

Report for 2003IA39B: Sequestration of phosphorus with iron mine tailings

- Articles in Refereed Scientific Journals:
 - Clayton, M.E., S. Liegeois, and E.J. Brown, 2004. Phosphorus sequestration in lake sediment with iron mine tailings. *Soil and Sediment Contamination*. (In press)
- Conference Proceedings:
 - Schwemm, A., R. Pasker, M. Clayton, and E.J. Brown, 2003. Phosphorus sorption by sediments from wetlands in the Cedar River watershed. 26th Annual Midwest Environmental Chemistry Workshop, Iowa City, IA.
 - Boyce, Matthew D., Heather J. Bailey, Mohammad Z. Iqbal, and Edward J. Brown, 2003. Lateral and vertical distribution of phosphorus in a northeast Iowa wetland system. Geological Society of America, 37th Annual Meeting, Kansas City.
 - Brown, E.J., S. Liegeois, and M. Clayton, 2003. Sequestration of phosphorus with iron mine tailings. Iowa Academy of Science Annual Meeting, Des Moines, IA.
 - Schwemm, A., R. Pasker, M. Musgrave, and E. Brown, 2003. Transport of phosphorus through a wetlands system. UG Summer Research Program, University of Northern Iowa, Cedar Falls, IA.
 - Schwemm, A., R. Pasker, M. Clayton, and E. Brown, 2004. Phosphorus sorption to wetlands sediments. Fourth Annual Water Monitoring Conference, Iowa Department of Natural Resources.

Report Follows

Sequestration of Phosphorus with Iron Mine Tailings

Edward J. Brown

Problem and Research Objectives

Orthophosphate (PO_4^{3-}) is found in surface and ground waters as a result of the natural weathering and solution of minerals; soil erosion and transport; use of soluble phosphate compounds in detergent manufacture, water treatment and industry; and soil fertilization. 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 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 the most 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.

In this project, we investigated whether this 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 ferric iron as contained in low cost 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 ferrous iron 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 during anaerobic respiration. We hypothesized that the soluble ferrous iron 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.

Methodology:

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). 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. 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 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.

Principal Findings and Significance:

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 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 hematite 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 in year 2 of this study.

Achievements & Awards

During the first year of this project, we proved the concept that ferric iron present in hematite can be reduced to ferrous iron in anaerobic waters through anaerobic respiration by certain microorganisms and that this ferrous iron can react with P or can be re-oxidized chemically or biologically back to ferric iron which forms P-sequestering particulate hydrous ferric oxides (HFO). The results will assist in formulation of pollution reduction and remediation plans for eutrophic lakes in Iowa and other locations where P is the major pollutant.