

Phosphorus Sequestration in Lake Sediment with Iron Mine Tailings

MAUREEN E. CLAYTON
SARAH LIEGEOIS
EDWARD J. BROWN

University of Northern Iowa
Cedar Falls, IA, USA

Internal phosphorus loading can lead to eutrophication in lakes when anoxic sediments release bioavailable phosphorus into the water column. In laboratory experiments, iron mine tailings helped to sequester phosphorus in sediment from a eutrophic lake. Phosphorus release from the sediments after extraction with distilled water or 0.02 N H₂SO₄ was significantly reduced when mine tailings were added (1:1 w/w), even when the system was anaerobic (~1 mg O₂/L). The degree of sequestration was enhanced when glucose (1% w/w) was added to stimulate the growth of microorganisms, suggesting that the process was microbially mediated. We suggest that oxidized iron in the mine tailings served as an electron sink for microbial respiration via dissimilatory Fe³⁺ reduction. The reduced iron released into solution sequestered phosphorus, either as it re-oxidized and formed hydrous ferric oxide complexes containing phosphorus (HFO-P), or through precipitation. Since mine tailings are inexpensive, they may prove useful for preventing phosphorus from entering surface waters, as well as reducing internal phosphorus loading.

Keywords Nutrients, phosphorus, lakes, wetlands, soil, remediation, sequestration.

Introduction

Orthophosphate (PO₄³⁻) is found in surface and ground waters as a result of the natural weathering and solution of minerals, soil erosion and transport, soil fertilization, and the use of soluble phosphate compounds in detergent manufacture, water treatment and industry. Controlling the total load of phosphorus in a lake is critical to controlling eutrophication since phosphorus is usually the biomass limiting nutrient in natural aquatic ecosystems. The phosphorus cycle does not allow atmospheric venting (as the nitrogen cycle does), so phosphorus tends to accumulate in the sediments of lakes. In a healthy, well aerated lake, this does not cause a problem because the phosphates precipitate or are tightly adsorbed to common minerals in the sediments and are thus unavailable for biological uptake. In oxygen-depleted waters, however, the internal loading of phosphorus results from a problem known as the “phosphorus trap.” Phosphorus accumulated in the sediments is mobilized through dissolution or desorption to the aqueous phase under low-oxygen conditions in the sediments, resulting in a stimulation of biomass production and ultimately a further

Address correspondence to Maureen E. Clayton, Department of Biology, University of Northern Iowa, Cedar Falls, IA 50614-0421, USA. E-mail: maureen.clayton@uni.edu

decrease in the levels of oxygen in the water column and sediments. If phosphorus in lake sediments can be sequestered in a form which is not released under anaerobic conditions, internal phosphorus loading would be reduced.

Iron, in both the ferric (Fe^{3+}) and ferrous (Fe^{2+}) oxidation states, is known to react with phosphate (PO_4^{3-}), leading to precipitates and hydrous ferric oxides that tie up the phosphorus so that it becomes unavailable for the growth of plants in general and algae in particular. Fe^{3+} is a common metal in soils and rocks and is the form of iron that is primarily found in both aerobic water and many naturally occurring minerals, including hematite. Most forms of this ion are insoluble but, if solubilized (usually under acidic conditions), Fe^{3+} will react with phosphate. The simplest reaction that immobilizes phosphate is the direct precipitation of solids such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), which is essentially insoluble (Hutchinson, 1957).

Because Fe^{3+} is insoluble, many current methods for the treatment of wastewater phosphate consist of reducing Fe^{3+} to Fe^{2+} under anaerobic conditions and then precipitating the phosphate either before or during re-oxidation of the iron to Fe^{3+} . One of those methods treats phosphate by the reductive iron dissolution (RID) process in which Fe^{2+} is made available by the reductive dissolution of Fe^{3+} solids that are contained in a reactive porous media. The media is placed in direct contact with the unoxidized sewage so that reducing conditions are maintained. As a result, Fe^{3+} is reduced to Fe^{2+} and subsequently solubilized (Freeze and Cherry, 1979). Fe^{2+} in solution can then attenuate phosphate in two ways (Robertson, 2000). The Fe^{2+} can react with phosphate, resulting in the precipitation of Fe^{2+} -P solids, for example vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). If the effluent is also subsequently oxidized, Fe^{3+} -P solids can precipitate in the same way as described above under aerobic conditions.

Another wastewater treatment method is based on the same principle, but the reduction of Fe^{3+} is enhanced by microorganisms. In this case, a flow-through chamber providing Fe^{2+} for treatment of wastewater contains a quantity of Fe^{3+} material such as taconite or magnetite and a consortium of microbes that utilize Fe^{3+} as a terminal electron acceptor to degrade organic compounds in wastewater. The chamber is constructed to maintain anaerobic conditions, and nutrients (e.g. from wastewater and sewage) are added to initiate the generation of soluble Fe^{2+} . When the aqueous output containing Fe^{2+} is introduced to oxygenated water, it is oxidized to Fe^{3+} , which binds and precipitates phosphorus in the sewage (Hogen and Robin, 1996).

In this paper, we investigate whether this wastewater treatment principle can be applied to runoff catchment basins and constructed wetlands for treatment of phosphate pollution in lakes and other surface waters. In this case, large amounts of Fe^{3+} as contained in low cost iron mine tailings would serve as the biological oxidant for sediment organic material as well as serving as a phosphate sink. We hypothesized that the iron would be reduced by anaerobic bacterial respiration because Fe^{3+} is an electron acceptor in a wide variety of film-forming bacteria and the biological reduction of Fe^{3+} is a major mechanism leading to the production of Fe^{2+} in natural systems. The potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is very electropositive, and because of this, Fe^{3+} reduction can be coupled with oxidation of several organic and inorganic electron donors (Frossard *et al.*, 1995) during anaerobic respiration. We hypothesized that the soluble Fe^{2+} that would be produced could then react with phosphate present in the sediment/water interface or be re-oxidized by other soluble electron acceptors (i.e. nitrate), leading to precipitates that immobilize phosphorus in the sediment by the reactions described above.

Ore from the Cuyuna iron range in east-central Minnesota contains multiple carbonate micronodules comprised of a rhodonite core surrounded by calcite, rhodochrosite and

hematite (Fe_2O_3) (McSwiggen and Cleland, 2003). Therefore, iron mine tailings from the Cuyuna range contain various amounts of hematite. Hematite has a simple, repeating crystalline structure: iron and oxygen atoms coordinate to form two-dimensional layers, leaving small open spaces between them (Blake *et al.*, 1966; Smith, 1998). Hematite can fix atoms or molecules when they are introduced into those spaces by absorption, or molecules can adsorb to the surface of the mineral. In either case, the attraction can be physical or chemical, involving ionic or covalent bonds. Furthermore, it has been shown that reactions of water with hematite can involve dissociation of water, resulting in the formation of surface hydroxyl groups (Kendelewicz *et al.*, 1998), which may increase its ability to sorb compounds such as phosphates. Additionally, depending on its chemical environment, hematite can also make available iron and oxygen ions for chemical reactions such as oxidation/reduction. In particular, hematite releases iron ions in aqueous solutions.

In this study, we designed experiments to investigate whether the oxidized iron in mine tailings will serve as electron acceptor (oxidant) for anaerobic respiration of organic matter, become soluble, and then immobilize sediment phosphate. The experiments were designed to measure sediment phosphorus available for algal uptake and growth in Silver Lake, Iowa. This phosphorus includes soluble reactive phosphorus (SRP) in sediment slurries as well as phosphorus released from sediments after extraction with dilute acid.

Materials and Methods

Sediment Source

Approximately 1000 cm^3 of wet sediment was collected by grab sample from the middle of Silver Lake in Delhi, IA in May 2002. Silver Lake is highly eutrophic, with total phosphorus concentrations ranging from $504\text{--}926\text{ }\mu\text{g P/L}$ in surface water and varying from $12\text{--}1279\text{ }\mu\text{g P/g}$ dry weight in the top 5 cm of the sediment (unpublished data). The Silver Lake sediment used for these experiments contained $206\text{ }\mu\text{g P/g}$ dry weight sediment. Aliquots of the same sediment sample were stored in a sealed plastic bag at 4°C and were used in all of the experiments. The water content of the sediment was determined after drying a sediment aliquot to a constant weight at 105°C .

Phosphorus Concentrations in Sediment and Iron Mine Tailings

All glassware used in the experiments was acid washed in 1 N HCl and rinsed with deionized (DI) water. Total phosphorus was measured in the Silver Lake sediment sample and in a sample of the hematite obtained from mine tailings from the Cuyuna iron range in east-central Minnesota (courtesy of Emily Sand and Gravel, Emily, MN) according to the method of Clesceri *et al.* (1998). Briefly, a known volume of deionized (DI) water was added to 2 g sediment (wet weight) and the samples were subjected to persulfate ($\text{S}_2\text{O}_8^{2-}$) digestion (Clesceri *et al.*, 1998). Following digestion, the samples were centrifuged for 10 min at $5000 \times g$, after which phosphate concentrations in the supernatant were measured by the ascorbic acid method (Clesceri *et al.*, 1998).

To quantify the amount of phosphorus in sediment that was potentially available for algal growth, the sediment was extracted with various strengths of acid (H_2SO_4) and the amount of phosphorus released into solution was compared with the total phosphorus in the sediment as determined above. Total P as determined by the persulfate ($\text{S}_2\text{O}_8^{2-}$) digestion procedure is generally assumed to include sediment organic P and most forms of inorganic P, although some highly insoluble minerals may not hydrolyze with persulfate ($\text{S}_2\text{O}_8^{2-}$)

digestion. However, the operational definition of total P (Clesceri *et al.*, 1998) relates quite well to the amount of phosphorus which may be ultimately available for algal growth and is often used to describe the trophic status of surface waters. Phosphorus released with mild acid (H_2SO_4) extraction (about 0.02 N) is an operational definition which generally represents sediment phosphorus immediately available for algal and plant growth (e.g. Bray's P; Tiessen and Moir, 1993).

Deionized (DI) water amended with various volumes (V) of 3.571 M H_2SO_4 was added to each sediment or hematite sample (volume V_0) to reach the desired acid concentration (0, 0.02, 0.05, or 0.1 N). After the addition of DI water or acid, the sample was shaken vigorously by hand for 1 minute, allowed to settle for 5 minutes, shaken again for 1 minute and allowed to settle for an additional 5 minutes. Following this procedure, 2–5 mL of the solution were removed with a syringe and filtered through a 0.45 μm membrane filter. The filtrate (1 mL for acidic solutions or 5 mL for solutions containing only DI water) was diluted to 50 mL with DI water and analyzed for soluble reactive phosphate (SRP) by the ascorbic acid method (Clesceri *et al.*, 1998).

Phosphorus Release from Sediment

The various treatments for each experiment were conducted in duplicate or triplicate. For each experiment, 2 g of wet sediment were placed in a known volume (V) of DI water. For some experiments, mine tailings were mixed with wet sediment in a 1:1 ratio by weight. The mine tailings were dried, ground and sieved prior to use so that the particles used in this study were <2 mm. Treatments to the sediment slurries included variations in the oxygen level, biological activity and incubation time. Phosphorus concentrations in the sediment and in solution were measured in triplicate at various times for each treatment as described above. All phosphorus concentrations were standardized to sediment dry weight.

Oxygen levels influence the redox state of iron which, in turn, affects phosphorus sequestration. We employed two methods to make the sediment environment anaerobic in order to study the effects of oxygen on phosphorus chemistry. One method was to purge sediment slurries with N_2 (physical removal of oxygen), and the other was to incubate slurries under conditions favorable for microbial growth (biological removal of oxygen). To physically remove oxygen from the sample, the sediment was placed in a 60 mL glass vessel designed for anaerobic work, which was then filled with 30 mL of deionized water. The vessel was sealed with an airtight septum through which a needle was inserted to purge the vial with N_2 gas for approximately 30 minutes. The dissolved oxygen concentration in the sample was measured with a CHEMets kit (Fisher, Chicago, IL; indigo carmine method with detection limit of 1 mg/L). Purging continued until the dissolved oxygen concentration was less than 2 mg/L. After the purge, the samples were allowed to equilibrate for 2 days. The required time for reaching anaerobic equilibrium was determined in a separate experiment (data not shown).

In order to remove oxygen from the sample by biological processes, approximately 0.4 g of the sediment was placed in a 15 mL glass vessel designed for anaerobic work. The vessel was then filled with 13 mL of DI water containing 1% (w/w) glucose, leaving just enough headspace for phosphorus extraction (about 1 cm^3), and sealed with an airtight septum. The samples were left to incubate at room temperature for approximately 1 week, at which point dissolved oxygen was measured as above. Phosphorus concentrations were measured by the method outlined above after the 1 week incubation.

Data Analysis

The percent of available phosphorus released from the sediment was determined by dividing the phosphorus released under each treatment condition by the total phosphorus available in the sediment sample ($206 \mu\text{g P/g}$ dry weight sediment). In order to compare sediments treated with hematite to the controls (untreated sediment), paired Student *t*-tests were performed. Significance was determined at the 0.05 level.

Results

Total phosphorus in the Silver Lake sediment sample used for these experiments was $206 \mu\text{g P/g}$ dry weight sediment. The mine tailings also contained some phosphorus ($82 \mu\text{g}$ total P/g dry weight), although only a small portion of this phosphorus could be considered to be biologically available, as only $11 \mu\text{g P/g}$ dry weight was extracted with $0.02 \text{ N H}_2\text{SO}_4$.

Under aerobic conditions (dissolved oxygen concentration approximately 5.6 mg/L), little phosphorus was released into solution, but significant amounts of phosphorus could be extracted from both the untreated lake sediment and from sediment mixed 1:1 with mine tailings as extraction conditions contained increasing concentrations of acid (Figure 1). As expected, the degree of phosphorus release was related to the extraction conditions. Under conditions which represent phosphorus availability for algal growth (extraction with $0.02 \text{ N H}_2\text{SO}_4$), the untreated sediment released approximately twice as much phosphorus as the sediment mixed with mine tailings containing hematite (102.2 and $50.9 \mu\text{g P/g}$ dry weight sediment, respectively). However, phosphorus release from sediments and iron-containing compounds would be expected to be low under oxidizing conditions. Therefore, further experiments were done to measure the release of phosphorus from sediments under anaerobic conditions.

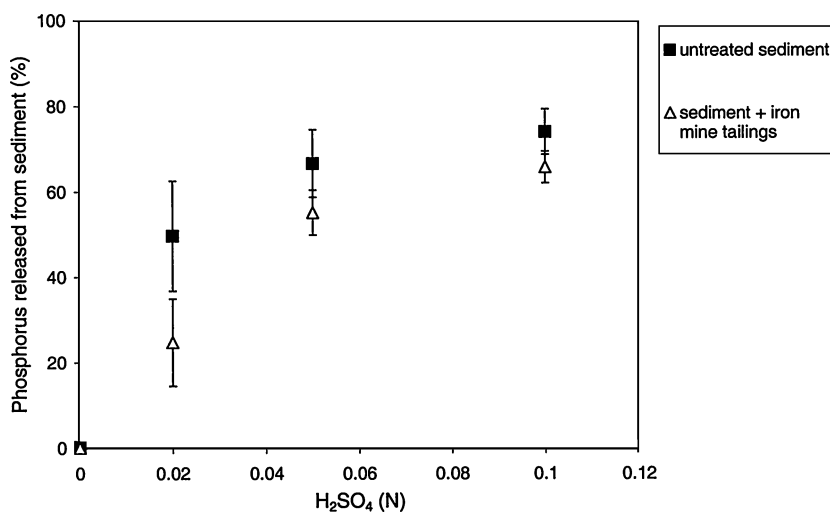


Figure 1. Release of phosphorus from Silver Lake sediment under aerobic conditions. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with iron mine tailings (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was $206 \mu\text{g P/g}$ dry weight. Means \pm standard deviation of duplicate experiments are plotted. Phosphorus release from the sediment samples treated with iron mine tailings was not significantly different ($p > 0.05$) from that of the untreated sediment samples.

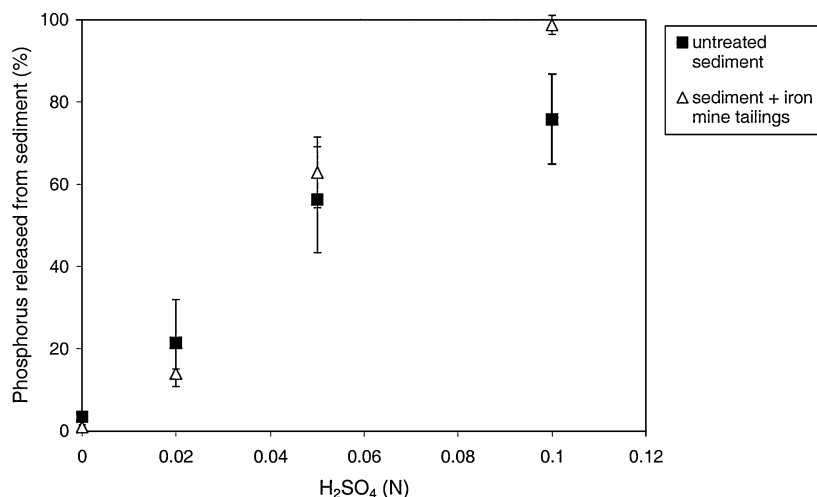


Figure 2. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was purged with N₂ and allowed to equilibrate for 2 days. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with iron mine tailings (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was 206 $\mu\text{g P/g}$ dry weight. Means \pm standard deviation of triplicate experiments are plotted. Phosphorus release from the sediment samples treated with iron mine tailings was not significantly different ($p > 0.05$) from that of the untreated sediment samples.

Following incubation for 2 days under anaerobic conditions (dissolved oxygen concentrations ~ 1 mg/L) generated by purging the system with N₂, mine tailings added to sediment did not increase phosphorus sequestration (Figure 2). After extraction with 0.02 N H₂SO₄, phosphorus release from the sediment (whether untreated or treated with mine tailings) was similar to that from aerobic sediment treated with hematite (44.2 and 41.3 $\mu\text{g P/g}$ dry weight sediment for untreated and treated sediment, respectively).

When the Silver Lake sediment was incubated for 1 week with an added carbon source (glucose) to stimulate microbial growth, approximately half of the phosphorus in the sediment was released into solution, even without the addition of acid (Figure 3). However, when these sediments were mixed with mine tailings and subjected to similar conditions, the phosphorus remained sequestered until the sediment was extracted with acid at concentrations in excess of 0.05 N. Oxygen concentrations in these samples were similar to those in the samples purged with nitrogen (~ 1 mg O₂/L).

When the glucose addition was combined with the nitrogen purge, approximately 40% of the total phosphorus in the Silver Lake sediment was released into solution (Figure 4), and nearly 60% was released with mild acid extraction (0.02 N). With hematite present in the system, most of the phosphorus remained sequestered in the sediment until the sediment was extracted with 0.1 N sulfuric acid. This sequestration is comparable to the situation in which the system is aerobic (Figure 1), although the final oxygen concentrations were ≤ 1 mg O₂/L in all of the anaerobic treatments.

Discussion

Iron mine tailings from the Cuyuna Range in Minnesota containing hematite proved to be effective for preventing the release of phosphate into aqueous solution from phosphorus-laden

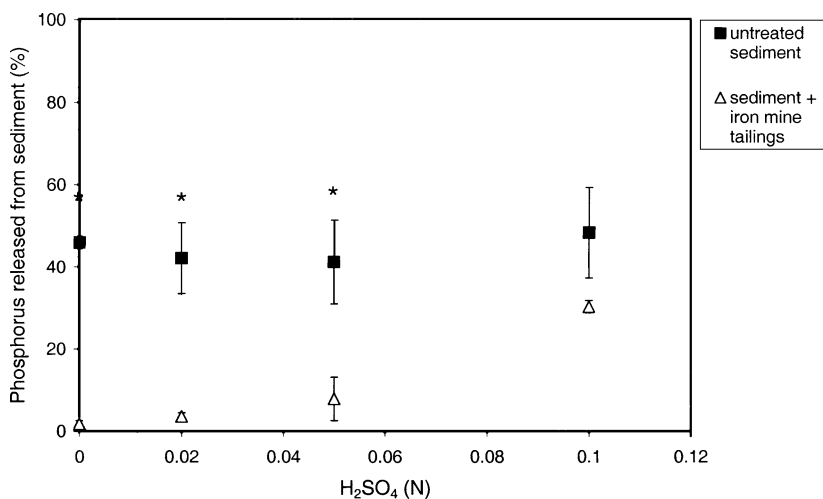


Figure 3. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was incubated with glucose (1% w/w) for one week. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with iron mine tailings (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was $206 \mu\text{g P/g}$ dry weight. Means \pm standard deviation of triplicate experiments are plotted. Statistically significant differences ($p < 0.05$) between the treated and untreated sediment samples are indicated by an asterisk.

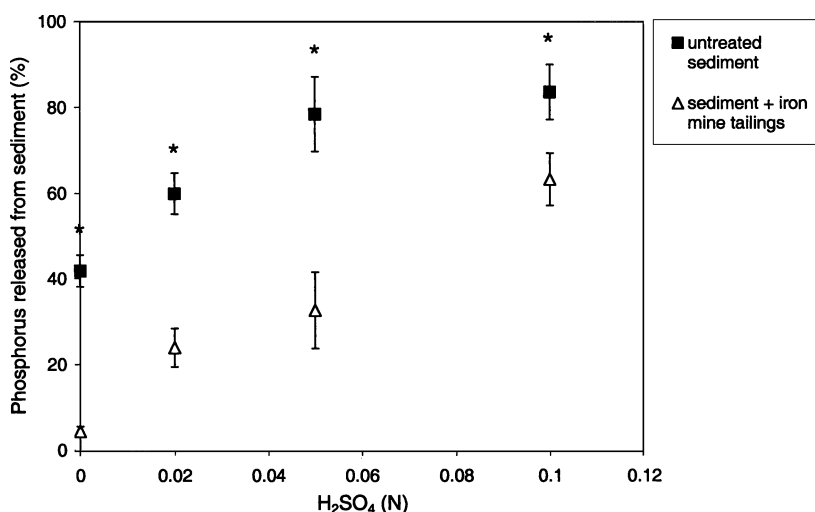


Figure 4. Release of phosphorus from Silver Lake sediment under anaerobic conditions after the sediment was purged with N_2 and incubated with glucose (1% w/w) for one week to stimulate microbial growth. Sediment samples (filled squares) and sediment mixed in a ratio of 1:1 (w/w) with iron mine tailings (open triangles) were extracted with deionized water and increasing concentrations of sulfuric acid. The total phosphorus content of the sediment was $206 \mu\text{g P/g}$ dry weight. Means \pm standard deviation of triplicate experiments are plotted. Statistically significant differences ($p < 0.05$) between the treated and untreated sediment samples are indicated by an asterisk.

Silver Lake sediments, even under anaerobic conditions. In both of the treatments in which anaerobic conditions were initiated biologically, the release of bioavailable phosphorus was significantly reduced in the sediments mixed with iron mine tailings as compared to sediment solutions alone, even though the dissolved oxygen concentrations were similar to those of the nitrogen purged system. The fact that the best results were seen in samples in which glucose was added to stimulate the growth of microorganisms suggests that the process of phosphorus sequestration was microbially mediated. We suggest that the hematite in the mine tailings served as an electron sink for microbial respiration, but that the reduced iron released into solution continued to sequester phosphorus, either as it re-oxidized, forming hydrous ferric oxide complexes containing phosphorus (HFO-P), or through precipitation as vivianite. The nature of the iron-phosphorus compound(s) formed in these reactions will be investigated further in future studies.

Conventionally, the presence or absence of O₂ is considered to be the main determinant of both iron and phosphorus chemistry in surface water. Indeed, anoxia does initiate the release of both Fe and P from the sediment into the water column. For this reason, aerators are commonly used in the restoration and management of shallow basins to oxygenate the water for aquatic organisms and to help prevent the release of phosphorus from surface sediments. However, it is known that Fe³⁺, as well as oxygen, can serve as an electron acceptor in some microbes through dissimilatory Fe³⁺ reduction (Fe³⁺ respiration) which leads to the oxidation of organic matter and the reduction of Fe³⁺ (Lovley, 2000, 2001). This process is likely to be particularly important in shallow basins with high concentrations of organic matter (Lovley, 2001), a common situation in eutrophic surface waters. We suggest that this process is responsible for the sequestration of phosphorus observed in our glucose-treated sediment amended with mine tailings. Further studies are planned to study the microorganism(s) involved and to better understand the mechanism of phosphorus sequestration by studying the effect of adding other carbon sources (e.g., acetate or glutamate) to optimize their growth under laboratory conditions. The addition of exogenous carbon sources would not be required for *in situ* treatment, however, as eutrophic lakes contain abundant sources of carbon for microbial respiration.

Other treatments for phosphorus sequestration in lake sediment have been described previously. These remediation techniques include the addition of aluminum (Rydin and Welch, 1998; Kopáček *et al.*, 2001; Van Hullebusch *et al.*, 2002; Lewandowski *et al.*, 2003), ferric sulfate (Perkins and Underwood, 2001), ferric aluminum sulfate (Foy, 1985), ferrous iron (Deppe *et al.*, 1999; Deppe and Benndorf, 2002), gypsum (Bastin *et al.*, 1999; Varjo *et al.*, 2003), CaO (Dittrich *et al.*, 1997), iron-based layered double hydroxides (Seida and Nakano, 2002), or hydroxyapatite seed crystals (cow bone; Jang and Kang, 2002). We believe that phosphorus sequestration with iron mine tailings containing hematite offers additional benefits in that this microbially mediated technique also has the potential to remediate other contaminants in the system.

Dissimilatory Fe³⁺ reduction has also been shown to influence the mobility of a variety of contaminants in aquatic systems. For example, some iron reducers can also transfer electrons to uranium, reducing mobile U⁶⁺ to insoluble U⁴⁺; similar results have been seen with technetium, chromium, and cobalt (Lovley and Anderson, 2000). Dissimilatory Fe³⁺—reducing microorganisms can also utilize organic contaminants (including toluene and phenol) as carbon sources, oxidizing them to carbon dioxide and providing an added environmental benefit (Lovley and Anderson, 2000).

Nitrate is also a powerful oxidant for anaerobic respiration (denitrification). Senn and Hemond (2002) found that in the presence of nitrate (NO₃⁻) under anaerobic conditions, Fe²⁺ can be oxidized biologically to produce hydrous ferric oxides (HFO). The reduction

of nitrate was shown to be coupled with the oxidation of As^{3+} , resulting in the formation of As^{5+} which, like phosphate, is more reactive with particles (including HFOs) and is thus sequestered. Harvey and colleagues observed a similar process when they added nitrate to arsenic-contaminated groundwater and observed a decrease in dissolved arsenic concentrations (Harvey *et al.*, 2002). If surface waters or runoff are enriched in nitrate as well as phosphate, these reactions could sequester PO_4^{3-} by a mechanism similar to that of arsenate sequestration and remove nitrate by denitrification in the process (Foy, 1986). Cooper *et al.* (2003), however, suggest that this process may be limited. When *Shewanella putrefaciens* was incubated in medium containing nitrate and goethite as a source of Fe^{3+} , the production of Fe^{2+} was inhibited for approximately 200 hours at aqueous nitrate concentrations of 2.5 mM and was not observed at timepoints up to 600 hours at nitrate concentrations of 5 mM. Therefore, dissimilatory Fe^{3+} reduction may be inhibited in the presence of more energetically favorable oxidants. However, in natural systems, a spatial separation of Fe^{3+} reduction (surface) and re-oxidation (solution) may actually help drive the reaction. In addition, Cooper *et al.* (2003) suggest that there may have only been an apparent inhibition of dissimilatory Fe^{3+} reduction in this system if the simultaneous presence of NO_3^- , NO_2^- and Fe^{2+} in the solution resulted in the coupling of the chemical reoxidation of Fe^{2+} to the reduction of NO_2^- to N_2O .

In theory, other oxidized iron compounds could be used in place of iron mine tailings. Since mine tailings are very inexpensive, however, they may prove to be useful for preventing phosphorus from entering surface waters. While seeding lakes and other large surface water bodies with oxidized iron may be impractical, large amounts of mine tailings could be used in runoff catchment basins, mixed with dredge spoil or used to filter outflow from wetlands drainage systems. For example, we suggest that the tile lines draining cropland in the Silver Lake watershed could be lined with iron mine tailings or routed through a tailing-lined catchment basin in order to sequester phosphorus before such drainages enter the lake.

Acknowledgements

The authors appreciate constructive comments on the manuscript from M. Iqbal, K. Dhanwada, A. Schwemm and three anonymous reviewers. This study was funded by the Roy J. Carver Charitable Trust, the Iowa Space Grant Consortium, the Iowa State Water Resources Research Institute and Environmental Programs at the University of Northern Iowa. S. Liegeois was supported by an exchange program between UNI and the Ecole Nationale Supérieure de Chimie de Rennes, France.

References

- Bastin, O., Janssens, F., Dufey, J., and Peeters, A. 1999. Phosphorus removal by a synthetic iron oxide-gypsum compound. *Ecol. Engineering* **12**, 339–351.
- Blake, R.L., Hessewick, R.E., Zoltai, T., and Finger, L.W. 1966. Refinement of the hematite structure. *Am. Mineralogist* **51**, 123–129.
- Clesceri, L.S., Greenburg, A.E., and Eaton, A.D. (eds.). 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. American Public Health Association, Washington, DC.
- Cooper, D.C., Picardal, F.W., Schimmelmann, A., and Coby, A.J. 2003. Chemical and biological interactions during nitrate and goethite reduction by *Shewanella putrefaciens* 200. *Appl. Environ. Micro.* **69**, 3517–3525.
- Deppe, T. and Benndorf, J. 2002. Phosphorus reduction in a shallow hypereutrophic reservoir by in-lake dosage of ferrous iron. *Wat. Res.* **36**, 4525–4534.

- Deppe, T., Ockenfeld, K., Meybohm, A., Opitz, M., and Benndorf, J. 1999. Reduction of *Microcystis* blooms in a hypereutrophic reservoir by a combined ecotechnological strategy. *Hydrobiologica* **408/409**, 31–38.
- Dittrich, M., Dittrich, T., Siever, I., and Koschel, R. 1997. A balance analysis of phosphorus elimination by artificial calcite precipitation in a stratified hardwater lake. *Wat. Res.* **31**, 237–248.
- Foy, R.H. 1985. Phosphorus inactivation in a eutrophic lake by the direct addition of ferric aluminium sulphate: Impact on iron and phosphorus. *Freshwat. Biol.* **15**, 613–629.
- Foy, R.H. 1986. Suppression of phosphorus release from lake sediments by the addition of nitrate. *Wat. Res.* **20**, 1345–1351.
- Freeze, R.A. and Cherry, J.A. 1979. *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ.
- Frossard, E., Brossard, M., Hedley, M.J., and Metherell, A. 1995. Reactions controlling the cycling of P in soils. Chapter 7, In: *SCOPE 54 Phosphorus in the Global Environment—Transfers, Cycles and Management* (Tiessen, H., ed.), Wiley & Sons, London.
- Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F., and Ahmed, M.F. 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science* **298**, 1602–1606.
- Hogen, D.R. and Robin, J.R. 1996. Microbial mediated water treatment. United States Patent number 5 667 673.
- Hutchinson, G.E. 1957. *A Treatise of Limnology, Volume 1*. Wiley & Sons, New York.
- Jang, H. and Kang, S.-H. 2002. Phosphorus removal using cow bone in hydroxyapatite crystallization. *Wat. Res.* **36**, 1324–1330.
- Kendelewicz, T., Liu, P., Brown, Jr., G.E., Nelson, E.J., and Chambers, S.A. 1998. Reaction of water with clean surfaces of hematite and magnetite. *1997 Activity Report*, Stanford Synchrotron Radiation Laboratory, 339–340.
- Kopáček, J., Ulrich, K.-U., Hejzlar, J., Borovec, J., and Stuchlík, E. 2001. Natural inactivation of phosphorus by aluminum in atmospherically acidified water bodies. *Wat. Res.* **35**, 3783–3790.
- Lewandowski, J., Schauser, I., and Hupfer, M. 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser See (Germany). *Wat. Res.* **37**, 3194–3204.
- Lovley, D.R. 2000. Fe(III) and Mn(IV) reduction. In: *Environmental Microbe-Metal Interactions*, pp 3–30 (Lovley, D.R., ed.). ASM Press, Washington, D.C.
- Lovley, D.R. 2001. Reduction of iron and humics in subsurface environments. In: *Subsurface Microbiology and Biogeochemistry*, pp 193–217 (Fredrickson, J.K. and Fletcher, M., eds.). Wiley-Liss, New York.
- Lovley, D.R. and Anderson, R.T. 2000. Influence of dissimilatory metal reduction on fate of organic and metal contaminants in the subsurface. *Hydrogeol. J.* **8**, 77–88.
- McSwiggen, P. and Cleland, J. 2003. The Cuyuna Iron Range—Geology and Mineralogy. Available from: <http://www.geo.umn.edu/mgs/cuyuna/cuyuna.htm>.
- Perkins, R.G. and Underwood, G.J.C. 2001. The potential for phosphorus release across the sediment-water interface in an eutrophic reservoir dosed with ferric sulphate. *Wat. Res.* **35**, 1399–1406.
- Robertson, W.D. 2000. Treatment of wastewater phosphorus by reductive dissolution of iron. *J. Environ. Qual.* **5**, 1678–1685.
- Rydin, E. and Welch, E.B. 1998. Aluminum dose required to inactivate phosphate in lake sediments. *Wat. Res.* **32**, 2969–2976.
- Seida, Y. and Nakano, Y. 2002. Removal of phosphate by layered double hydroxides containing iron. *Wat. Res.* **36**, 1306–1312.
- Senn, D.B. and Hemond, H.F. 2002. Nitrate controls on iron and arsenic in an urban lake. *Science* **296**, 2373–2376.
- Smith, D.L. 1998. Have method, will travel. *Engineering & Science* **3**, 21–29.
- Tiessen, H. and Moir, J.O. 1993. Characterization of available P by sequential extraction. In: *Soil Sampling and Methods of Analysis*, pp 75–86 (Carter, M.R., ed.). Lewis Publishers, Boca Raton, FL.

- Van Hullebusch, E., Deluchat, B., Chazal, P.M., and Baudu, M. 2002. Environmental impact of two successive chemical treatments in a small shallow eutrophied lake: Part I. Case of aluminium sulphate. *Env. Poll.* **120**, 617–626.
- Varjo, E., Liikanen, A., Salonen, V.-P., and Martikainen, P.J. 2003. A new gypsum-based technique to reduce methane and phosphorus release from sediments of eutrophied lakes: Gypsum treatment to reduce internal loading. *Wat. Res.* **37**, 1–10.