	91.0	78.9
	s.d.	76.3	28.9	25.3	9.0	24.2	28.9
<i>Temperature</i>							
78-79	\bar{x}	17.7	17.8	17.4	18.2	17.6	18.3
	s.d.	9.9	8.2	8.9	9.6	8.3	9.8
79-80	\bar{x}	17.4	19.3	18.9	19.6	17.6	19.3
	s.d.	10.3	9.2	8.9	8.2	7.9	9.1
80-81	\bar{x}	15.0	17.8	16.9	18.5	17.4	15.7
	s.d.	8.4	8.4	9.0	8.2	8.0	9.2

* During this year, a pH value of 8.6 was reached in March. That was the highest value ever obtained, and deletion of that reading would lower the average pH for 1980-81 to 6.3. Similarly, deletion of an extremely low reading of 4.3 at F1 in May 1981 would raise the average pH at that station to 6.5.

with $F1 > A2 > C1$ (Wassel & Mills, 1983). Similar results were obtained for the same time period in 1979–1980 and again in 1980–81.

If all the stations included in the AODC determinations are examined, a more refined relationship is seen in the results. While statistical significance could not be demonstrated for differences in AODC values among the various stations, an interesting trend was observed (Fig. 4). Bacterial numbers in the unpolluted situation (Freshwater Creek) decreased from a maximum in the shallow productive areas near the stream mouth to a minimum in the deeper, open waters of the lake. However, the presence of acid mine drainage in the Contrary Creek arm has altered the situation there to one in which the bacterial densities increase in a downstream direction as the intensity of the pollution damage becomes less and less. The shape of the curve closely resembles that of the general recovery model presented in Fig. 2. The convergence of the AODC curves for the two arms of the lake prior to the point where the waters mix is an important observation indicating essentially complete recovery of the water column microbes within the Contrary Creek arm itself.

The usual criticism of cultural count methods notwithstanding, the lack of significant differences among stations for the AODC results is likely due to an abundance of chemoautotrophic bacteria such as *Thiobacillus* sp. in the acid impacted areas. Using the FAINT procedure (fluorescent antibody for identification combined with INT reduction to indicate an active cytochrome system), the contribution of *T. ferrooxydans* to the AODC was determined to be about ten percent of the AODC obtained at C1, but only one percent at station A2 (Baker & Mills, 1982). The numbers of *T. ferrooxydans* and *T. thiooxydans* in Contrary Creek are approximately equal (Scala *et al.*, 1982), and if it is assumed that the relative proportions of organisms hold for the entire year, the points shown at station C1 in Fig. 4 would be lower, yielding an even more significant recovery of the heterotrophic fraction in the Contrary Creek arm.

The diversity of the heterotrophic communities was examined on a quarterly basis by isolating organisms from the enumeration plates, subjecting

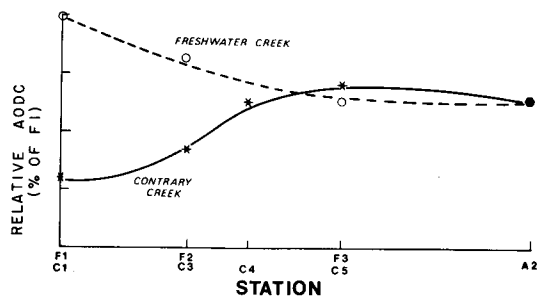


Fig. 4. Annual average of the AODC for several stations in the Contrary Creek and Freshwater Creek arms of Lake Anna. Reproduced with permission from Mills (1985).

the cultures to a battery of physiological tests, clustering the isolates into groups using numerical taxonomic techniques, and using these resultant clusters to perform diversity analysis using the rarefaction method (Mills & Wassel, 1980; Wassel & Mills, 1983). Organisms from both sediment and water showed similar diversity patterns, viz., the community at F1 was more diverse than at either A2 or C1, which, in turn, were not significantly different. The low diversity in the areas receiving the mine wastes was explained by the absence of strains found at station F1 but not at the affected sites. That is, a community exists for the entire area (both polluted and unaffected sites) which has, as a large portion of its makeup, a series of common organisms.

At station F1 however, a large number of individuals present had no counterparts at the other stations sampled. Furthermore, on the basis of the patterns of response of the bacterial isolates to the battery of physiological tests, the strains unique to F1 (not present elsewhere, resulting in a reduced diversity at A2 and C1) were different from the general community (common strains) and from the unique strains found at the sites receiving the mine drainage. The F1 unique strains had a lower ability to withstand the metals Pb, Cu, Zn, and Cd in the culture medium. All of those metals are abundant in the Contrary Creek AMD. There was no difference, however, in the ability of the organisms from the various stations to withstand acidity as determined by culturing each isolate at pH 4.0.

In contrast, the sessile bacterial communities at sites C1 and F1 were highly dissimilar in composition (L.A. Mallory & A.L. Mills, unpublished

data), and displayed a great difference in their ability to tolerate the conditions at sites other than their native habitat. These findings imply that, in fact, the planktonic bacteria are transients, whereas the attached forms are able to grow because of an enhanced resistance to the extreme conditions in the acid mine drainage.

The effects of the acid mine drainage on the rate of leaf litter decomposition were investigated at two sites in the Contrary Creek arm (C1 and C5) in comparison to a control site (F1) in the Freshwater Creek arm (Carpenter *et al.*, 1983). Litterbags containing leaves of yellow birch (*Betula lutea*), flowering dogwood (*Cornus florida*), white oak (*Quercus alba*), and soft rush (*Juncus effusus*) were incubated for up to 149 days in the littoral zone at each site. The decomposition rate was measured by loss of ash free dry weight of the leaf litter, and was expressed as both a linear and an exponential decay rate. Interspecific differences in decomposition rates were found at all sites, with dogwood decaying the most rapidly, followed by birch, oak, and rush (Fig. 5). The decomposition rates also differed significantly among the study sites. For all leaf species, the decay rate coefficients at F1 were at least twice those obtained at C1. At C5, values were generally intermediate between those obtained for the other two sites. Bacterial counts (AODC) in the decomposing material did not differ significantly among the sites at any time. The decomposition process was primarily microbially mediated, as very few direct detritus processors (e.g. shredding and scraping invertebrates) were ever found in the litter bags. Thus, although microbial activity in the Contrary Creek arm was inhibited by the presence of the acid mine drainage, some activity was seen even in the most severely affected area.

Glucose assimilation measurements made in various parts of the lake (Carpenter *et al.*, 1983) supported the observations of the litter bag incubations. A pattern of assimilation was observed that resembled that of the distribution of AODC in the two arms, and the pattern was valid for the 10 month period from spring of 1980 to late winter of 1981 (Table 3). Assimilation of ^{14}C -glucose over the sampling period was lowest at C1 and increased

in a downstream direction moving away from the acidic environment. Conversely, the activity was highest at station F1 and decreased in a downstream direction in that arm; the general recovery pattern (Fig. 2) was seen in a more integrated examination. The heterotrophic activity results are entirely consistent with those of both the direct and cultural count analyses and show a recovery of the heterotrophic community that is essentially complete before the water from the two arms mix.

Actual rates of heterotrophic activity were consistent with all of the other results (Table 4). Values of V_{max} and turnover time (T_1) showed a depression of activity at the acid impacted area as compared with the other sites examined (Carpenter *et al.*, 1983). The time for glucose turnover at C1 was an order of magnitude longer than at F1, supporting the observation of a reduced rate of decomposition of organic matter there.

The microbiological effects of acid mine drainage observed in Lake Anna are quite similar to those obtained in ponds and streams artificially acidified to study the effects of acid precipitation, and others which have become acidified by the precipitation itself. Early observations on acidified Swedish lakes reported that particulate organic matter (litter) accumulated faster in those lakes than in unacidified ones (Grahn *et al.*, 1974), and

Table 3. Comparative levels of ^{14}C -glucose assimilation in the Contrary Creek area of Lake Anna. To clarify the relationships, all values are expressed as the percentage of the activity observed at station F1. Values presented are the averages of 10 months from November, 1979 to August, 1980. Comparisons are made on equal sized water samples. Reproduced by permission from Mills (1985).

Station	Heterotrophic activity	
	(% of F1)	S.D.
C1	8.3	11.9
C3	15.0	14.1
C4	29.0	19.2
C5	31.0	22.0
A2	36.0	22.6
F3	46.1	30.0
F2	49.0	38.2
F1	100	-

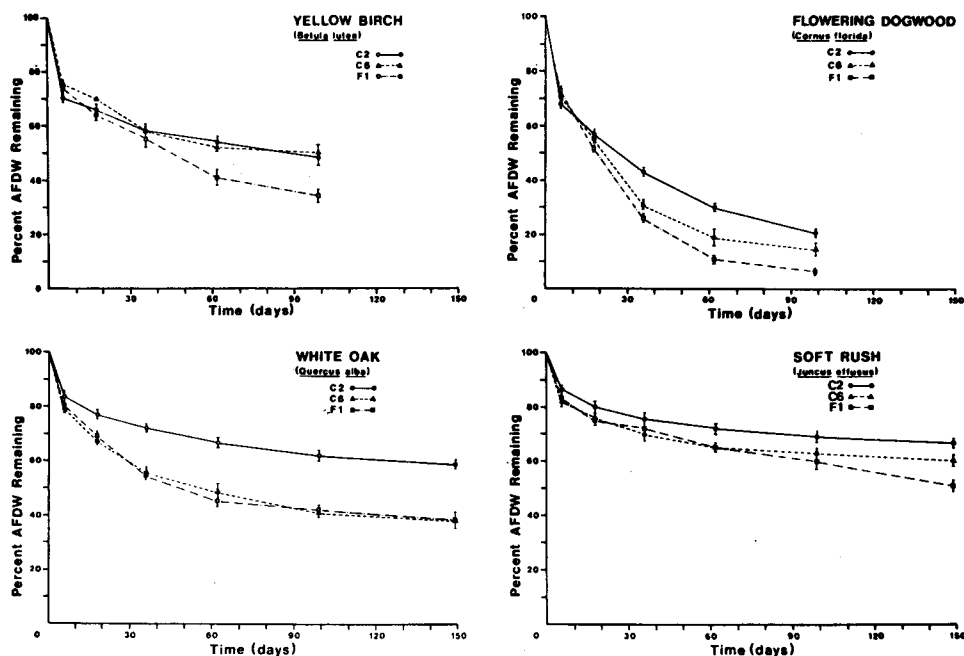


Fig. 5. Decomposition of leaf litter at sites in Lake Anna receiving different amounts of the drainage from Contrary Creek. Reproduced with permission from Carpenter *et al.*, 1983.

that mats of fungal hyphae also were found in the more acidic lakes. Given that acidic environments are thought to select for fungi over bacteria, Grahn *et al.* (1974) hypothesized that decomposition in the acid lakes was accomplished by fungi and that overall decomposition in the acidified lakes was reduced.

Because of the low pH of waters contaminated with AMD, it has been suggested that fungi may play an exceptionally important role. In strip mine soils, filamentous fungi are prolific and diverse (Wilson, 1965). Uptake of organic pollutants from AMD contaminated waters by fungi may result in the removal of iron by the production of organ-

ically stabilized colloids, but the observed reduction in acidity in such streams cannot be attributed to those microbes. (Weaver & Nash, 1968). Representatives of the yeasts *Candida*, *Rhodotorula*, and *Trichosporon* have often been isolated from streams carrying acid mine wastes (Rogers & Wilson, 1966; Weaver & Nash, 1968).

Transformations of other nutrients

Concomitant with decomposition of organic matter is transformation of nutrient elements such as sulfur and nitrogen. The biogeochemistry of sulfur in waters acidified by acid precipitation or acid mine drainage is currently the focus of a great deal of research. The transformations are intimately related to the ecosystem response of a reservoir to acidification, and the reactions will be treated in detail in a later section.

Literature on the effects of acidification on nitrogen transformations in impoundments is non-existent. In fact, only soil microbes have been examined with regards to the impact of acid pollutants

Table 4. Kinetic values for heterotrophic uptake of ^{14}C -glucose at stations in the Contrary Creek area (April, 1981). Reproduced by permission from Carpenter *et al.* (1983).

Station	$V_{\max-1}$ (nMh)	T_i (h)
C1	10.2	133
A2	78.2	52.6
F1	124.3	9.38

on the nitrogen cycle. For the heterotrophic reactions, the effects are linked to general effects on heterotrophs. That is, if heterotrophic activity is reduced, the nitrogen cycling reactions associated with the community will likewise be reduced. For autotrophic reactions such as nitrification, evidence from soil studies suggests that small amounts of acidity may be detrimental to the process (Alexander, 1980). In the presence of simulated acid rain, the amount of nitrate formed from added ammonium was much lower than in unamended controls. In a set of samples amended with nitrapyrin, the amount of nitrate formed during the incubation period was no different for amended or unamended samples. Alexander (1980) concluded that the autotrophic nitrifiers in the soil samples were more acid sensitive than the heterotrophic nitrifiers. The relationship of results such as these to lakes and/or impoundments remains to be determined.

As pointed out later, it is conceivable that acid precipitation might induce an increase in the rate of nitrate reduction (denitrification or dissimilatory nitrate reduction) in sediments or anoxic hypolimnia. To this date; however, no data have been published on such a stimulation, nor has anyone speculated as to the potential contribution of denitrification in buffering acid pollutants.

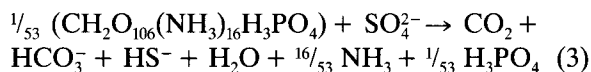
Microbiological effects on acid pollutants

There are a number of internal lake processes that can buffer or otherwise affect acidic inputs. Photosynthesis is a net consumer of H^+ but most of the fixed carbon is subsequently decomposed and the reaction is probably of little importance in buffering acidification. The production of organic acids during decomposition may contribute to alkalinity if their pK_a is greater than 1.92, the pK_1 of H_2SO_4 . However, the concentration of these organics is usually small so that they are of minor quantitative importance in acid neutralization. The release of Fe^{2+} or manganese from the sediment under anoxic conditions results in an increase in alkalinity (Mortimer, 1971) as bicarbonate forms from dissolved inorganic carbon to balance the input of the posi-

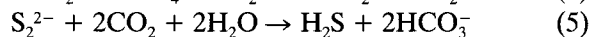
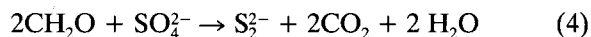
tive cations. However upon the introduction of oxygen into the hypolimnion during turnover, these metals are oxidized and the alkalinity is lost when bicarbonate is turned into CO_2 (Schindler *et al.*, 1980).

Due to the increased concentrations of sulfate and nitrate in acidic pollution, the most important reactions involved in acid neutralization in lakes are bacterial sulfate reduction and nitrate reduction (denitrification). The reason these reactions are effective is that they generate alkalinity and yield end products that can be stable in the presence of oxygen so that the alkalinity is conserved after turnover. The nitrogen gas formed by denitrification can easily escape the system and the sulfide from sulfate reduction can escape the immediate system as H_2S or can react with ferrous iron and precipitate into the sediment as iron sulfide.

A generalized reaction for sulfate reduction (SR) is given in equation 3 (Richards, 1965).



Equation (3) shows that SR will generate carbonate alkalinity (bicarbonate) which can raise the pH of acidic waters. Berner *et al.* (1970) concluded that SR was the principal factor affecting carbonate alkalinity in the pore waters of coastal marine sediments. Berner formulated the generation of alkalinity from SR as a two step process.



Ben-Yaakov (1973) used a chemical model of anoxic pore waters, to show that SR is the most important process controlling pH. In equation (4), there is a net transfer of charge from a non-protolytic species (sulfate) to a protolytic species (weak acid or base, i.e. HS^-) which can remove protons from solution. Ben-Yaakov's model predicted a pH of 6.9 in an anoxic sulfate reducing sediment in which all the produced sulfide remained in solution. If all the sulfide precipitated out of solution, the pH was predicted to be 8.3 because a weak acid would have been removed from the system.

Kelly *et al.* (1982) derived the following equa-

tions to predict the change in hypolimnetic alkalinity based on the changes in concentrations of the major cations and anions. The major protolytic species contributing to alkalinity in freshwater systems can be written as:

$$\text{alk} = 2\text{CO}_3^{2-} + \text{HCO}_3^- - \text{H}^+ + \text{HS}^- + 2\text{S}^{2-} + \text{NH}_3 \quad (6)$$

A neutral or lower pH values CO_3^{2-} , S^{2-} , and NH_3 are insignificant and equation 6 reduces to:

$$\text{alk} = \text{HCO}_3^- - \text{H}^+ + \text{HS}^- \quad (7)$$

A charge balance of the major hypolimnetic ions can be expressed as:

$$\text{O} = 2\Delta\text{Fe}^{2+} + 2\Delta\text{Mn}^{2+} + \Delta\text{NH}_4^+ + \Delta\text{H}^+ - \Delta\text{HCO}_3^- - \Delta\text{NO}_3^- - 2\Delta\text{SO}_4^{2-} - \Delta\text{HS}^- \quad (8)$$

Rearranging equation (8) and substituting in equation (7) yields:

$$\Delta\text{alk} = 2\Delta\text{Fe}^{2+} + 2\Delta\text{Mn}^{2+} + \Delta\text{NH}_4^+ - \Delta\text{NO}_3^- - 2\Delta\text{SO}_4^{2-} \quad (9)$$

Equation (9) demonstrates that the removal of sulfate or nitrate or the release of ferrous iron or manganese will increase the alkalinity. However the alkalinity generated by iron, manganese, and NH_4^+ is not permanent and is lost upon oxidation of these cations. Also, any sulfide that has not precipitated as FeS may also be oxidized so the equation for persistent alkalinity formation is best represented by:

$$\Delta\text{alk} = \Delta\text{NO}_3^- + 2\Delta(\text{SO}_4^{2-} - \text{H}_2\text{S}) \quad (10)$$

where $(\text{SO}_4^{2-} - \text{H}_2\text{S})$ represents the fraction of the sulfate reduced that is resistant to oxidation. Using equations (6–10), Cook (1981) observed good agreement between calculated and measured alkalinities in the hypolimnion of Lake 223.

Several examples from the literature demonstrate the ability of sulfate and nitrate reduction to neutralize acidic pollution. Tuttle *et al.* (1969a) described an AMD stream blocked by a porous wood dust dam. The wood dust provided organic matter for the sulfate reducers. The pH increased from 2.84 to 3.38, and sulfate level decreased from 8.8 mM to 6.1 mM from the pond upstream of the dam to the downstream pond. No sulfate reducing

bacteria were observed in the upstream pond but were numerous in the wood dust and the downstream pond. Black iron sulfide precipitates were also observed in the lower pond. In laboratory incubations with AMD waters and wood dust, the pH increased and sulfate concentrations decreased over time. Tuttle *et al.* (1969b) further investigated this system as a potential AMD pollution abatement procedure, and concluded that once anaerobic conditions are established, and a carbon source supplied, it is theoretically possible for SR to alleviate AMD pollution.

During the experimental acidification of Lake 223 with sulfuric acid, Schindler *et al.* (1980) observed that the pH did not decrease as much as predicted. Weatherable bedrock or weak organic acids could have accounted for the observed buffering, but they were not found in sufficient concentrations in this region. An input-output mass balance for sulfate suggested significant sulfate reduction in the anoxic hypolimnion, enough to cause the observed neutralization.

In a follow-up study, Schindler & Turner (1982) reported that after five years of acidification, one fourth to one third of the added sulfate has precipitated into the sediment as FeS, reducing the efficiency of acidification. In modeling the same region, Kelly *et al.* (1982) demonstrated that as sulfate and nitrate inputs from acid rain increased, the dominant anaerobic metabolic pathway shifted from methanogenesis (no alkalinity generation) to sulfate and nitrate reduction (alkalinity generation). The alkalinity generated from this shift was enough to neutralize 'typical' acid deposition in eutrophic lakes.

Kilham (1982), in studying records of Weber Lake in Michigan over the last 25 years, reported an increase in alkalinity despite a twenty fold increase in proton loading from acid precipitation. His budget showed that alkalinity from SR and nitrate uptake by plants was sufficient to neutralize the incoming acidity.

Recently, Wieder & Lang (1982) observed a freshwater wetland which receives AMD. Although Tub Run Bog in West Virginia receives AMD along its eastern edge, the stream draining the bog showed little or no influence from the

AMD. The interstitial water in the bog showed a general decline in acidity and sulfate concentration with increasing distance from the mines, and hydrogen sulfide was present in the pore water. In this environment, SR may also be the important process in modifying the AMD.

Sulfate reduction and denitrification require both organic substrates and anoxic conditions. Thus the major factors controlling the capacity of a lake to neutralize incoming acidity are the amounts of organic matter input and lake hydrology. Campbell *et al.* (1965) observed a series of acid strip mine lakes in Missouri and found that there was a natural succession in these lakes to an alkaline state with a corresponding increase in the abundance and diversity of the biota. King *et al.* (1974) attributed the recovery to biological sulfate reduction and in a series of microcosm studies showed that the addition of raw wastewater sludge to acid strip mine lake water caused a decrease in sulfate, iron and acidity. They concluded that the amount of mine spoils remaining in the watershed and the rate of organic matter input controlled the recovery process in these lakes.

Schindler & Turner (1982) concluded that the alkalinity generated by sulfate reduction in Lake 223 was a function of hypolimnetic volume, light penetration, and the concentrations of sulfate and oxygen. Larger anoxic hypolimnia will entrap more sulfate for reduction so that more alkalinity will be produced. The amount of mixing that occurs during turnover will determine the oxygen and sulfate concentration in the hypolimnion. While less mixing means less oxygen in the hypolimnion and a quicker start to sulfate reduction, it also means that sulfate movement to the reducing zone will similarly be impeded. Schindler & Turner (1982) found that with more complete mixing more sulfate was reduced. It is also interesting to note that in experimentally acidified Lake 114 there was no anoxic hypolimnion; however, sulfate reduction still occurred as the sulfate diffused into the anoxic sediments beneath the aerobic water. Although the calculated rates of sulfate reduction were lower in Lake 114 than in Lake 223, the percentages of added sulfate precipitated as iron sulfides were almost the same (Schindler & Turner, 1982).

Acidic pollution has different attributes in impoundments than it does in natural lakes primarily due to the differing hydrological characteristics of the two water bodies. Impoundments usually have more shoreline than lakes and a higher drainage area to surface area ratio indicating the potential for higher organic matter inputs (Gunnison, 1981). Also, there is often a supply of organic matter on the bottom of the reservoir resulting from the flooding of a terrestrial environment. Water flow into impoundments is usually dominated by one or two major tributaries and the residence times are shorter than natural lakes (Thornton *et al.*, 1980; Gunnison, 1981). Thus pollutants entering the reservoir will be carried to the outflow faster.

Acid mine drainage is different from acid rain in terms of input source and chemistry. Acid rain is a diffuse, dilute source of acidity while acid mine drainage is a concentrated, point source of acidity that enters from streams. Acid mine drainage will often enter an impoundment as a coherent mass either overflowing, interflowing, or underflowing depending on the thermal density stratification of the lake and the temperature of the inflow. Koryak *et al.* (1979) observed all three types of flow in the Tygart River Impoundment. In spring the lake was homothermal and the more easily warmed acid inflow overflowed on the surface of the lake. During the summer a thermal stratification developed and interflow was observed. In the fall the lake was again homothermal but the inflow water was cooler than the warm lake water and caused an underflow. Underflows can be a problem in impoundments with hypolimnetic withdrawal since acid mine waters will not mix in the lake and be diluted but will plunge directly to the outflow resulting in a release of acidic waters that can cause fish kills downstream (Koryak *et al.*, 1979). The same problem can occur with surface withdrawals and overflows. Since neutralization of acidity occurs in the anoxic hypolimnion and sediments, the flow pattern of acid mine drainage inflows is also important in determining how fast neutralization can occur. Underflows would concentrate the acidity in the region where neutralization occurs. On the other hand, overflows and acidity from acid rain enter the epilimnion and lake mixing processes are

needed to bring the acidity down to the hypolimnion. These mixing processes can be quite slow especially if a thermal stratification is present.

The chemical composition of the two types of acidic pollution are different. Acid rain has enhanced concentrations of nitrate and sulfate so both denitrification and sulfate reduction are important. On the other hand, the dominant anion in acid mine drainage is sulfate so sulfate reduction is the most important alkalinity producing reaction. Also the elevated metal concentration in acid mine drainage is important in buffering the acidity. Most heavy metals form insoluble precipitates with sulfides (Hutchinson, 1975). Thus in lakes receiving acid mine drainage most of the sulfide produced by sulfate reduction will precipitate in the sediment conserving the alkalinity generated by sulfate reduction. Since acid rain generally has low concentrations of heavy metals the effectiveness of sulfate reduction in removing acidity is dependent on the iron content of the lake and the soil of the surrounding watershed. In iron poor regions sulfate reduction will not be as important a mechanism in reducing acidity since a significant fraction of the produced sulfides will be oxidized with the concomitant loss of alkalinity.

In many impoundments acid rain will probably not be a major problem in the near future due to the high alkalinities and organic matter present in most of these systems. Due to the increases in coal mining and reservoir construction, acid mine drainage is the more serious acid problem in impoundments. Bacterial sulfate reduction can reduce the effect of the AMD given sufficient organic matter and the right kind of flow pattern. However, if a large part of the inflow into an impoundment is made up of strong AMD or if the reservoir has a short residence time, sulfate reduction may be incapable of buffering the acid inflow.

In the Lake Anna study site, the concentration of the pollutants from the acid mine drainage decreases in a down lake direction at a rate faster than can be explained by dilution alone (Mills, 1985; Herlihy & Mills, 1985, Rastetter *et al.*, 1984). A conceptual model was formulated that would explain the observed removal of the AMD (Fig. 6). Sulfate diffuses into the sediment where it is re-

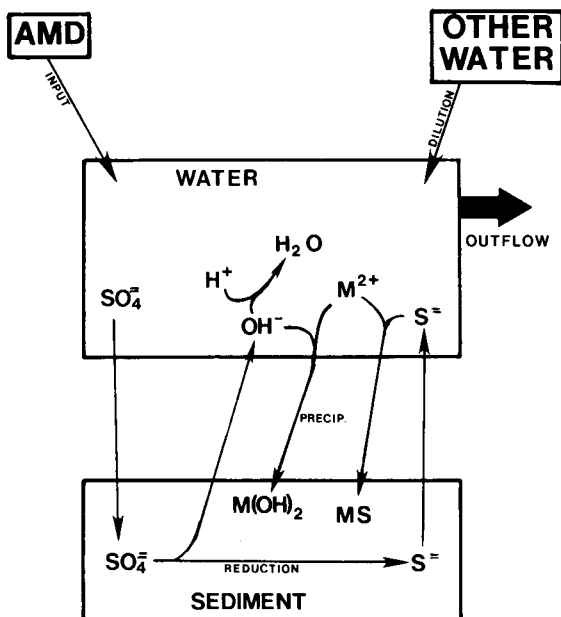


Fig. 6. Conceptual model of the relationship of SO_4^{2-} reduction in sediment and the removal of AMD from the overlying water column. Although SO_4^{2-} reduction generates alkalinity as carbonate, OH^- has been used here for simplicity in depicting the subsequent reactions. Reproduced by permission from Mills (1985).

duced. Sulfate reduction in the lake sediment generates alkalinity to neutralize the pH, and the produced sulfide causes metals to precipitate as metal sulfides. Sulfate reduction is modeled as occurring in the sediments because most of the Contrary Creek arm is shallow and the water is oxygenated to the bottom all year. Only at station A2, and then only for brief periods in the summer, is the bottom water anaerobic. Thus, little or no sulfate reduction occurs in the water column.

In order to see if the addition of acid mine drainage to freshwater lake sediments enhanced sulfate reduction rates, sediment sulfate reduction rates were measured seasonally over a one year period at four stations in the Contrary Creek arm of Lake Anna (Herlihy & Mills, 1985). One of the stations (F1 in the Freshwater Creek section, Fig. 3) receives 'clean' water ($\text{SO}_4^{2-} = 10\text{--}80\ \mu\text{M}$, $\text{pH} = 5.6\text{--}7.1$) from Freshwater Creek and was used as a control for comparative purposes.

Sulfate reduction rates in the Contrary Creek section of the lake were significantly higher than in

the Freshwater Creek section in the summer (Table 5). Rates in the two sections were similar in the fall, winter, and spring, presumably due to low sediment temperatures limiting the reaction. Acid volatile sulfide concentrations in the Contrary Creek section were always an order of magnitude higher than those in the Freshwater Creek section (Fig. 7).

In order to verify the model, an input-output budget for sulfate was calculated for the Contrary Creek arm of Lake Anna (Herlihy & Mills, in review). The sulfate inputs included Contrary Creek, Freshwater Creek, and a direct input component. The direct input component included precipitation and all surface water that did not enter the lake via Contrary or Freshwater Creeks. The sulfate output was based on the water leaving the arm under the Route 652 bridge near station A2. Sulfate input-output loads were determined on a daily basis from October 1, 1982 to September 30, 1983 by multiplying the appropriate discharge by its sulfate concentration. The daily discharges for all components of the lake were based on the daily Contrary Creek discharge values. The discharges for Freshwater Creek, the direct input component, and the outflow were calculated from the Contrary Creek discharge on the basis of watershed area ratios. The sulfate concentration of the outflow was based on the depth averaged monthly sulfate concentration at station A2. The average sulfate

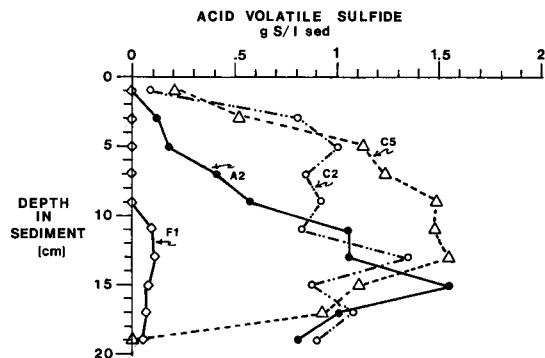


Fig. 7. Acid volatile sulfide concentration with depth in the sediment in the winter of 1983. Data points are the mean of triplicate samples. Coefficients of variance were usually between 10 and 60%. Fall, summer, and spring acid volatile sulfide concentration profiles were similar in shape and magnitude to the winter profile. Reproduced with permission from Herlihy & Mills (1985).

Table 5. Integrated SO_4^{2-} reduction rates in Lake Anna sediment. Rates are mmol SO_4^{2-} reduced $\text{m}^{-2}\text{day}^{-1}$. Data from Herlihy and Mills (1985).

	Station			
	C2	C5	A2	F1
Fall 1982	.720 (.045)	1.81 (1.02)	.227 (.041)	2.10 (.119)
Winter 1983	2.10 (.486)	39.8 (60.6)	.409 (.095)	4.78 (1.96)
Spring 1983	5.46 (2.48)	.551 (.648)	1.27 (.452)	.730 ^b (.051)
Summer 1983	225 (192)	26.8 (3.43)	31.9 (3.58)	8.39 (2.45)

^a Values in parentheses are one SD of triplicate sediment cores

^b Data obtained from duplicate, not triplicate cores

concentration of Freshwater Creek was $46.3 \mu\text{M}$ (SD = 18.6) based on 9 observations taken during the last half of 1983. The sulfate concentration of the direct input component was assumed to be equal to the Freshwater Creek concentration. The sulfate concentration in Contrary Creek was found to be related to creek discharge. The sulfate concentration in the creek for any given day was interpolated from a graph of the sulfate-discharge relationship. The daily sulfate input loads were summed to determine the amount of sulfate added over the year. The outflow sulfate load for the year was subtracted from the input load to determine the amount of sulfate that remained within the system.

The integrated SR rates from Herlihy and Mills (1985) were used to calculate the amount of sulfate removed by SR in the Contrary Creek arm of Lake Anna. The lake was divided into four regions (C2, C5, A2 and F1) and the surface area of that region (m^2) was multiplied by the seasonal SR rate ($\text{mmol m}^{-2}\text{day}^{-1}$). Each season was taken to be 91.25 (365/4) days long. The amount of sulfate reduced in each region and each season was summed to yield the total sulfate removal via SR for the year. These calculations assumed that the SR activity was uniform within the four lake regions. Sulfide oxidation was assumed to be equal to the

difference between the measured SR rates and the sulfate input-output budget.

The sulfate fluxes (Table 6) shows that 57 percent of the sulfate that enters the lake does not leave. Of the sulfate that remains in the lake, 125 percent (± 55 percent) can be accounted for by measured rates of SR (Herlihy & Mills, in review). Despite the large variances in the budget, the good agreement between observed rates of SR and sulfate disappearance from the lake indicates that sulfate reduction is the major mechanism removing AMD derived sulfate.

The depth distribution of sulfate concentration in Lake Anna demonstrates the spatial and temporal inflow pattern of the AMD (Fig. 8). The observed summer minimum and winter maximum in sulfate reported by Herlihy and Mills (in review) can be explained by the observed SR rates and Contrary Creek discharge. Contrary Creek has a winter-spring maximum and a late summer minimum in discharge (USGS/Va. State Water Control Board, 1979). Even though the AMD pollutants were more concentrated in the creek in the summer, the low flow rate reduced the pollutant load entering the lake. Also, in the summer, SR rates were highest, so more sulfate was being removed from the water. The combination of these two factors caused the observed minimum and maximum in sulfate, acidity, and conductivity.

Throughout much of the year there was a strong stratification of sulfate and pH. In July, the top water at C2 had a pH of 5.5 and a sulfate concentra-

tion of 304 μM . The bottom water had a pH of 3.9 and a sulfate concentration of 638 μM . The stratification was even more striking in August. C2 water pumped from the bottom had a sulfate concentration of 198 μM . Pumped bottom water samples were usually taken about 20–30 cm above the sediment to avoid sucking up the loose iron floc on the sediment surface. C2 bottom water from an equilibrator right at the sediment-water interface had a sulfate concentration of 1190 μM , a five-fold increase in 20–30 cm. The plunging of AMD increases rates of sulfate removal from the lake by concentrating sulfate in the bottom water where it would more rapidly diffuse into the sediment and be reduced.

In an attempt to better understand the causes of the observed stratification a modified version of DYRESM-6 was applied to the Contrary Creek arm of Lake Anna. DYRESM-6 is a one dimensional computer simulation model for predicting temperature and salt structure in medium sized lakes (Imberger & Patterson, 1981). Ferrous sulfate was used as the dominant salt to compute salt density and the model was modified to simulate the outflow under the bridge near station A2. The results of the simulation indicate that thermal stratification in the lake is much stronger than salt stratification, however, a strong thermal stratification effectively traps the sulfate, acid plume in the hypolimnion. A weak salt stratification did develop when lake temperatures were homogeneous. When a strong wind was added to the model it inhibited the formation of the thermocline and caused the lake to mix (Rastetter *et al.*, 1984). The results of the computer simulation in conjunction with the observed increase in sulfate reduction rates in the summer indicate that the sediments are most effective at sulfate removal during calm summer days when thermal stratification is strong.

Conclusions

It should be clear that present knowledge of the behavior of acidic pollutants in impoundments is not well understood. For small reservoirs that are overwhelmed by concentrated pollutants like acid

Table 6. Sulfate budget for the Contrary Creek arm of Lake Anna.

	10 ⁶ moles of SO ₄ ²⁻
INPUTS	
Contrary Creek	6.3
Freshwater Creek	0.23
Direct input	0.10
Input sum	6.6
OUTPUT	
Outflow under bridge	3.0
Input - Output	3.6
Sulfate reduction	4.5 (125%)

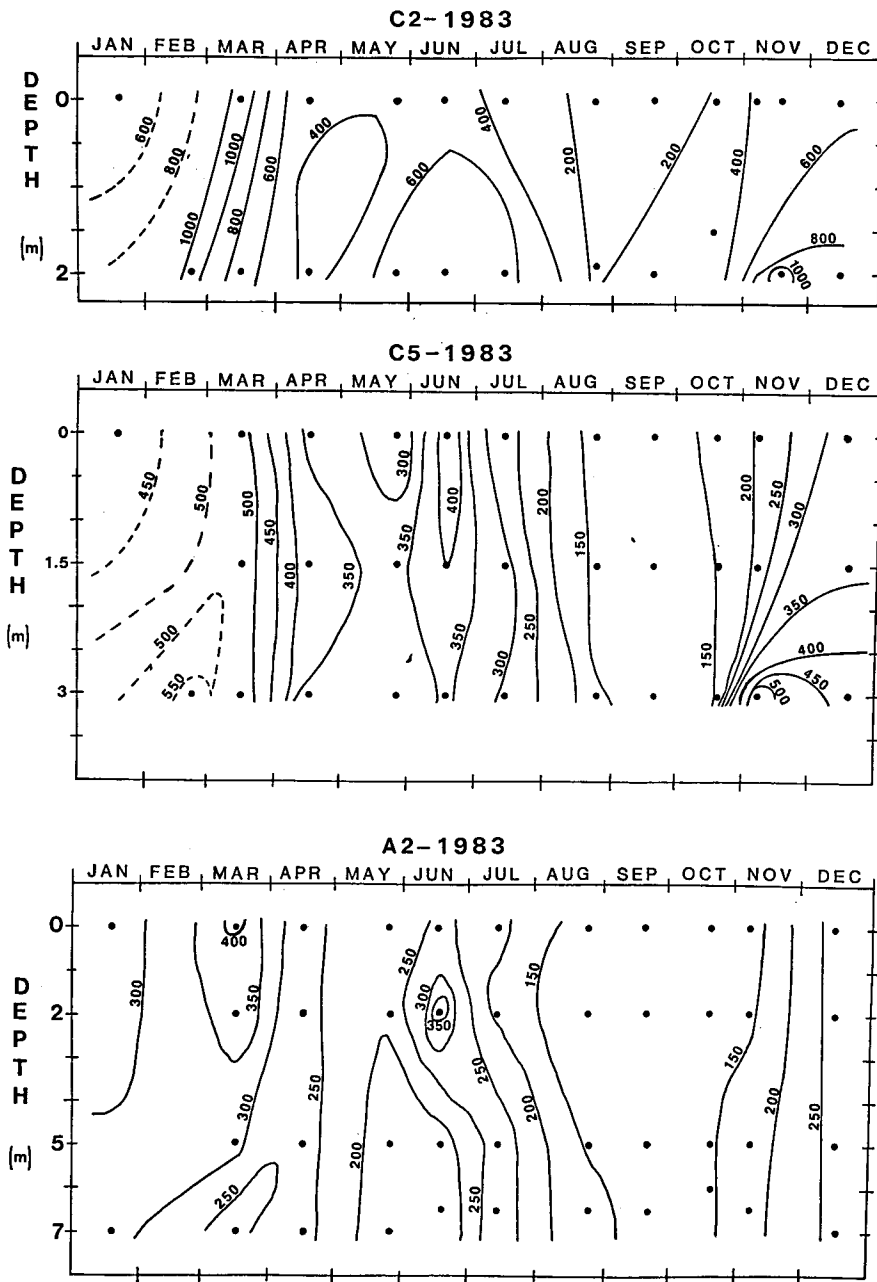


Fig. 8. Sulfate concentration (μM) isopleths in the Lake Anna water column at stations C2, C5, and A2 during 1983. Isopleths are given in 200 μM intervals at C2 and 50 μM intervals at C5 and A2. Dashed lines indicate approximate isopleths due to the scarcity of the surrounding data points. Reproduced with permission from Herlihy & Mills (1985).

mine drainage, the damage may be complete and the water converted to that similar to an acid mine stream. The more prevalent cases are those in which a small proportion of the inflow water is acidified, or the precipitation is acidic. In such

instances, many factors, physical, chemical, and microbiological, combine to buffer the acidity. The current lack of information prevents definitive statements about the combined effects at present. Continued research in the area should be aimed at

those interactions, and attempt to quantify the processes involved so that accurate predictions of the behavior of the polluted impoundments may be made.

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