

Mechanisms of Phosphate Dissolution from Soil Organic Matter

Amanda J. Morris and Dean Hesterberg

Dept. of Soil Science, North Carolina State University, Raleigh, NC, Email ajzelask@ncsu.edu, dean_hesterberg@ncsu.edu

Abstract

Wetlands serve a critical role in removing nutrients and other contaminants from water moving from terrestrial to aquatic ecosystems. While reduced soils remove nitrogen from porewater by denitrification, these conditions are less conducive for retaining phosphate. The objective of this research was to determine the relative effects of pH and dissolved organic matter (DOM) on the retention of inorganic phosphate by soil organic matter. Sorption of phosphate was measured as a function of pH on Pahokee peat. Ferric iron was pre-sorbed to the peat at 1200 mmol/kg, and phosphate was added at 300 or 600 mmol/kg and equilibrated at pH ranging from 3 to 8.5. With increasing pH, sorbed PO_4 decreased from 300 (low P input) or 500 mmol/kg at pH 3 to approximately 50 mmol/kg at pH 8.5. Between pH 5 and 8.5, dissolved organic carbon (DOC) increased from 10 to 200 mg/L. Given that DOM tends to increase along with pH as aerobic soils become reduced, quantifying the relative effects of DOM and pH on dissolution of phosphate in reduced soils is important for managing phosphorus retention in wetlands.

Key Words

wetlands, phosphorus, organics, redox, iron, DOC

Introduction

Dissolved phosphate often increases as soils become anaerobic, but the trend is not consistent across all soils. Mechanisms that potentially contribute to reductive dissolution of soil phosphate in acid soils include (i) reductive dissolution of Fe(III) from oxide mineral surfaces or Fe(III)-phosphate minerals and concomitant dissolution of associated PO_4 ; (ii) decreased sorption of phosphate with a redox-coupled increase in pH; and (iii) competitive sorption of DOM displacing phosphate from soil components (Patrick and Khalid 1974; Roden and Edwards 1997; Hutchison and Hesterberg 2004). To help ensure that wetlands are created on soils that have suitable properties for retaining phosphate under reducing conditions, the relative importance of these and other dissolution mechanisms should be quantified.

Here we discuss the effects of pH and DOM on retention of inorganic phosphate in organic matter. Organic matter tends to accumulate in wet soils and DOM serves as an energy source for microbial reduction of nitrate, Mn-oxides, Fe-oxides, and sulfate. In addition to harbouring organic phosphorus, organic matter sorbs inorganic phosphate. Experimental evidence suggests that inorganic phosphate involves Fe(III) and Al(III) in organic matter as bridging cations (ternary complexes) (Bloom 1981; Gerke and Hermann 1992). The objective of this research was to determine the relative effects of pH and DOM on phosphate dissolution from soil organic matter.

Methods

Samples of organic-matter bound phosphate were prepared by first equilibrating Fe(III) then PO_4 with acid-washed Pahokee peat from the International Humic Substances Society. All reactions were done at 25°C. Binding of Fe(III) was accomplished by reacting FeCl_3 with peat (1200 mmol Fe/kg peat) at pH 2.5 in a 0.05 M KCl background and equilibrating for 2 hours. The sample was divided into separate subsamples, and 0.05 M KOH was added for pH adjustment to various levels between 3 and 8.5. The Fe-peat samples were equilibrated for 48 hours with periodic re-adjustment of pH before phosphate was added as 0.05 M KH_2PO_4 at concentrations of 300 or 600 mmol P/kg peat. The PO_4 /Fe/peat samples were equilibrated for 48 hour while maintaining target pH through periodic adjustment. Equilibrated samples were centrifuged, and the supernatant solutions were filtered to $<0.2 \mu\text{m}$ and analysed for dissolved reactive phosphate (DRP) colorimetrically, and dissolved organic carbon (DOC) by combustion. Auxiliary analyses not reported here included total dissolved Fe and Al. Sorbed inorganic PO_4 as a function of pH was determined as loss of added PO_4 from solution.

Results

Figure 1 shows sorption envelopes for PO_4 on Fe(III)-peat for additions of 300 or 600 mmol P/kg. The trend of decreasing PO_4 sorption with increasing pH is characteristic of sorption envelopes found for PO_4 on Fe(III)- and Al(III)-oxide minerals. However, our sorption envelopes were complicated by potential competitive effects of DOM. As shown in Figure 2, DOM increased with increasing pH, from a nearly-constant concentration of 10 mg/L between pH 3 and 5 up to 200 mg/L at pH 8.5. An increase in DOM with increasing pH is typical, but we also found that DOM increased during abiotic or biotic reduction of peat at constant pH (data not shown).

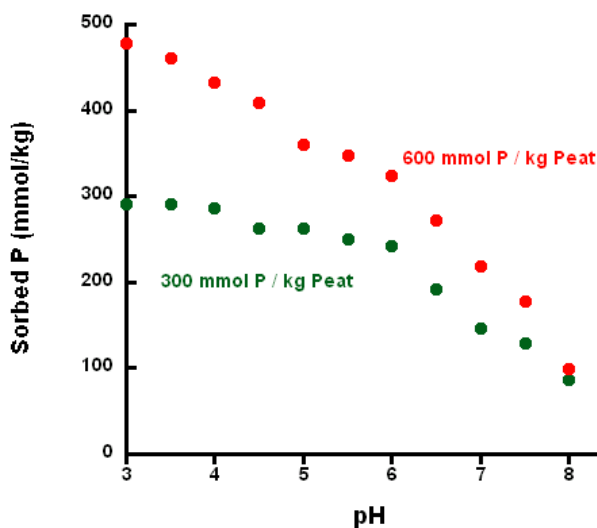


Figure 1. Sorption envelopes for phosphate on Pahokee peat containing 1200 mmol Fe/kg peat.

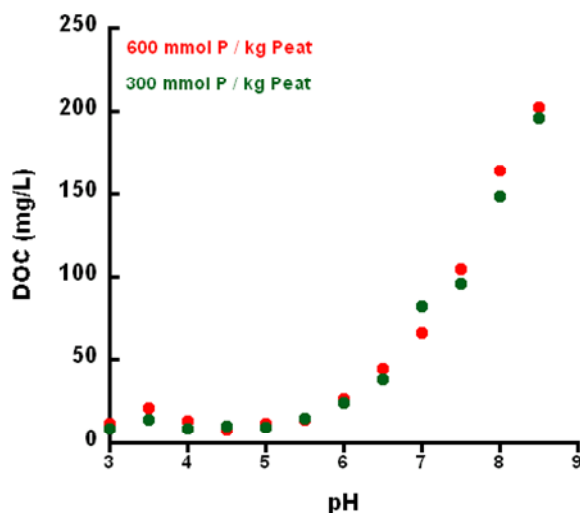


Figure 2. Dissolved organic C (DOC) in supernatant solutions (filtered to $<0.2 \mu\text{m}$) from the measurements of P sorption envelopes shown in Figure 1.

Between pH 3 and 5, where DOC is essentially constant (Figure 2), sorbed PO_4 decreased by 25% (from 482 to 364 mmol/kg peat) for the 600 mmol P/kg input, and by 10% (from 293 to 265 mmol/kg peat) for the 300 mmol P/kg input (Figure 1). These results highlight the pH dependence of PO_4 sorption at constant DOC, albeit over a narrow pH range. At pH > 5 , we cannot separate the effect of pH from that of DOM from these results. For example, Figure 3 illustrates that the pH-dependent increase in DOM could potentially be contributing to an increase in dissolved PO_4 , which is tied to a decrease in sorbed PO_4 . This effect, if independent of any pH effect, is consistent with a mechanism of competitive sorption of PO_4 and DOM for binding sites on the peat.

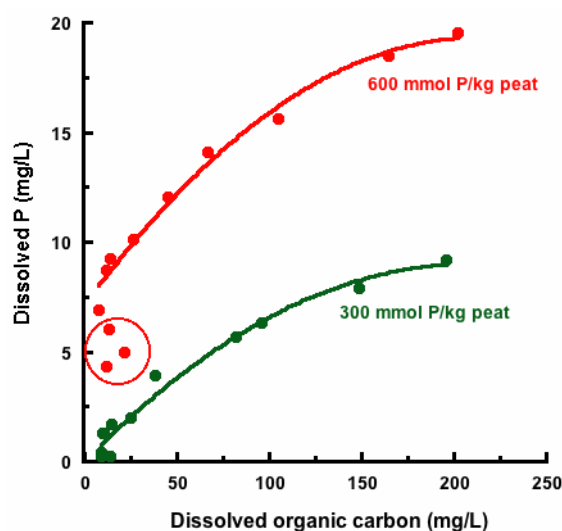


Figure 3. Dissolved phosphate increased with increasing dissolved organic carbon (DOC) concentration for Pahokee peat. Quadratic models are fit to the data to show trends (circled points were omitted from the model for the 600 mmol P/kg treatment).

Conclusions

Under the conditions of our experiments, pH-dependent sorption of inorganic phosphate on Fe(III)-peat showed sorption envelopes analogous to those for phosphate sorption on oxide minerals. However, for pH > 5, dissolution of organic matter from the solid-phase peat appeared to increase dissolved phosphate, probably by competitive binding to Fe(III). Accordingly, increases in both pH and DOM during reduction of soils likely contribute to phosphate dissolution and diminished phosphate retention capacity in reduced soils. The effects of pH and DOM on organic-matter bound inorganic phosphate are important, regardless of any direct effects of Fe(III) reduction on phosphate dissolution.

References

- Bloom PR (1981) Phosphorus adsorption by an aluminum-peat complex. *Soil Science Society of America Journal* **45**, 267-272.
- Gerke J, Hermann R (1992) Adsorption of orthophosphate to humic-Fe-complexes and to amorphous Fe-oxide. *Zeitschrift Fur Pflanzenernahrung und Bodenkunde* **155**, 233-236.
- Hutchison KJ, Hesterberg D (2004) Dissolution of phosphate in a phosphorus-enriched ultisol as affected by microbial reduction. *Journal of Environmental Quality* **33**, 1793-1802.
- Patrick WH, Khalid RA (1974) Phosphate release and sorption by soils and sediments. *Science* **186**, 53-55.
- Roden EE, Edmonds JW (1997) Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III)-oxide reduction versus iron-sulfide formation. *Archiv Fur Hydrobiologie* **139**, 347-378.