ENHANCING PHOSPHORUS SORPTION CAPACITY WITH TREATMENT WETLAND IRON OXYHYDROXIDES[1]

by

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Abstract. Substantial quantities of iron oxyhydroxide (FeOOH) accumulate in treatment wetlands that receive net alkaline coal mine drainage (CMD). Removal of this material may prolong effective wetland life but results in a waste disposal dilemma. A potential beneficial use may be to enhance soil phosphorous (P) retention capacity. Urban and agricultural nonpoint source pollution often contains elevated P concentrations. In some soil-water systems, ferric iron controls aqueous P concentrations via adsorption or precipitation mechanisms. Addition of FeOOH to soils could offer a P retention strategy. A laboratory batch study was conducted to examine the P sorption capacity of CMD wetland FeOOH and two FeOOH-supplemented soils. FeOOH was obtained from the Cedar Grove treatment wetland, Washington County, PA. Local Oklahoma soils examined included upland (sandy, mixed, thermic Typic Ustifluvent) and wetland (coarse-loamy, mixed, nonacid thermic Aquic Udifluvent) types. Total iron (Fe) concentrations in FeOOH, wetland and upland soils were $5x10^5$, $2.7x10^4$, and $1.3x10^4$ mg Fe/kg soil, respectively, while available P concentrations for these materials were 1.5, 2.2, and 3.3 mg P/kg soil, respectively. In an initial experiment, FeOOH and unamended soils were equilibrated with given aqueous P concentrations (0, 10, 20, 30, 40, 50 and 100 mg P/L) over a 24-hour period. Soil P sorption capacity was directly related to soil Fe content (FeOOH > wetland > upland.) P sorption capacities for wetland and upland soils were determined to be 523 ± 20 and 359 ± 40 mg P/kg soil, respectively. The P sorption capacity for FeOOH was not determined, but at the highest P concentration tested, $1.54x10^3$ ± 40 mg P/kg soil was retained. Sorption isotherms demonstrated a C-curve for FeOOH, an L-curve for wetland soil, and an S-curve for upland soil. In a second experiment, FeOOH was mixed with each soil on a mass ratio to equalize Fe content, and mixtures were equilibrated at the given P concentrations. P sorption capacities for the amended upland and wetland soils were 763 ± 9 and 757 ± 7 mg P/ kg soil, respectively. Both mixtures demonstrated L-shaped sorption isotherms, indicating that P sorption capacity had been reached. FeOOH waste products obtained from CMD treatment wetlands may be recycled to effectively enhance P sorption capacity.

Additional Key Words: iron oxide, coal mine drainage, phosphorous sorption, waste recycling, nonpoint source pollution

Introduction

Wetlands are a unique feature of nature. Not only do these systems provide the necessary habitat for many species of plants and wildlife, but they also have been shown to remove many of the pollutants entering them through runoff from agricultural sites, discharges from coal mines, and many other anthropogenic sources (Masscheleyn et al., 1992; Nairn and Hedin, 1993).

One source of pollution currently being treated in wetlands is coal mine drainage (CMD) (Nairn and Hedin, 1993). CMD is often high in dissolved metals (i.e., iron (Fe) and manganese (Mn)). There are two main types of treatment wetlands used to remove dissolved metals from CMD: anaerobic and aerobic (Robb and Robinson, 1995). In both anaerobic and aerobic wetlands, Fe is removed through precipitation. Anaerobic wetlands use bacteria to remove dissolved metals as metal sulfide precipitates while aerobic wetlands are designed to encourage Fe oxidation through exposure to air and are sometimes called "oxidation ponds".

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The most common form of Fe precipitate that forms in aerobic CMD treatment wetlands is amorphous iron oxyhydroxide (FeOOH). It is possible that FeOOH can accumulate to such an extent in these wetlands that it fills the oxidation pond and adversely affects treatment wetlands' ability to effectively remediate CMD. This is of greatest concern in treatment wetlands that receive net alkaline CMD. The alkaline conditions found in these wetlands cause FeOOH to precipitate much more rapidly than in treatment wetlands receiving net acidic CMD. This may drastically limit the length of time these systems can be used to treat CMD. A simple solution to this problem is to simply remove FeOOH from the treatment wetlands, however, this now creates a waste disposal problem. FeOOH must be disposed of in a landfill or by some other means.

The desire to find ways to beneficially use FeOOH to avoid disposal led to this study. Because Fe can react with phosphorous (P), an agricultural and urban pollutant, and remove it from solution via adsorption, it is hypothesized that FeOOH, when added to an upland or wetland soil, will be able to increase that soil's P sorption capacity.

P is of particular concern in freshwater ecosystems because it has been shown to often be the limiting nutrient (Caraco et al., 1990; Freedman, 1995). Elevated concentrations are often observed in agricultural runoff and sewage outfalls. When this runoff enters freshwater lakes and streams, the associated P loading can cause an increase in productivity (i.e., algal blooms and increased rates of eutrophication). These problems can harm an ecosystem by changing the trophic structure and causing deeper waters to become anoxic (Freedman, 1995). Therefore, the water quality of the receiving waters becomes degraded, and its use as a source of drinking water and recreation is limited.

Because of this, possible P sinks have begun to be examined more closely. Wetlands are currently being studied as potential P sinks (Nguyen et al., 1997; Boers et al., 1992; Masscheleyn et al., 1992; Gale et al., 1994). In these systems, both uptake by macrophytes and sediment deposition play a role in removing P from solution. However, it is believed that sediment deposition via adsorption and precipitation plays a more important role in P removal than biotic P removal (Cooke, 1992; Cooke et al., 1992).

Both adsorption and precipitation abiotically remove P from solution (Nguyen et al., 1997). In adsorption processes, P is adsorbed to soil particles through ligand exchange with oxides of Fe and aluminum (Al) (Sposito, 1989). In this way, phosphate ($RH_2PO_4^-$) is exchanged with a hydroxyl group (ROH) on the surface of an oxide molecule (Sposito, 1989). This forms a covalent bond between $RH_2PO_4^-$ and the oxide that is relatively strong. Clay minerals and calcium carbonate can also form a covalent bond with P and increase the rate of P removal from solution.

Precipitation is another method by which P can be removed from solution. This occurs when concentrations of P are relatively high (Sposito, 1989). However, unlike adsorption, precipitation is limited by the low solubility of calcium (Ca), Fe, and Al. These three metals are the primary elements with which P, in the form of phosphate, can form precipitates. Several studies have shown that a single wetland or a series of wetlands can decrease the amount of P in solution without causing damage to the wetlands or to the receiving waters based solely on adsorption and precipitation (Nguyen et al., 1997; Zhu et al., 1997; Gale et al., 1994; Masscheleyn et al., 1992).

This study indicated that adding FeOOH to soil used to build P treatment wetlands can increase these wetlands' P sorption capacity. Using FeOOH in this manner will not only help to solve the waste disposal problem associated with removing FeOOH from CMD treatment wetlands, but it will also help limit P loading of freshwater ecosystems by removing P from solution. In this way, two environmental problems will be solved without further damage to the environment.

Materials and Methods

To examine the impact of FeOOH addition on the P sorption capacity of soil, a batch study involving two Central Oklahoma soils (upland and wetland) was conducted. The upland soil was a sandy, mixed, thermic Typic Ustifluvent soil. The wetland soil was a coarse-loamy, mixed, nonacid thermic Aquic Udifluvent soil from a natural wetland. Both soils were analyzed for bulk density, pH, organic matter content, cation exchange capacity (CEC), total Fe, and available P according to standard methods (SSSA, 1996) with the exception of total Fe. Total Fe was analyzed using EPA Method 200.2 (USEPA, 1994), and analysis was performed at the University of Arkansas Agricultural Diagnostic Laboratory (Fayetteville, AR). Results for these analyses are given in Table 1.

FeOOH was collected from the Cedar Grove Treatment Wetland located in Washington County, PA. This material was subjected to the same characterization analyses as the two soils (Table 1). Both soils and FeOOH were air-dried before use and

Table 1: Soil Characterization Results for FeOOH and Soils Used in P Retention Experiments

	FeOOH	Upland Soil	Wetland Soil
Bulk Density *(g/cm^3)*	0.45	1.40	0.78
pH	6.99	7.85	5.56
Organic Matter Content *(%)*	9.64	1.82	4.04
Cation Exchange Capacity *($cmol_c/kg$)*	10.64	16.02	7.83
Total Fe *(mg Fe/kg)*	$5.0x10^5$	$1.3x10^4$	$2.7x10^4$
Available P *(mg P/kg)*	1.5	3.3	2.2

sieved to remove large particles (ASTM Sieve #10 (9 mesh)).

P sorption capacity of FeOOH and FeOOH-amended and unamended soils was determined through two batch studies. For both studies, a 1:20 soil to water ratio was used. In the first study, 5 g of FeOOH or unamended soil and 100 mL of one of the 7 P concentrations (0, 10, 20, 30, 40, 50, and 100 mg P/L) were added to triplicate 250 mL Erlenmeyer flasks (total of 21 flasks per soil type). The flasks were then placed on an orbital shaker set at 200 rpm and allowed to equilibrate for 24 hours. For the second batch study, the two soils were amended with FeOOH on a weight-by-weight basis. A 2:1 soil to FeOOH ratio was used for the upland soil and a 4:1 ratio was used for the wetland soil, based on unamended Fe concentration. These ratios were used to create similar Fe concentrations in both soils. Five g of the amended soil mixture was then placed in one of a set of three 250 mL Erlenmeyer flasks with 100 mL of one of the 7 P concentrations listed above and allowed to equilibrate on a shaker, as in the first study.

For both studies, P was analyzed after the samples were allowed to settle and were filtered through 0.45 μm filters to remove any suspended particles that would interfere with spectrophotometric analysis. Filtered samples were then analyzed immediately via the Ascorbic Acid Method (SSSA, 1996). A Beckman DU-65 spectrophotometer was used for P analyses, set at a wavelength of 880 nm. Absorbance readings were recorded and converted to P concentrations in mg P/kg as described in the Ascorbic Acid Method (SSSA, 1996).

Results and Discussion

From the first batch study, individual P sorption capacities were obtained for both soils and FeOOH. P sorption capacity for the upland soil was 359 ± 40 mg P/kg soil while P sorption capacity for the wetland soil was 523 ± 20 mg P/kg soil (Figure 1). At 100 mg P/L, FeOOH retained $1.54x10^3$ ± 40 mg P/ kg. As can be seen in Figure 1, it was unclear as to whether the P sorption capacity of FeOOH had been reached in this study because the amount of P retained was still increasing at the highest concentration tested. The adsorption isotherm for FeOOH in Figure 2 demonstrates a C-curve isotherm. This type of isotherm is typically associated with systems in which adsorption is independent of the concentration of the adsorptive until the maximum possible adsorption has been achieved. Both of these facts seem to indicate that the P sorption capacity had not been reached even at 100 mg P/L, a concentration which is two orders of magnitude higher than P concentrations usually observed in the environment. The testing of higher P concentrations may provide a better estimate of the P sorption capacity for FeOOH.

Adsorption isotherms were also developed for the unamended upland and wetland soils (Figure 2). The upland soil showed an S-curve. This indicated that P preferentially remained in solution at the lower concentrations (0, 10, 20, and 30 mg P/L). P was not retained by the soil until it reached a concentration that began to favor partitioning to soil. P had a stronger affinity for the aqueous phase until a concentration of 50 mg P/L. In contrast, the wetland soil showed an L-curve. This indicated that P had a high affinity for the soil and that adsorption increased quickly until the surface area available for adsorption began to decrease.

The ability of P to adsorb on all three solid materials (as indicated by P sorption capacity) can be related to the amount of Fe present. In the upland soil, a relatively low amount of Fe was present ($1.3x10^4$ mg/kg soil). The upland soil had the lowest P sorption capacity (359 ± 40 mg P/kg soil) when compared to the other two materials. The relatively low concentration of Fe in this soil had a small amount of surface area (potential P adsorption sites) associated with it. This small amount of surface area available for adsorption meant that P remained in solution until adsorption to soil became more likely because of the large number of P molecules in solution at high concentrations. The wetland soil had a greater concentration of Fe ($2.7x10^4$ mg/kg) than the upland soil and was expected to have

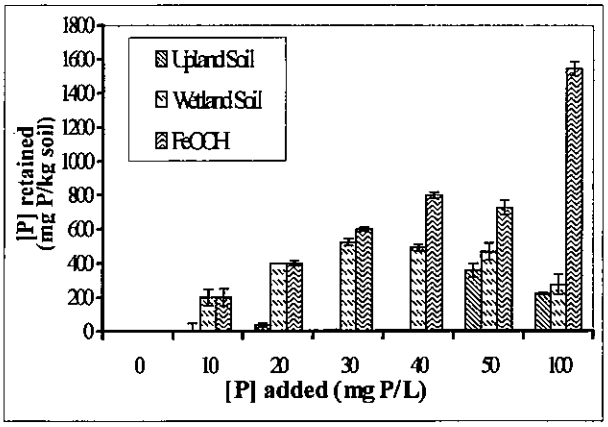

Figure 1: P retention as a function of [P] added by FeOOH, upland soil and wetland soil. Error bars indicate ± one standard deviation for three replicates.

a greater P sorption capacity, if Fe concentration and P adsorption were related. The wetland soil retained 523 ± 20 mg P/kg soil, which is 1.5 times more than was retained by the upland soil. The Fe-P relationship for the wetland soil may be explained by the relatively large number of easily accessible sites for P adsorption in this soil because of its higher Fe content. Adsorption increased as P concentration increased, as demonstrated by the first portion of the wetland soil isotherm (Figure 2), until the easily accessible sites were filled. Once these sites were taken up, the amount of P retained by the soil started to reach a saturation point where the amount of P retained remained the same despite increasing aqueous concentrations of P. Because FeOOH had the largest concentration of Fe (5.0×10^5 mg/kg) of the materials tested, it was expected to retain the greatest amount of P. It retained $1.54 \times 10^3 \pm 40$ mg P/kg at the highest P concentration tested and may possibly be able to retain even more P as indicated by the C-curve isotherm (Figure 2). The relationship between Fe concentration and P adsorption may be explained in this case by the fact that FeOOH is amorphous. The Fe surface area for adsorption is not only increased because there is more Fe present but this Fe also has more surface area because it lacks a crystalline structure unlike Fe in soil, which is assumed to be of a mostly crystalline nature. All three materials showed adsorption isotherms and maximum P retention capacities that indicate that Fe concentration and P retention were related.

The second batch study results also supported the fact that Fe concentration and P adsorption are related. Both soils, when amended with FeOOH to raise their Fe concentrations, showed greater P sorption capacities than their unamended counterparts. The amended upland soil had a P sorption capacity of 763 ± 9 mg P/kg while the amended wetland soil had a P sorption capacity of 757 ± 7 mg P/kg. These P sorption capacities are 1.5 to 2 times greater than the P sorption capacities of the unamended soils (359 ± 40 and 523 ± 20 mg P/kg, respectively). Also, FeOOH was added to both soils in ratios designed to raise the Fe content of both soils to a single common concentration (~150 mg Fe/kg). A similar Fe content was expected to yield P sorption capacities for both amended soils that were approximately equal because of the Fe-P relationship. This was shown to be the case with both amended soils adsorbing ~760 mg P/kg and having L-curve isotherms that were nearly the same (Figures 2 and 3).

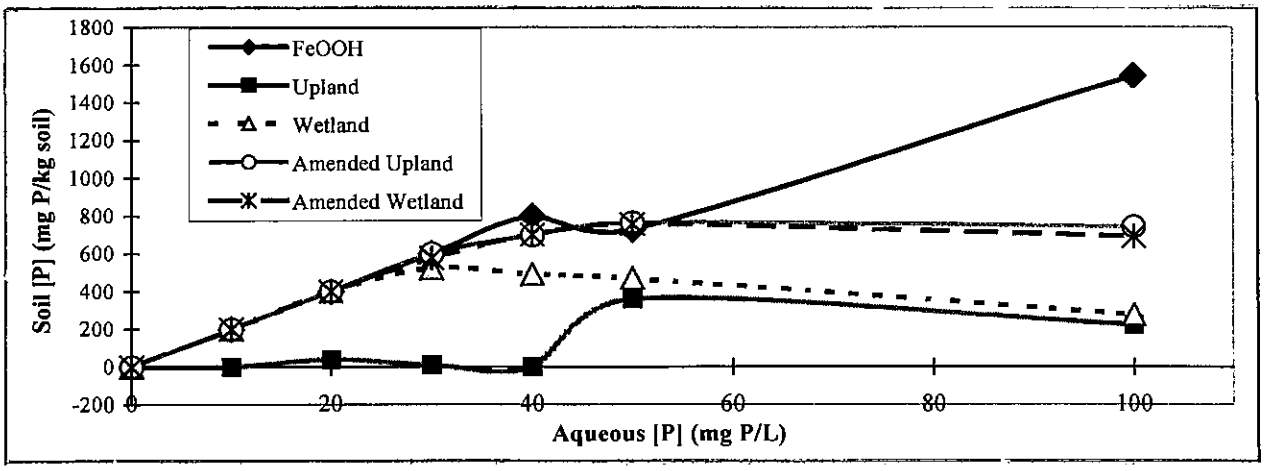

Figure 2: Adsorption isotherms for FeOOH, unamended upland soil, unamended wetland soil, amended upland soil, and amended wetland soil.

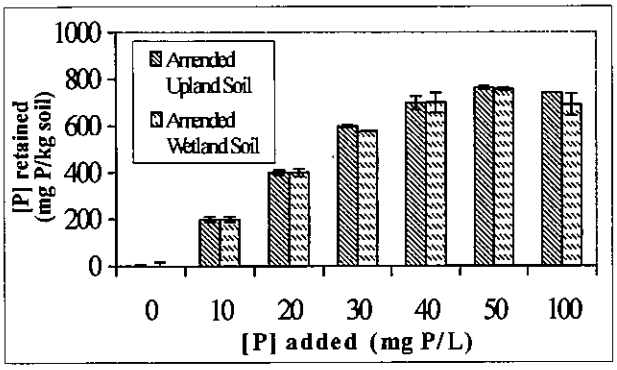

Figure 3: P retention as a function of [P] added for amended upland and wetland soils. Error bars indicate ± one standard deviation for three replicates.

Conclusion

Increasing either an upland or a wetland soil's Fe content with FeOOH increased that soil's P sorption capacity. Also, P sorption capacity was related to Fe concentration. The material with the lowest Fe concentration had the lowest P sorption capacity (upland soil) while the material with the highest Fe concentration had the highest P sorption capacity (FeOOH). These results indicate that FeOOH is a suitable material for use in wetlands treating P-contaminated waters. Using FeOOH in such a way will not only prevent anthropogenic P contamination of freshwater ecosystems, but it will also provide a solution to the waste disposal dilemma associated with the removal of FeOOH from CMD treatment wetlands.

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Literature Cited

Boers, P.J., J. Van der Does, M. Quaak, J. Van der Vlugt, and P. Walker. 1992. "Fixation of Phosphorous in Lake Sediments Using Iron (III) Chloride: Experiences and Expectations". *Hydrobiologia.* 233: 211-212. https://doi.org/10.1007/BF00016109

Caraco, N., J. Cole, and G.E. Likens. 1990. "A Comparison of Phosphorous Immobilization in Sediments of Freshwater and Coastal Marine Systems". *Biogeochemistry.* 9: 277-290.

Cooke, J.G. 1992. "Phosphorous Removal Processes in a Wetland". *Journal of Environmental Quality.* 21: 733-739. https://doi.org/10.2134/jeq1992.00472425002100040032x

Cooke, J.G., L. Stubb, and N. Mora. 1992. "Fractionation of Phosphorous in the Sediment of a Wetland after a Decade of Receiving Sewage Effluent". *Journal of Environmental Quality.* 21:726-732. https://doi.org/10.2134/jeq1992.00472425002100040031x

Freedman, B. 1995. Environmental Ecology. Academic Press, Inc. San Diego, CA. pp. 189-197.

Gale, P.M., K.R. Reddy, and D.A. Graetz. 1994. "Phosphorous Retention by Wetland Soils Used for Treated Wastewater Disposal". *Journal of Environmental Quality.* 23: 370-377. https://doi.org/10.2134/jeq1994.00472425002300020024x

Masscheleyn, P.H., J.H. Pardue, R.D. DeLaune, and W.H. Patrick Jr. 1992. "Phosphorous Release and Assimilatory Capacity of Two Lower Mississippi Valley Freshwater Wetland Soils". *Water Resources Bulletin.* 28(4): 763-773. https://doi.org/10.1111/j.1752-1688.1992.tb01498.x

Nairn, R.W. and R.S. Hedin. 1993. "Designing Wetlands for the Treatment of Polluted Coal Mine Drainage". *In:* M.C. Landin (ed.), Wetlands: Proceedings of the 13th Annual Conference of the Society of Wetland Scientists, New Orleans, LA, South Central Chapter, Society of Wetland Scientists, Utica, MS, pp. 224-229.

Nguyen, L.M., J.G. Cooke, and G.B. McBride. 1997. "Phosphorous Retention and Release Characteristics of Sewage-Impacted Wetland Sediments". *Water, Air, and Soil Pollution.* 100: 163-179. https://doi.org/10.1023/A:1018340028411

Robb, G.A. and J.D.F. Robinson. 1995. "Acid Mine Drainage from Mines". *The Geographical Journal.* 16(1): 47-55. https://doi.org/10.2307/3059927

Soil Science Society of America, Inc. (SSSA). 1996. Methods of Soil Analysis: Chemical Methods. J.M. Bigham, J.M.Bartels, D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnston, and M.E. Sumner, eds. Part 3, Book Series No. 5. Madison, WI. 1390 pp.

Sposito, G. 1989. The Chemistry of Soils. Oxford University Press, Inc. New York, NY. 148-160.

U.S. Environmental Protection Agency (USEPA). 1994. Methods for the Chemical Analysis of Water and Wastes. EPA/600/R-94/111. USEPA.

Zhu, T., P.D. Jenssen, T. Maehlum, and T. Krogstad. 1997. "Phosphorous Sorption and Chemical Characteristics of Lightweight Aggregates (LWA) – Potential Filter Media in Treatment Wetlands". *Water Science and Technology.* 35(5): 103-108.
https://doi.org/10.1016/S0273-1223(97)00058-9