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Impact of iron–organic matter complexes on aqueous phosphate concentrations

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ABSTRACT

The close linkage between iron (Fe) and phosphorus (P) suggests that changes in Fe speciation may have a strong effect on the bioavailability of P. At the same time Fe speciation in natural oxic environments is known to be affected by the presence of organic matter (OM), pH and total Fe concentrations, thus these parameters should also influence the Fe–P interactions. The main objective of the present work was to study how OM affected the distribution of P(V) in the presence of Fe(III) and to address the questions if and by what mechanism(s) OM influenced the concentration of aqueous phosphate. This was accomplished by investigating the ternary P(V)–Fe(III)–OM system over a wide range of chemical conditions; $[Fe]_{tot}$ = 5000–50,000 μg g^{-1}, Fe/P = 0.5–2.0 at pH 2.9–7. Iron speciation was probed via Fe K-edge X-ray absorption spectroscopy, P speciation and concentrations were analyzed via infrared spectroscopy, and chemical equilibrium modeling was conducted to simulate the distribution of chemical species of the system. The collective results showed that the dominating species were Fe(III)–OM complexes and ferric phosphate ($FePO_4$(s)). At low concentrations, the Fe(III)–OM complexes suppressed the formation of $FePO_4$(s), which resulted in elevated aqueous phosphate concentrations. At high concentrations, $FePO_4$(s) was formed and co-existed with Fe(III)–OM complexes; ternary P(V)–Fe(III)–OM complexes were not detected under any experimental condition. The collective spectroscopic and equilibrium modeling results offer a mechanistic and thermodynamic consistent explanation to why OM contributes to elevated concentrations of soluble P and thereby to increased bioavailability of P in soils and waters.

1. Introduction

The bioavailable soil solution concentrations of phosphate are typically very low (e.g., Schindler (1967); Frossard et al. (2000) and Hinsinger (2001)), and these concentrations are regulated by the presence of metal ions e.g., Al(III) and Fe(III). Abiotic processes that contribute to the limited phosphate concentrations are binding to soil constituents such as metal (hydr)oxides and precipitation of low-solubility compounds containing Al, Ca and Fe (Hinsinger, 2001). Also the formation of solid solutions, such as PO_4^{3-} bearing ferrihydrite-like compounds, has been identified as an important process for scavenging of phosphate (Thibault et al., 2009). The suggested limiting P:Fe stoichiometric ratio of 1:2 and low solubilities of these solid solutions would make them very efficient in removing phosphate from solution (Thibault et al., 2009). Similar limiting P:Fe stoichiometric ratios have also been reported for systems where phosphate is removed via precipitation caused by oxidation of ferrous ions in aerated bicarbonate media (Voegelin et al., 2013).

In addition to the inorganic reactions described, organic matter (OM) plays a crucial role in the fate of phosphate in soils. The formation of phosphate–metal–OM complexes has been proposed to be an important pool of phosphorus in soils, and these complexes are also suggested to be more bioavailable than phosphate bonded to inorganic surfaces or in precipitates (Gerke, 2010). A solid, ternary phase containing P(V), Fe(III) and organic ligands has been synthesized, via a hydrothermal process, and structurally characterized (Kizewski et al., 2010). OM may also increase the concentration of soluble phosphate as organic acids compete for binding sites at the soil mineral surfaces (Lindegren and Persson, 2009), or indirectly as organic substrates for microbes inducing the reduction of Fe(III) oxides and the subsequent release of phosphate (Chacon et al., 2006). Indeed, in a recent study of strongly weathered soils, OM from leaf litter was shown to decrease the fraction of immobilized phosphate and increase the soluble, bioavailable phosphate concentration (Schreeg et al., 2013). The underlying mechanism responsible to this phenomenon, however, remains unclear due to the

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lack of molecular-scale information. This motivated the present laboratory study aimed at investigating the speciation in the phosphate–Fe(III)–OM system.

We have addressed the question of whether Fe(III)–OM interactions affect the distribution of phosphate. This was accomplished by studying the influence of pH, total Fe concentrations, and the Fe:P ratio as those parameters control the partitioning between Fe(III)–OM complexes and precipitated Fe(III) (hydr)oxides as well as the composition of the solid phases and adsorption to mineral surfaces (Karlsson and Persson, 2010, 2012; Neubauer et al., 2013; Sundman et al., 2014a). The molecular structures of the Fe(III) species were probed with Fe K-edge X-ray absorption spectroscopy (XAS), which previously has been shown to provide detailed information about Fe(III)–OM interactions (Karlsson et al., 2008; Mikutta, 2011). These measurements were complemented with infrared (IR) spectroscopy that enabled in-situ quantification of phosphate in solution in the presence of Fe(III)–OM species. A chemical equilibrium model was developed based on these collective experimental results, and this model facilitated extrapolation to conditions in natural waters and provided a possible thermodynamic explanation for the increase in soluble phosphate caused by OM.

2. Materials and methods

The sample preparation was similar to Karlsson and Persson (2010), (2012) and Sundman et al. (2014b). The aquatic OM was purchased from the International Humic Substances Society (Suwannee River natural organic matter (SRN; 1R101N)). This material originates from a blackwater river, with high DOC (25–75 mg L^{-1}) and pH below 4.0 (Averett et al., 1994). Chemical data for SRN are reported in Table S1, Supplementary material (SM). A stock solution of phosphate was prepared by dissolving NaH_2PO_4 (p.a. MERCK) in Milli-Q water. Stock solutions of Fe(III) were prepared by dissolving either $FeCl_3 \times 6H_2O$ (p.a. Sigma-Aldrich) or $Fe(NO_3)_3 \times 9H_2O$ (p.a. MERCK) in Milli-Q water. The nitrate salt was used for the Fe(III)–OM reference samples previously published by Karlsson and Persson (2012) and for half of the OM XAS samples (Table 1). Due to possible interference of nitrate in the IR spectra, the chloride salt was used in the preparation of all IR samples. 40.0 mg of the aquatic organic material was weighed into 1.5 mL Eppendorf test tubes, and water and Fe(III) stock solution were added to reach the desired concentration. After 20 min, NaOH was added to reach the predetermined pH-values. To avoid light-induced reactions, the samples were covered with aluminum foil before equilibrated for 2 h on an end-over-end rotator. The samples were further equilibrated for 22 h in an upright position prior to the addition of the phosphate stock solution. After further equilibration, following the same 2 h + 22 h procedure, pH was measured using a pH combination electrode (InLab®Micro, Mettler Toledo) that was calibrated at pH 3 and 7. When needed pH was adjusted and the samples were diluted to final concentrations with Milli-Q water. The samples were then further equilibrated for 3 days and the pH was measured again; these pH values are the ones reported in Table 1. The samples were stored in a refrigerator for a few days prior to XAS and IR measurements. A series of $H_2PO_4^-$ standard solutions at pH 4.5 ranging from 2 mM to 128 mM was prepared by diluting the $H_2PO_4^-$ stock solution with Milli-Q water.

Table 1
Sample characteristics of the P(V)–Fe(III)–OM samples prepared for XAS and IR analysis.

Sample[a]	[Fe] (μg g^{-1})[b]	[Fe] (mM)	[Fe(III)]/[P(V)][c]	pH
SRN1	5000	18.0	1.2	5.0
SRN2	6504	16.7	2.0	2.9
SRN3	6504	16.7	2.0	5.1
SRN4	6504	16.7	1.0	2.9
SRN5	6504	16.7	1.0	5.0
SRN6	6504	16.7	1.0	6.5
SRN7	11,971	30.3	1.1	3.2
SRN8	11,971	30.3	1.0	5.2
SRN9	11,971	30.3	1.1	6.9
SRN10	22,916	55.4	2.1	5.0
SRN11	22,916	55.4	2.1	7.0
SRN12	22,916	55.4	1.1	2.9
SRN13	22,916	55.4	1.1	5.0
SRN14	22,916	55.4	1.1	7.0
SRN15	22,916	55.4	0.5	2.9
SRN16	22,916	55.4	0.5	4.9
SRN17	22,916	55.4	0.5	6.9
SRN18	50,000	146.9	1.0	5.0
SRN IR1	22,918	58.2	1.0	3.5
SRN IR2	22,918	58.2	1.0	4.1
SRN IR3	22,918	57.5	1.0	4.6
SRN IR4	22,918	58.2	1.0	5.2
SRN IR5	22,918	58.2	1.0	5.5
SRN IR6	22,918	58.2	1.0	5.9
SRN IR7	22,918	58.2	1.0	6.5

For more information see Table S2 in SM.
[a] On a dry mass basis, the concentration of carboxylic functional groups is 4807 μmol g^{-1}.
[b] Based on a dry mass basis.
[c] Expressed as a molar ratio.

2.1. XAS measurement and data analysis

Fe K-edge XAS spectra were collected at beamlines 4–1 and 4–3 at Stanford Synchrotron Radiation Lightsource (SSRL), California, USA. The ring current was 150–350 mA and the energy was 3.0 GeV. Spectra were collected at room temperature using a Lytle detector, filled with Ar gas, in fluorescence mode. Si ([2 2 0], $\Phi = 90$) and Si ([1 1 1], $\Phi = 90$) double-crystal monochromators were used at 4–1 and 4–3, respectively, and a Mn 3-μx filter was used to reduce unwanted fluorescence and scattering contributions to the signal. To reduce higher order harmonics, a nickel coated harmonic rejection mirror was used at 4–3 and at 4–1. The monochromator was detuned ca. 30%. The hutch slits were set at 2×10 mm. The samples were mounted in Teflon sample holders and sealed with Kapton Tape (CHR-Furon). 2–8 spectra were recorded per sample, depending on the sample concentration, and spectra of a Fe foil were simultaneously recorded to allow for internal calibration. All spectra were energy calibrated and averaged using SixPack (Webb, 2005). Investigation of self-absorption effects and quantitative shell-by-shell extended X-ray absorption fine structure (EXAFS) data fitting was accomplished by means of Viper (Klementiev, 2001), and wavelet transform (WT) analysis by means of an Igor Pro script (Funke et al., 2005). Each spectrum was carefully studied prior to averaging, and spectra displaying signs of beam damage (detected as shifts in the edge position of the 1st derivative spectra) were excluded. Standard procedures for background subtraction, normalization and shell-by-shell fitting were followed (Karlsson et al., 2008). The samples were modeled in *k*-space from 2.8 to 10.2–12.6 $Å^{-1}$, depending on the data quality, using theoretical phase and amplitude functions from FEFF calculations (Zabinsky et al., 1995). Trisoxolatoiron (Persson and Axe, 2005), $FePO_4 \times 2\ H_2O$, strengite (Taxer and Bartl, 2004) and goethite (Szytula et al., 1968) were used as input structures to the FEFF calculations. The amplitude reduction factor (S_0^2) was set to 0.85, obtained by fitting the first coordination shell in a Fe–OM reference sample, assuming a coordination number of 6 for the Fe–O path in the first shell. The numbers of free variables were restricted by correlating coordination numbers and when available, fixing the Debye–Waller factors (σ^2) found in literature or separately determined for new reference compounds. Furthermore, the E_0-shift was assumed to be identical for all shells beyond the first. Consequently, the number of free variables in the fitting never exceeded the limit given by the Nyquist theorem ($N_{max} = 2 \times \Delta k \times \Delta R/\pi$, where Δk is the k-range of the EXAFS spectrum and ΔR is the R-range of the Fourier transforms).

2.2. IR measurements and data analysis

The IR measurements were performed according to the procedure by Sundman et al. (2014b), and conducted using a Bruker Vertex 80 vacuum spectrometer equipped with a DTGS detector. Spectra were