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common assumptions and misconceptions

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Eutrophication control by sediment treatment common assumptions and misconceptions

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Sediment processes influencing eutrophication

Sediments are a major problem in aquatic ecosystem management and restoration. Sediments contain a much higher concentration of nutrients than the water column and can be a major source of nutrients to the water column. Recent studies in Sweden indicate that in summer, as much as 99% of the gross nutrient flux comes from the sediments (Rydin and Brunberg, 1998). Typhoon sediment agitation in Lake Biwa, Japan seems to be associated with the initiation of *Microcystis* blooms (Frenette et al., 1996). The southern basin of Lake Biwa has become more eutrophic and part of the problem appears to be related to sediments (Kurata, 1994).

Unfortunately, when external sources of nutrients are controlled, this rapid seasonal reflux of nutrients from sediment can maintain eutrophication for decades (Sas, 1989). Improvements in the quality of the overlying water and associated components of the aquatic ecosystem often cannot be achieved without some form of sediment treatment. The control of excessive algal growth is still the biggest aquatic environmental problem, and the concern over algal toxins is growing (Carmichael, 1992). Advocates of environmental restoration often promote the hypothesis that directly treating a lake will enhance the utility of source control. Huge dredging projects to control eutrophication are taking place in Lake Biwa and other lakes in Japan.

Sediment redox reactions – iron phosphate reactions

Before sediment treatment can be effectively implemented, the project manager must understand the basic processes influencing nutrients in sediment. Some concepts that pervade limnology are classic and in need of revision. For example, the work of Mortimer on iron phosphate reactions was profound in 1941, but if he had current geochemical analytical methods, he would be the first to amend his theories. Most sediment phosphorus studies have stressed the importance of ferric iron adsorption of phosphorus (Mortimer, 1941, 1971; Williams et al., 1971; Krom and Berner, 1981). Ferric iron is well known to adsorb and precipitate more phosphorus than ferrous iron. Thus, when eutrophication results in sediments becoming more reduced, phosphorus is dissolved which can eventually be released to the surface water (Murray, 1995). This scenario is important but overly simplistic.

Although ferric reactions are probably mainly controlling the solubility of phosphorus in the surface sediments, the flux of phosphorus from deeper sediments in Lake Biwa, and presumably many other lakes, is controlled by vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] formation (Murphy et al., 2001, Fig. 1). Ferrous iron is well known to react with phosphorus to form the mineral vivianite. It can be an important sink for phosphorus in lakes. Usually its presence is detected indirectly using geochemical calculations and chemical analyses of sediment extractions or porewaters (Emerson and Widmer, 1978), but it has also been

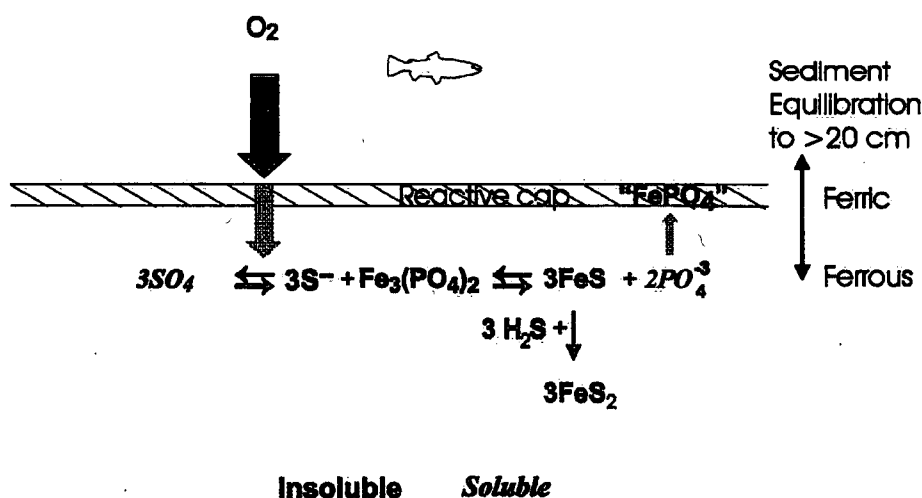


Fig. 1. Major sediment phosphorus reactions in Lake Biwa.

identified with microscopic and X ray diffraction methods (Cornwell, 1987). It has been demonstrated in lakes (Olsson et al., 1997, Hupfer et al., 1998) and groundwater (Griffioen, 1994) that the formation of vivianite is partly controlled by the ratio of iron to phosphate and that as long as the iron concentration exceeds sulphide concentration, vivianite will be stable. In Lake Biwa, vivianite was detected with a combination of magnetic separation, XRD and other procedures. There are important exceptions where geochemical calcula-

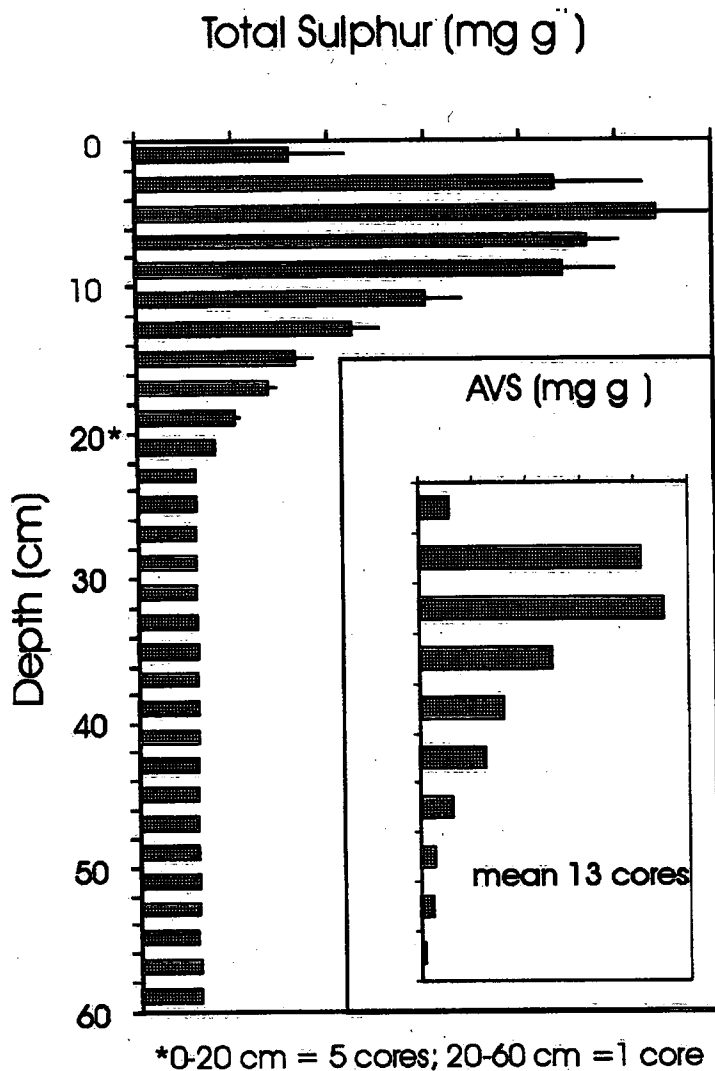


Fig. 2. Concentration of total sulphur and acid volatile sulphide in Lake Biwa sediments.

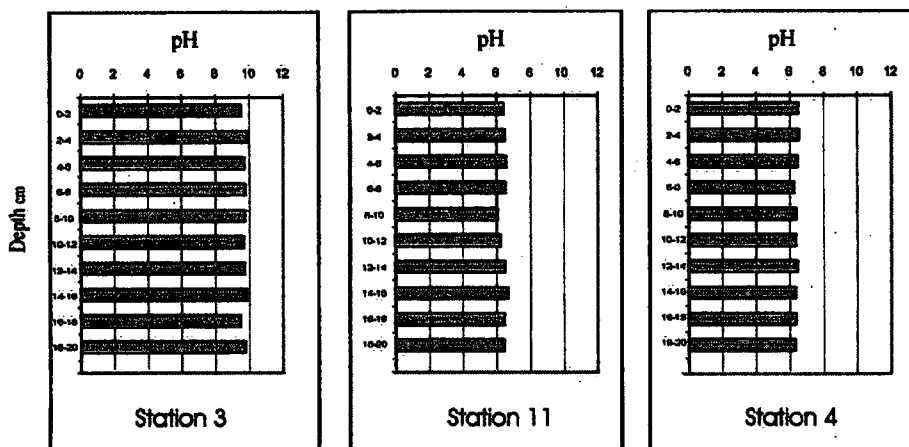


Fig. 3. Equilibration of pH in sediments.

tions indicate vivianite should precipitate, but it does not (Stauffer, 1987; Boers and de Bles, 1991).

Interaction of deeper sediments with surface sediments

The importance of ferrous iron reactions does not dispute the importance of the surface cap of oxic iron. The absence of an oxic cap reflects severe anoxia where vivianite is not stable in the subsurface sediments. The exchange of the surface 2 cm oxic layer of sediments with 20-30 cm of deeper sediments has been observed in Lake Biwa (Murphy and Kumagai, unpublished). In a Canadian lake with a much higher sedimentation rate than Lake Biwa, Carignan and Lean (1991) observed that 50-100 cm of sediment was involved with sediment phosphorus release. Although this concept of deeper sediments being part of sediment nutrient release has been known since at least 1988 (Carignan, 1988), it has not been widely recognized. In Lake Ontario, we have observed the depth of the seasonal change in sulphate in the sediment porewaters to exceed 30 cm (Moller et al., 1993). The increased concentration of sulphate during winter reflects the oxygenation of reduced sulphur. Another example of diffusion or diagenesis is illustrated in Fig. 2 where the peak of total sulphur in Lake Biwa is subsurface. The lower concentration of sulphur on the surface sediments cannot represent reduced sulphur loading; it reflects movement of sulphate to a zone of sulphide precipitation in subsurface sediments. The rapid equilibration in the porewater pH (Fig. 3) or redox (not shown) is another illustration. In figure 3, the porewater of stations 11 and 4 are typical of the usual values but during the extremes of reduction observed at station 3, the pH of entire depth of sampled sediments (>20 cm) changed. A final example of diagenesis is

the formation of surface crusts and nodules of manganese and iron in parts of Lake Biwa (Takamatsu et al., 1993). These elements migrate from deeper sediments and precipitate on the oxic surface.

Diagenesis is not independent of physical mixing. The actual release of phosphorus from sediments into the overlying water has often been related to physical factors such as currents, waves, storms, and boats. Diffusion is too slow to explain the observed phosphorus release rates. Holdren and Armstrong (1980) observed in laboratory studies that bioturbation had the greatest effect on phosphorus release rates. However, other physical forces are probably at times more important. In Norway, studies have shown that fluxes of phosphorus are highly dependent on water circulation (Skogheim and Erlandsen, 1979). In Denmark, phosphorus release from sediments can increase 20-30 fold during resuspension events (Sondergaard et al., 1992). Little data exists on the way water depth affects the depth of sediments that influence water chemistry, but our unpublished data from Lake Biwa indicates it varies from about 20 cm in deep water (>90 m) to at least 35 cm in shallow water (2 m). Presumably wind speed and fetch affect this relationship in a similar manner to the way they influence sediment resuspension (Stefan and Hanson, 1980), i.e. strong winds with a long fetch enhance sediment mixing and phosphate release.

Microbial processes in sediments cannot be ignored. Bacteria store phosphate in polyphosphate granules, and under reducing conditions, these granules dissolve. Another biological factor of significance for sediment phosphorus release is algal recruitment. Hansson (1996) states that about 32% of algal taxonomic groups exhibit recruitment from sediments and that this process is an important aspect influencing formation of algal blooms. Barbiero and Welch (1992) observed that a substantial portion of internal phosphorus loading was due to recruitment of the blue-green algae *Gleotrichia* from lake sediments. The algae of concern in Lake Biwa are *Microcystis*. Since *Microcystis* has a high K_s and low V_{max} for phosphorus (Nalewajko and Murphy, 2001), it would not compete well with other algae unless it had occasional access to high phosphorus concentrations as found on the sediments. Recruitment of *Microcystis* from lake sediments was observed by Reynolds and Rogers (1976) and Trimbee and Harris (1984), but little is known on how this process is regulated. It is possible that changes in sediment redox and physical processes could trigger release of algae from sediments.

Oxic surface sediment phosphate desorption – importance of pH

Iron rich sediments with low buffering are well known to release phosphorus into high pH water (Jacoby et al., 1981; Boström, 1984; Drake and Heaney 1987). Andersen (1975) observed maximal release of phosphorus at a pH

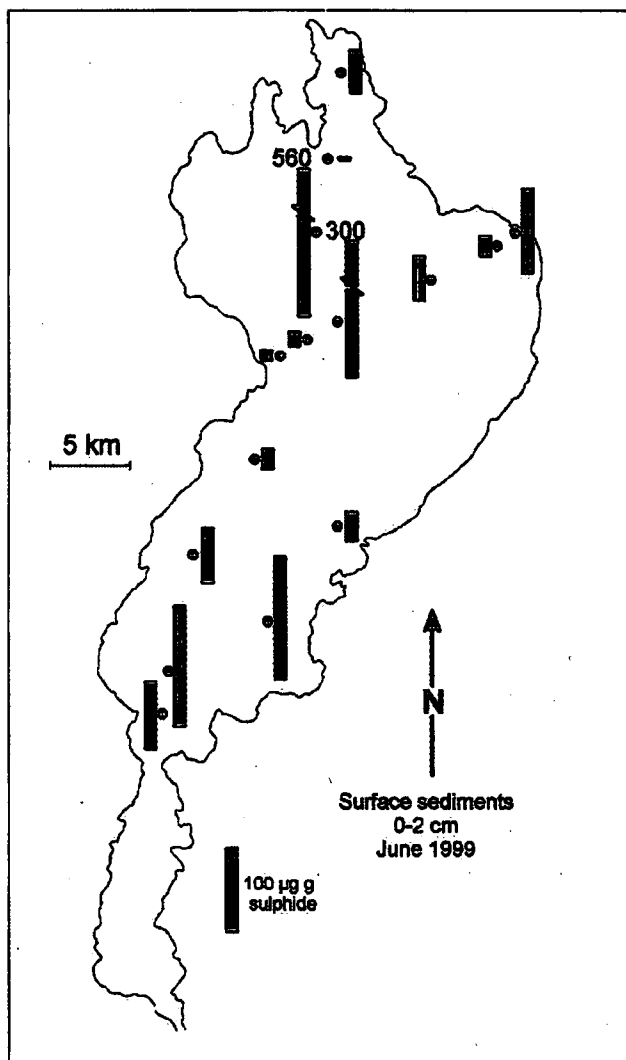


Fig. 4. Distribution of sulphide in Lake Biwa, Sept. 1999.

around 9-9.2. These studies assumed that the primary process influencing the pH of sediments was algal production. Thus, sediments above the thermocline would potentially show this pH mediated response much more than the sediments in deeper water. However, in spite of algal blooms and a pH of surface water exceeding 9, in our studies in a shallow bay of Lake Biwa (Akanoi Bay) we did not observe high pH values in sediments. We did observe a high pH of

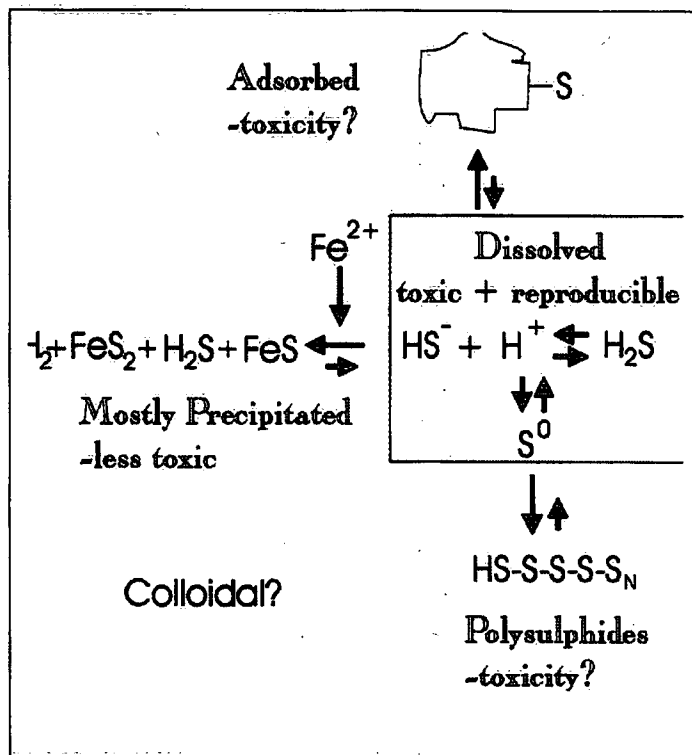
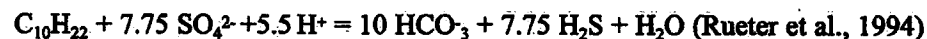


Fig. 5 Sulphide sediment chemistry.

9.95 in sediments located in deep water (>90 m) where the acid volatile sulphide concentrations were highest (560 mg g⁻¹, Fig. 4). Bacterial sulphate reduction is a process by which organic matter is oxidized under anaerobic conditions (Fig. 5). The process produces alkalinity and the following two equations indicates that the degree of pH shift would reflect the degree of reduction of the organic matter being metabolized:



and



The acid consumed in this reaction presumably accounts for the high pH observed in these sediments in deep water. It is probably too simple to consider only reduction reactions to be responsible for sediment release of phosphorus. The pH of 9.95 is in the range where 50% of the phosphorus adsorbed to ferric iron

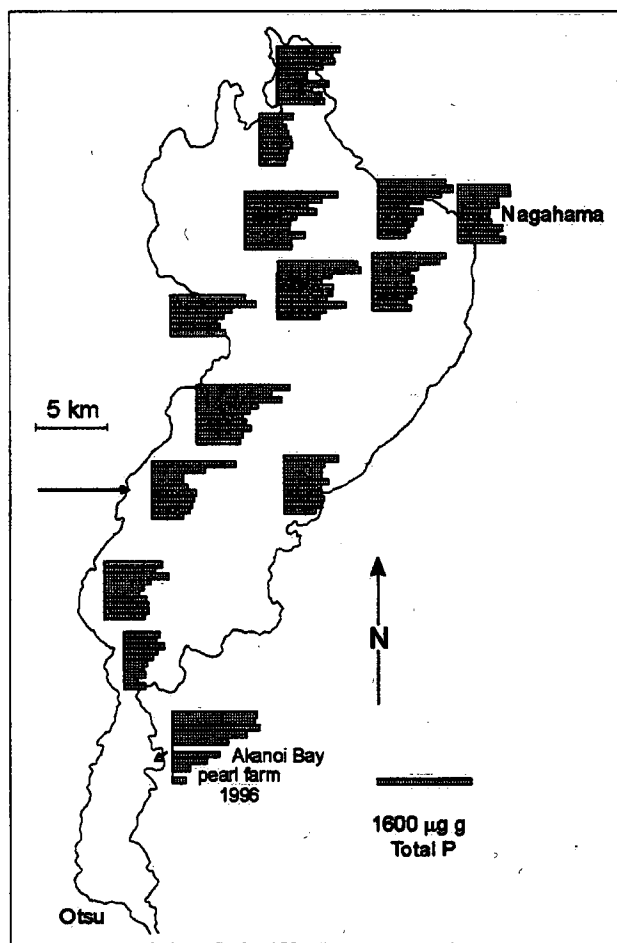


Fig. 6. Distribution of total phosphorus in Lake Biwa sediments. With the exception of the Akanoi Bay data, the samples were collected in 1999.

should be dissolving and presumably is (Stumm and Morgan, 1981, page 638). The idea of reduction reactions occurring in association with oxic particulate iron reflects that porewater reduction can proceed faster than the solid phase reactions. It seems that most of the phosphorus in surface sediments does not dissolve. The profile of total phosphorus in the sediments (Fig. 6) supports the idea that phosphorus is being mobilized from deeper sediments and is moving upwards where currently most of it precipitates. Using a sediment rate of 2 mm yr^{-1} (Kashiwaya, personal communication) and the most extreme data (surface three samples from station 11, 1999 data), the rate of phosphorus diagenesis in

Lake Biwa can be estimated to be as much as $1.5 \text{ mg m}^{-2} \text{ d}^{-1}$. This rate is less than the highest sediment release rates of 2.8 and $14 \text{ mg m}^{-2} \text{ d}^{-1}$ observed by Kurata (1994) and Murphy et al. (2001) respectively in Akanoi Bay of Lake Biwa. The highest rates of sediment release probably represent pulses of microbial activity or physical mixing events.

Sulphate enhancement of eutrophication

The increased loading of sulphur into Lake Biwa presumably with additional organic matter resulted in higher sulphide concentrations in the sediments (Fig 2). Unfortunately, the elevated sulphide concentration resulted in the dissolution of vivianite (Fig. 7, 8). Probably the first concern about sulphur loading stimulating eutrophication was raised by Caraco et al. (1989). The mechanism of sulphate stimulation of eutrophication was shown by Smolders and Roelofs (1993) to be related to enhanced formation of iron sulphides leading to iron limitation, phosphorus dissolution and eutrophication. The work of Smolders and Roelofs was confirmed in the Netherlands by Bellemakers and Maessen (1998). The Australians have also documented similar concerns that sulphate from fertilizers and organic wastes enhances phosphorus release from sediments (Donnelly et al., 1997).

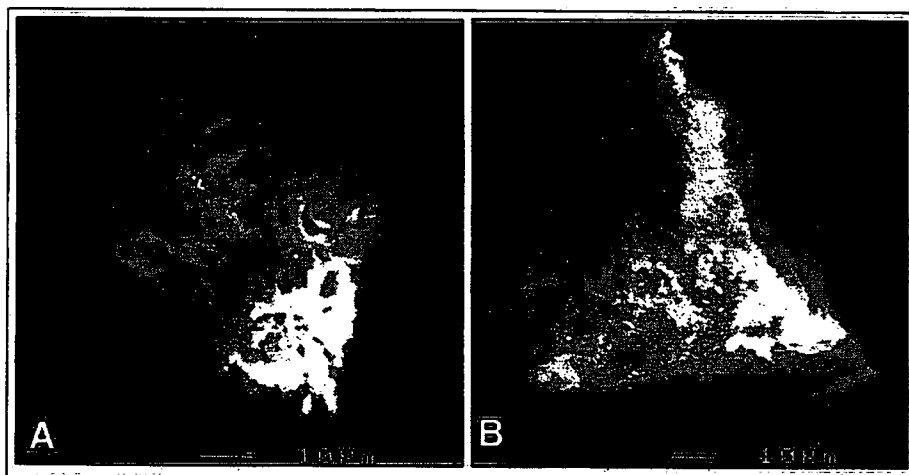


Fig. 7. Vivianite crystals collected in 1996 in Lake Biwa sediments A was collected from sulphide rich sediments from the pearl farm of Akanoi Bay. B was collected from station 9, 35 deep from the sediment surface in the North Basin and below when the sulphide concentrations increased.

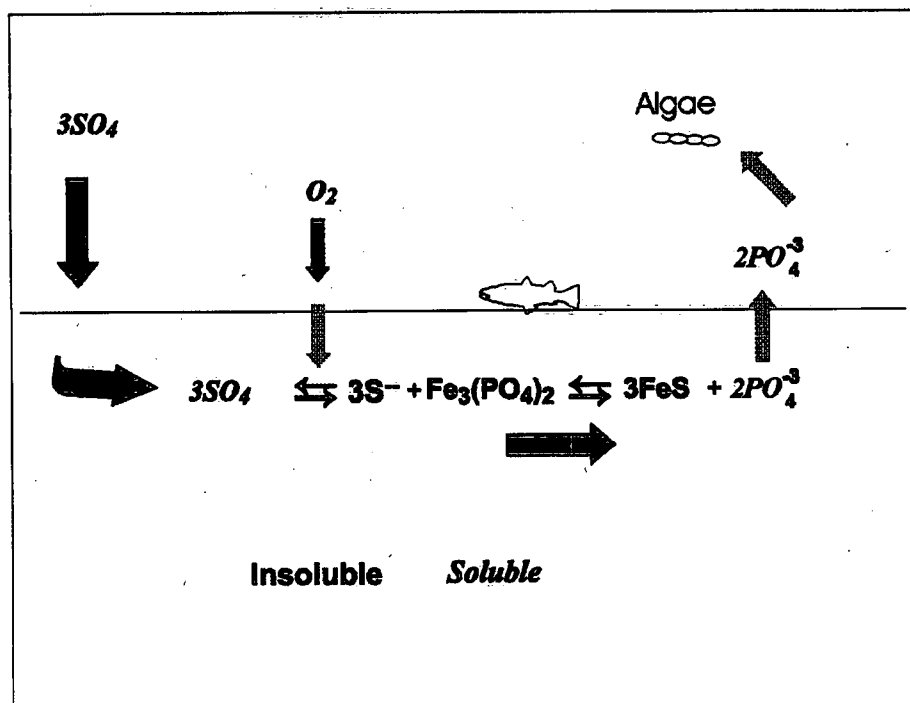


Fig. 8 Sulphate loading dissolves vivianite.

Relevance of sediment eutrophication processes to sediment treatment

Dredging

Dredging will remain an important lake restoration procedure, but it is easier to justify its use for maintaining lake volume than as a treatment for eutrophication. Certainly there are some famous examples of lake restoration with dredging (Andersson et al., 1973). Most dredging for environmental purposes attempts to remove the nutrient enriched surface layer. Many years ago, Yoshida (1982) stressed the uncertainty of the long-term effectiveness of such dredging. Some dredging strategies emphasize the importance of creating a deeper water column (Hanson and Stefan, 1984). A deeper water column reduces sediment resuspension and maintains most nutrients in stratified deeper water. However, dredging to produce stratification in an entire lake is very expensive. Dredging to create a stratified water column in part of a shallow lake has worked well (Murphy et al., 1999). These dredged areas become sediment traps to focus the most nutrient rich organic material for subsequent removal or treatment. This

concept has particular relevance to controlling blue-green and red tide algae, which at times rest upon, or access nutrients from sediments. It is not just the major nutrients (N and P) that are important. Chelated iron in sediment porewaters can stimulate red tides (Nishio and Ishida, 1990). These chelators appear very similar to those observed to stimulate blue-green algae (Murphy et al., 1976). Lakes with high sedimentation might also benefit from sediment traps built in areas where subsequent sediment removal is easier and hence more cost-effective.

Dredging may fail to reduce eutrophication for many reasons including:

1. inadequate control of external nutrient loading
2. undesirable habitat alteration such as macrophytes replaced by phytoplankton
3. inadequate suppression of sediment phosphorus release.

The first and third items are not necessarily independent. A newly formed layer of organic rich sediment can still have intense sulphate reduction, a high pH and phosphorus dissolution. Sediment diagenesis can also result in the failure of dredging to reduce eutrophication. If the external sources continue to cause sediment conditions that result in mobilization of phosphorus from deeper sediments, a surface layer rich in phosphorus will reform, and surface sediment phosphorus concentrations will likely return to pre-dredging rates. In Lake Biwa, sand capping is done after dredging. This practise will suppress diagenesis, but perhaps more reactive materials than sand should be considered.

Sediment oxidation

Most attempts to oxidize sediments have been done via lake aeration (Babin et al. 1999). However, there are remarkably few measurements of sediment sulphides in lake aeration projects. Oxygen is sparingly soluble, and sediment oxygen demand can exceed oxygen supply several fold. Furthermore, in one study it was demonstrated that oxygenation through forced aeration of two Swiss lakes with high sedimentation rates was not sufficient to oxidize the surface sediments or reduce internal phosphorus loading (Gächter and Wehrli 1998).

Since nitrate is much more soluble than oxygen, it is possible to inject enough nitrate to overcome the sediment oxygen demand (Murphy et al., 1995, Fig. 9). In laboratory and in situ treatments of Akanoi Bay, Lake Biwa, >97% and 80%, respectively of the porewater phosphorus was precipitated (Murphy et al., 2001). Furthermore, high purity nitrate is available in bulk from agricultural sources at a relatively low price. Repeated treatments would still be

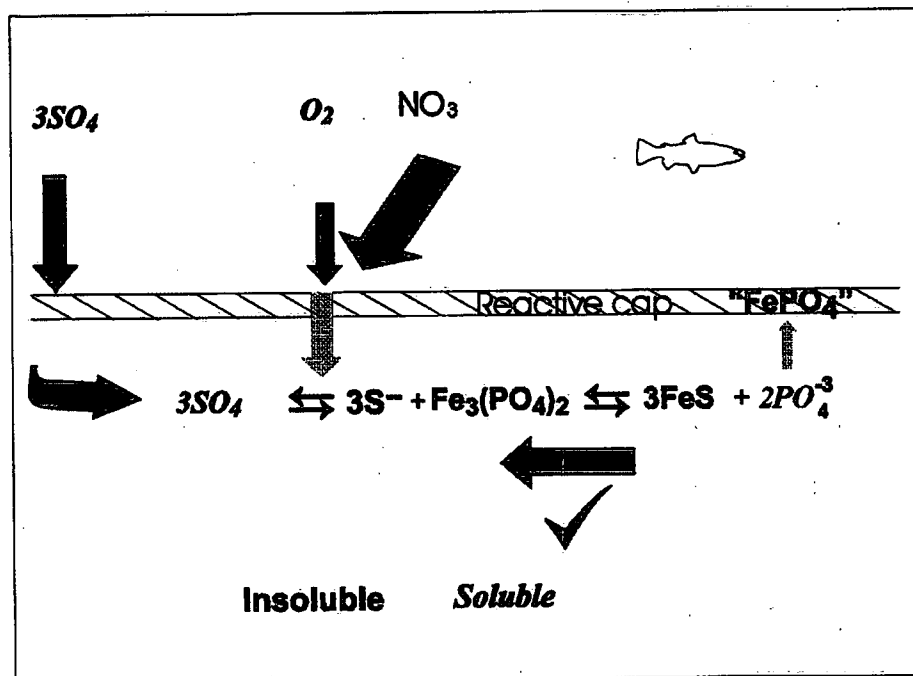


Fig. 9. Effect of nitrate treatment on vivianite stability.

expensive so, as always, source control must be evaluated relative to in situ treatment. Detailed budgets of sulphate loading are lacking in Japan, where much of the loading is likely atmospheric and difficult to control. Recent studies indicate that much of the winter acid rain in Japan comes from China and Korea (Kyodo News, 2000). It should be possible to calculate the sulphide formation rates in sediments and the cost of both external sulphur loading and in situ injection of sulphate. Source control of sulphur must be done for other reasons, but some in situ treatment would likely be required. The hesitations associated with nitrate treatment of sediments are usually associated with it being a nutrient and a health concern in drinking water. With proper engineering, including standardization and monitoring, the risks of implementation are much less than expected in relation to other nitrogen sources at most sites. For example, the nitrogen loading into Akanoi Bay, Lake Biwa as measured by the Shiga Prefecture exceeds 300 kg d⁻¹.

Ferric chloride is another oxidant that has been added to sediments either with nitrate or by itself (Ripl, 1976, 1986; Murphy et al., 1996). In situ sediment treatment is a relatively new option. Ripl's system was relatively small but the process was effective. A much larger but similar process was used by

Volker Stevin, a Dutch firm. The Dutch sediment treatment of a shallow lake with ferric chloride was not successful, and apparently sources of nutrients were not well controlled (Boers et al., 1992). Two concerns that have limited iron use are contamination and the high reactivity and acidity of most iron solutions. Two other oxidants that have been utilized in small treatments of lake sediments are calcium peroxide and magnesium peroxide. Vendors market these products as slow acting oxidants. One concern is the high pH that these oxidants create. Without pH buffering, the high pH dissolves phosphorus from sediments.

Phosphate inactivation

Iron can be both an oxidation agent and a complexation agent. Ferrous iron can react with phosphorus to form vivianite (Nriagu, 1972). Frossard et al. (1997) demonstrated that iron addition to sewage treatment plants resulted in formation of vivianite. Since sewage treatment plants have a short residence time, the rate of formation of vivianite must be relatively fast. Iron has been added to both the water column and sediments of lakes. Two compounds used more commonly in lake treatment for phosphorus precipitation are lime (calcium hydroxide) and alum (aluminum sulphate). Unlike iron, these two chemicals are almost always added to the water column. Addition of alum or lime to the water column deposits a new reactive layer on the sediment surface (Murphy et al., 1988, 1990, 1993; Murphy and Prepas, 1990; Prepas et al., 1990). These chemicals readily react with phosphorus diffusing from sediments and prevent phosphorus from being released into the water column. Lime is purported to form apatite; although there is considerable indirect evidence, the argument is still incomplete. In North America, these lake treatments are focused on precipitation and flocculation of phosphorus and organic particles from lake water, and little attention has been directed at their ability to treat sediments or block algal recruitment. In Japan, lime is added to seawater to inactivate phosphorus in sediments and to reduce the odour associated with high concentrations of hydrogen sulphide. At times, there are concerns that these chemical treatments can damage biota. Lime can enhance toxicity of ammonia (Hillaby and Randall, 1979); iron and alum could potentially foul the gills of fish. However, both lime and alum are often used without any damage to fish. Concerns about contaminants or impurities in these lake treatment chemicals should be considered carefully. Lime and nitrate are almost always free of contaminants. Iron solutions that come from steel making which uses recycled metals can be badly contaminated with cadmium and other metals. The presence of sulphate in alum and some iron solutions requires specific attention.

Alum

For softwater lakes like in Japan, the first consideration with alum treatment is to buffer the solution with sodium aluminate (Cooke et al., 1986). It is important to maintain a neutral pH so that aluminum does not dissolve. Titrations of Lake Biwa sediments in small field treatments with alum and sodium aluminate achieved pH values of pH 6.1-6.5 (Murphy et al., 2001). Titrations of poorly buffered sediments in large-scale treatments are unlikely to be much better, and patches of slightly alkaline or slightly acidic sediments are expected. These small sediment treatments in Lake Biwa resulted in extremely high concentrations of porewater sulphate (Fig. 10). The alum/aluminate buffer should work well for small lakes where the whole site was treated. A partial treatment of bays or hotspots of a large lake might not be the best thing for a softwater

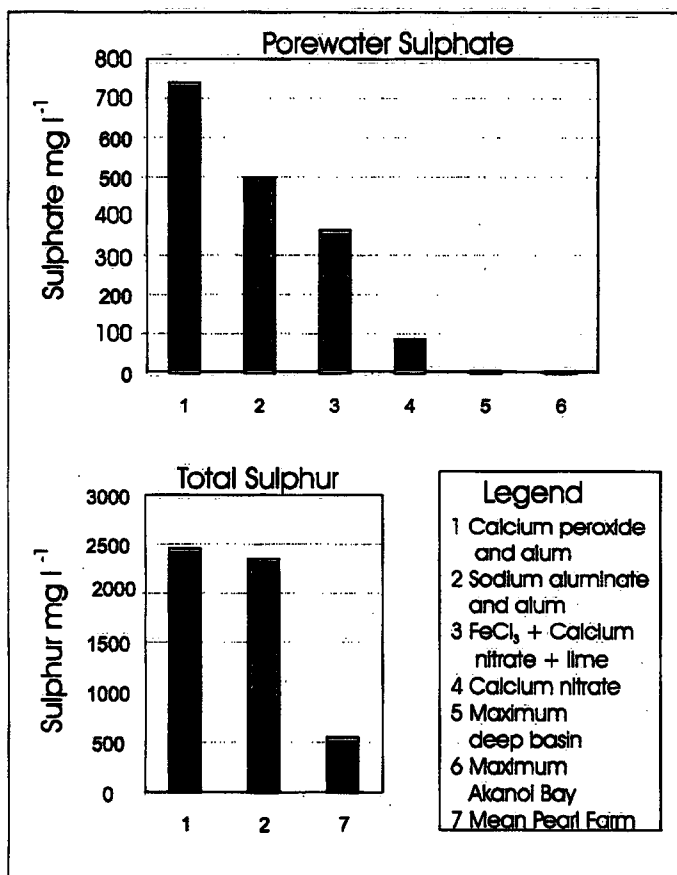


Fig.10. Porewater sulphate after in situ chemical treatments.

lake. Any major increase in porewater sulphate is a concern. Some of the sulphate will get flushed from the lake, but some of it would move to areas not treated and facilitate enhanced sulphide formation and, in turn, dissolution of vivianite. This topic does not appear to have been considered and warrants further attention.

Equally as perplexing was the high sulphate content in a ferric chloride/lime treatment (Fig. 10). One or both of these compounds must have contained a significant amount of an impurity. It is possible to buy these compounds without sulphate, but if the prices were too high, they would not be useful for lake treatment. Of course, the information is new, and more evidence is required, but considerations for sulphate free products for sediment treatment should begin. In North America, sulphate free lime is readily available, and presumably the same applies in Asia. However, the availability of sulphate free ferric chloride at reasonable prices is less certain. Ferric chloride is usually derived from primary steel makers. At one time, sulphuric acid was used extensively in steel making, but now many North American steel mills use hydrochloric acid instead of sulphuric acid. The availability of sulphate free ferric chloride in bulk at prices suitable for sediment treatment will reflect the local steel making processes.

The nitrate treatment of Lake Biwa increased the concentration of sulphate slightly (Fig. 10), but this sulphate came from the oxidation of other sulphur compounds, not impurities. In the nitrate treatments, only 16% of the total sulphur was converted to sulphate. Presumably, most sulphur in Lake Biwa is associated with organic matter. Changes in sulphur speciation or availability resulting in higher concentrations of sulphide are critical to vivianite stability and the future sediment phosphorus release in Lake Biwa. Our results indicate that enhanced external loading, especially of sulphur and organic matter will increase the internal loading of phosphorus. The effect of increased sulphur loading could be confirmed via in situ incubations. The mechanisms of vivianite dissolution and phosphorus dissolution are not completely resolved. We discussed the processes that we observed, especially the high pH associated with sulphate reduction, but there must be periods of low pH associated with sulphide oxidation too. Our data does not absolutely prove that sulphur loading has increased; diagenesis in sediments can result in redistribution of sulphur. It is important to evaluate the sources of increased sulphur loading. Potential sources include garbage incineration, fuel combustion, agricultural fertilizers, and sewage. If more source control is to be implemented, the relative proportion of long-range vs. local loading is also important. Evaluations could provide clarification in the degree of source control possible and the relative costs of in situ treatment. These vivianite reactions strongly influence ongoing sediment and lake treatments. Diffusion from deeper sediments will reduce the

effectiveness of dredging, but the rate that sediment phosphorus release returns to predredging rates and relative importance of external and internal phosphorus sources is unclear. Capping of sediments should be more effective with the addition of more reactive ingredients to buffer pH, oxidize sulphide or complex phosphorus. Ideally, lake aeration should be designed to oxidize sediment AVS, and it should at least be monitored prior to and during treatment.

Summary

Sediment treatment traditionally is centred on sediment dredging. It is a basic process that has been modified several times to increase efficiency. Some aspects, such as sediment traps, probably could be used more to improve the cost-effectiveness of dredging. The rate that a layer of contaminated sediment forms after dredging must be well understood so that the life cycle of dredging can be forecasted. External sources are not the only cause of the formation of a surface layer enriched with metals and nutrients. For example, transformations in the sediment such as sulphide dissolution of vivianite can result in diagenesis or upward movement of phosphorus to form a new surface layer enriched with phosphorus. Some of the enhanced eutrophication of Lake Biwa is associated with increased sulphate loading resulting in higher sulphide concentrations. Phosphorus inactivation with reactive caps should be evaluated with chemicals that stabilize vivianite.

Acknowledgements

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