Phosphate sorption to organic matter/ferrihydrite systems as affected by aging time

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Abstract

It's been hypothesized that organic matter (OM) can complex iron (Fe) from oxides minerals, which provide sorption sites for phosphate (PO_4) via the formation of Fe-PO_4-OM ternary complexes. To elucidate such mechanism, the coordination structure of Fe was examined, as well as PO_4 sorption capacity and crystallinity of ferrihydrite as it aged with OM. Stock suspensions containing 1 g ferrihydrite/kg and 0 to 3.1 g OM/kg were created at pH 6.8. PO_4 sorption capacities were measured as they have aged for 1, 7, 21, 40, and 55 days. After aging for 55 days, all systems had a 20% to 50% decrease of PO_4 sorption capacity. Extended X-ray absorption fine structure (EXAFS) analyses on selected aged peat/ferrihydrite samples showed no evidence of Fe(III)-OM complexation. With the same amounts of Fe(III) and peat, mixtures of Fe(III)-peat complexes and ferrihydrite provided higher PO_4 sorption capacity per unit Fe than ferrihydrite only. Indicated by HCl extractable Fe, ferrihydrite crystallinity increased during aging. For ferrihydrite itself, crystallization was the main cause for its decreased PO_4 sorption capacity. It is very likely that the continuous competition between OM and PO_4 resulted in the decreased PO_4 sorption capacity as ferrihydrite aged with OM.

Key Words

Ferrihydrite, phosphate, organic matter, EXAFS, iron, DOC.

Introduction

As an important soil component, soil organic matter (OM) has been extensively studied for its role on phosphate sorption to oxide minerals. Many studies have found that OM has instantaneous inhibitory effect on phosphate sorption to oxide mineral, although the mechanism is under debate (Antelo, Arce *et al.* 2007; Hiradate and Uchida 2004; Kreller, Gibson *et al.* 2003). With longer time, however, the scenario is different. After the studied soils and PO_4 have equilibrated for 7 days in calcium acetate background electrolyte, organic matter did not alter the soils' PO_4 sorption capacity (Borggaard, Jorgensen *et al.* 1990). When PO_4 was added to Fe- or Al-oxide/humic acid (HA) mixtures, the system's PO_4 sorption capacity was lower than the mineral itself after equilibration for three days. However, as longer equilibration time (up to 28 days) was given, the mineral/HA systems had about the same PO_4 sorption capacities as the mineral itself (Borggaard, Raben-Lange *et al.* 2005). While the change of PO_4 sorption to oxide minerals appears to be a kinetic issue since PO_4 sorption can take scores of days before reach equilibration (Bolan, Barrow *et al.* 1985), Gerke and Mt (1993) proposed that the increased PO_4 sorption to Fe-oxide/humic mixtures involved a change of sorption mechanism. In this study, PO_4 sorption capacities of mixture of poorly crystalline Fe-oxide and humic substances first decreased (pH 7), then increased by 15% after aging for 56 days, parallel with increased Fe-humic complexes. The author hypothesized that Fe from oxide was complexed by humic substances. These complexes provided more sorption sites for PO_4 via the formation of PO_4-Fe-OM ternary complexes, resulting in the increased PO_4 sorption capacity.

Although the published results support the ternary complexation mechanism, molecular understanding of such mechanism remains little. Direct evidence for such Fe-PO_4-OM complexes has yet to be found. Applying the technique of EXAFS and other analytical methods, this study aims to explore how OM affects PO_4 sorption to ferrihydrite as they age and elucidate the underlying mechanisms. The specific objectives were: 1) determine any change of PO_4 sorption capacity of ferrihydrite/OM systems as they age; 2) determine if Fe(III) from ferrihydrite is complexed by OM and how the Fe-OM complexation contributes to the change of the system's PO_4 sorption capacity, if any. The findings of this study add to the very much needed understanding of the long term effect of organic matter on PO_4 sorption on oxide minerals.

Methods

Pahokee peat (PP) and Pahokee peat humic acid (PPHA) were purchased from International Humic Substance Society and were hydrated prior to use. Stock suspensions containing 1 g ferrihydrite/kg and 80 mg DOC from PPHA, or 0~3.1 g peat/g of ferrihydrite were prepared in 0.05 M KCl at pH 6.8. These stock suspensions were shaken at 0.5 s^{-1} in a water-bathed shaker at 25°C for aging. For each system when it had aged for 1, 7, 21, 40 and 55 days, KH_2PO_4 solution was added to 30 g of subsample. After equilibration for 42 hours, the adsorbed PO_4 was determined by the difference between added PO_4 and dissolved PO_4 in the supernatants.

To mimic the formation of Fe(III)-peat complex (Fe-peat), $FeCl_3$ solution was added to peat suspension (at pH 2.5) prior to addition of ferrihydrite. These Fe-peat/peat/ferrihydrite mixtures had the same amounts of peat and total Fe(III) as those in system of 1 g peat/g, but differed in the percentage of Fe(III) that was complexed with peat out of total Fe(III), ranging from 0 to 20%. These systems did not age. PO_4 sorption capacities of these systems were determined by 8-point sorption isotherm experiments.
For EXAFS analysis, stock ferrihydrite and peat/ferrihydrite suspensions with peat input as 3.1, 6.2, and 12.5 g/g were prepared with different aging time. Stock Fe-peat/peat/ferrihydrite systems (no aging) were also created with total peat and Fe(III) the same as those in system 3.1 g/g. The percentages of Fe-peat out of total Fe(III) were 0%, 50%, and 100%. All these suspensions were first centrifuged and the solids were mounted to sample holders for EXAFS data collection at beamline X-11B of National Synchrotron Light Source (NSLS) at the Brookhaven National Lab (Upton NY).
* DOC=dissolved organic carbon from Pahokee peat humic acid

Results

Figure 1 shows the change of PO_4 sorption capacities of OM/ferrihydrite systems as they aged. For ferrihydrite or system A, there was an approximately 20% decrease of PO_4 sorption capacity after aging for 55 days. PO_4 sorption capacity decreased by 38% and 56% when peat input was 1 and 3.1 g/g, respectively. Regardless of the amount of OM, all systems showed decreasing PO_4 sorption capacities during aging. The decrease is greater with higher OM. For the same aging time, more OM resulted in lower PO_4 sorption capacity, which indicates the competition between OM and PO_4 for sorption sites on ferrihydrite surface.

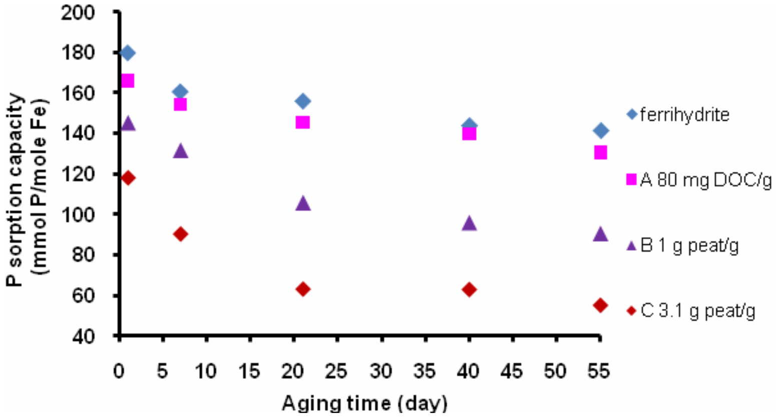


Figure 1. Change of PO_4 sorption capacities of OM/ferrihydrite systems as they aged for 55 days.

The systems presented in Figure 2 have the same Fe(III) and peat as those in system of 1g peat/g, but different amounts of Fe(III) that is complexed with peat. When all Fe(III) was in the form of ferrihydrite (0% Fe-peat), the system's PO_4 sorption capacity was the lowest as 125 mmol P/mole Fe. The system's PO_4 sorption capacity increased as Fe(III)-peat complexes increased, reaching the maximum capacity of 166 mmol/mole when 10% of total Fe(III) was complexed with peat. More Fe(III)-peat complexes did not further increase the system's PO_4 sorption capacity. These results suggest that if Fe(III) from ferrihydrite were complexed by peat, the PO_4 sorption capacities of these peat/ferrihydrite systems would have increased.

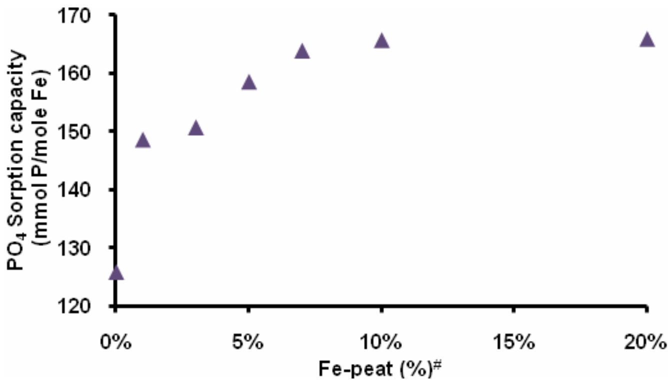


Figure 2. PO_4 sorption capacity of Fe-peat/peat/ferrihydrite systems increased as Fe(III)-peat complexes increased. Total peat and Fe(III) in these systems are equal to those in system B (1 g peat/g ferrihydrite).
Fe-peat (%) denotes the percentage of total Fe(III) that is complexed with peat.

Figure 3 displays the Fe K-edge EXAFS spectra of peat/ferrihydrite systems that have aged for 1 day. Essentially these spectra show no structural difference of Fe, regardless of the amount of peat present with ferrihydrite.

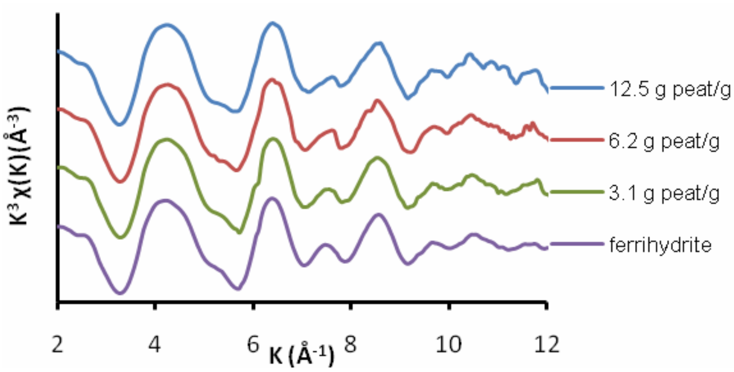
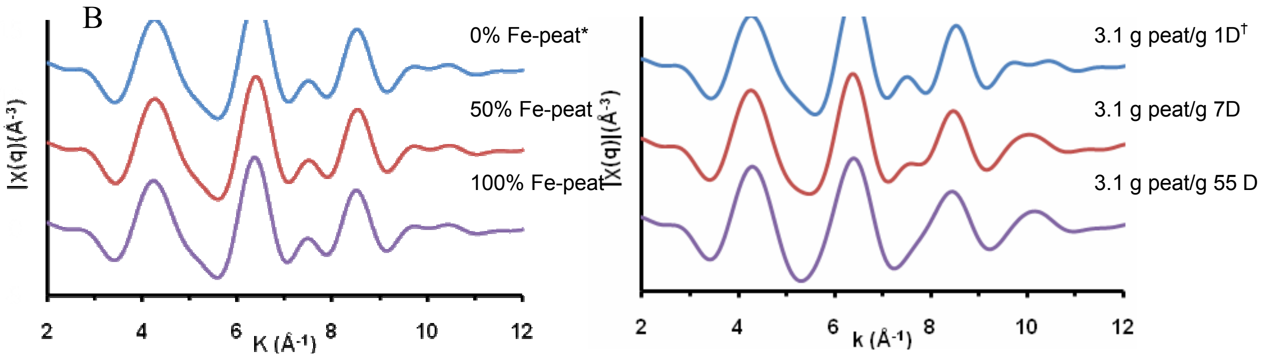


Figure 3. Fe K-edge EXAFS spectra of ferrihydrite/peat systems that have aged for 1 day.

The systems displayed in Figure 4A have the same amounts of total Fe(III) and peat as those in the systems displayed in Figure 4B (3.1 g peat/g), but different amounts of Fe(III)-peat complexes. Fe(III)-peat complexation illustrates distinct spectral features from Fe(III) in ferrihydrite (from bottom to top), as highlighted by the vertical bars. The spectral features of Fe(III)-peat complexation are absent in the spectra displayed in Figure 4B, which are essentially the same to each other, regardless of aging time. EXAFS analyses provided no evidence to show Fe(III)-peat complexation during aging.



* peat-Fe denotes Fe(III) that is complexed with peat. †D denotes aging time in days.

Figure 4. (A) Fourier-filtered (*R*+Δ*R*=1-3.5 Å) EXAFS spectra of Fe-peat/peat/ferrihydrite systems (total Fe(III) and peat are equal to those in 3.1g peat/g); (B) Fourier-filtered (*R*+Δ*R*=1-3.5 Å) EXAFS spectra of peat/ferrihydrite systems (3.1 g/g) that have aged for 1, 7 and 55 D. Vertical bars highlight the change or no change of spectral features.

As an indication of crystallinity (Cornell and Schneider 1989), 0.4 M HCl extractable Fe from ferrihydrite decreased by 10% after aging for 55 days (data not shown), although the change of crystallinity was not detected by x-ray diffraction (XRD). B.E.T. surface area of ferrihydrite decreased from 330 to150 m^2/g after aging for 55 days. No crystallization was detected by XRD in all OM/ferrihydrite systems.

Conclusions

Crystallization of ferrihydrite caused its decreased PO_4 sorption capacity by 20% after aging for 55 days. We did not find increasing PO_4 sorption capacity as ferrihydrite aged with OM as reported in the literature. On the contrary, these OM/ferrihydrite systems had a 20% to 50% decrease of PO_4 sorption capacity after aging for 55 days. EXAFS analyses of peat/ferrihydrite systems that have aged for different time did not show any change of Fe coordination structure as induced by the amount of peat or aging time. On the other hand, Fe(III)-peat complexation did contribute to higher PO_4 sorption capacity than the same amount of Fe(III) in the form of ferrihydrite. The competition between organic matter and PO_4 appeared to be responsible for the decreasing PO_4 sorption capacity as ferrihydrite aged with organic matter.

Acknowledgement

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References

Antelo J, Arce F, Avena M, Fiol S, Lopez R, Macias F, Kq (2007) Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma* **138**(1-2), 12-19.

Bolan NS, Barrow NJ, Posner AM (1985) Describing the effect of time on sorption of phosphate by iron and aluminum hydroxides. *Journal of Soil Science* **36**(2), 187-197.

Borggaard OK, Jorgensen SS, Moberg JP, Rabenlange B, Eb (1990) Influence of organic-matter on phosphate adsorption by aluminum and iron-oxides in sandy soils. *Journal of Soil Science* **41**(3), 443-449.

Borggaard OK, Raben-Lange B, Gimsing AL, Strobel BW, Bj (2005) Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma* 127(3-4), 270-279.

Cornell RM, Schneider W (1989) Formation of goethite from ferrihydrite at physiological ph under the influence of cysteine. *Polyhedron* **8**(2), 149-155.

Gerke J, Mt (1993) Phosphate adsorption by humic/fe-oxide mixtures aged at ph-4 and ph-7 and by poorly ordered fe-oxide. *Geoderma* **59**(1-4), 279-288.

Hiradate S, Uchida N (2004) Effects of soil organic matter on pH-dependent phosphate sorption by soils. *Soil Science and Plant Nutrition* **50**(5), 665-675.

Kreller DI, Gibson G, Novak W, Van Loon GW, Horton JH, Zm (2003) Competitive adsorption of phosphate and carboxylate with natural organic matter on hydrous iron oxides as investigated by chemical force microscopy. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **212**(2-3), 249-264.