1 Impact of iron-organic matter complexes on aqueous phosphate concentrations

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11
12 Abstract

13 The close linkage between iron (Fe) and phosphorus (P) suggests that changes in Fe speciation
14 may have a strong effect on the bioavailability of P. At the same time Fe speciation in natural
15 oxic environments is known to be affected by the presence of organic matter (OM), pH and total
16 Fe concentrations, thus these parameters should also influence the Fe-P interactions. The main
17 objective of the present work was to study how OM affected the distribution of P(V) in the
18 presence of Fe(III) and to address the questions if and by what mechanism(s) OM influenced the
19 concentration of aqueous phosphate. This was accomplished by investigating the ternary P(V)-
20 Fe(III)-OM system over a wide range of chemical conditions; $[\text{Fe}]_{\text{tot}}=5000\text{-}50\,000\text{ }\mu\text{g g}^{-1}$,
21 $\text{Fe/P}=0.5\text{-}2.0$ at pH 2.9-7. Iron speciation was probed via Fe K-edge X-ray absorption
22 spectroscopy, P speciation and concentrations were analyzed via infrared spectroscopy, and
23 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 ($\text{FePO}_4(\text{s})$). At low concentrations, the Fe(III)-OM complexes suppressed the formation of $\text{FePO}_4(\text{s})$, which resulted in elevated aqueous phosphate concentrations. At high concentrations $\text{FePO}_4(\text{s})$ 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 contribute to elevated concentrations of soluble P and thereby to increased bioavailability of P in soils and waters.

Keywords

Iron; phosphate; organic matter; X-ray absorption spectroscopy

1. Introduction

The bioavailable soil solution concentrations of phosphate are typically very low (e.g. Schindler, 1967; Frossard et al., 2000; 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 -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, 2010). OM may also increase the concentration of soluble phosphate as organic acids compete for binding sites at the soil mineral surfaces (Lindgren 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 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 was 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., 2004). Chemical data for SRN are reported in Table S1, supplementary material (SM). A stock solution of phosphate was prepared by dissolving NaH₂PO₄ (p.a. MERCK) in Milli-Q water. Stock solutions of Fe(III) were prepared by dissolving either FeCl₃×6H₂O (p.a. Sigma-Aldrich) or Fe(NO₃)₃×9H₂O (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 minutes 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 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] ($\mu\text{g g}^{-1}$) ^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

107 ^aOn a dry mass basis, the concentration of carboxylic functional groups is 4807 $\mu\text{mol g}^{-1}$.

108 ^bBased on a dry mass basis.

109 ^cExpressed as a molar ratio.

110 For more information see Table S2 in SM.

111

112 *2.1 XAS measurement and data analysis*

113 Fe K-edge XAS spectra were collected at beamlines 4-1 and 4-3 at Stanford Synchrotron

114 Radiation Lightsource (SSRL), California, USA. The ring current was 150-350 mA and the

115 energy was 3.0 GeV. Spectra were collected at room temperature using a Lytle detector, filled

116 with Ar gas, in fluorescence mode. Si ([2 2 0], $\Phi=90^\circ$) and Si ([1 1 1], $\Phi=90^\circ$) double-crystal
117 monochromators were used at 4-1 and 4-3, respectively, and a Mn 3- μ x filter was used to reduce
118 unwanted fluorescence and scattering contributions to the signal. To reduce higher order
119 harmonics a nickel coated harmonic rejection mirror was used at 4-3 and at 4-1 the
120 monochromator was detuned ca. 30 %. The hutch slits were set at 2x10 mm. The samples were
121 mounted in Teflon sample holders and sealed with Kapton Tape (CHR-Furon). 2-8 spectra were
122 recorded per sample, depending on the sample concentration, and spectra of a Fe foil were
123 simultaneously recorded to allow for internal calibration. All spectra were energy calibrated and
124 averaged using SixPack (Webb, 2005). Investigation of self-absorption effects and quantitative
125 shell-by-shell extended X-ray absorption fine structure (EXAFS) data fitting was accomplished
126 by means of Viper (Klementiev, 2001), and wavelet transform (WT) analysis by means of an Igor
127 Pro script (Funke et al., 2005). Each spectrum was carefully studied prior to averaging, and
128 spectra displaying signs of beam damage (detected as shifts in the edge position of the 1st
129 derivative spectra) were excluded. Standard procedures for background subtraction,
130 normalization and shell-by-shell fitting were followed (Karlsson et al., 2008). The samples were
131 modeled in *k*-space from 2.8 to 10.2-12.6 Å⁻¹, depending on the data quality, using theoretical
132 phase and amplitude functions from FEFF calculations (Zabinsky et al., 1995). Trisoxolatoiron
133 (Persson and Axe 2005), FePO₄×2 H₂O, strengite (Taxer and Bartl, 2004) and goethite (Szytula
134 et al., 1968) were used as input structures to the FEFF calculations. The amplitude reduction
135 factor (S_0^2) was set to 0.85, obtained by fitting the first coordination shell in a Fe-OM reference
136 sample, assuming a coordination number of 6 for the Fe-O path in the first shell. The numbers of
137 free variables were restricted by correlating coordination numbers and when available, fixing the
138 Debye-Waller factors (σ^2) found in literature or separately determined for new reference
139 compounds. Furthermore, the E₀-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 collected using an attenuated total reflectance (ATR) accessory equipped with a ZnSe crystal as internal reflection element. The samples were transferred to the crystal surface using a pipette and were then sealed from the atmosphere using a stainless steel lid that was not in contact with the sample. 1000 scans, ranging 400-5000 cm^{-1} at a resolution of 4 cm^{-1} , were recorded for each sample. The spectra of a pH-adjusted 0.27 M NaCl solution, and SRN dissolved in water adjusted to pH 3 and 6 were also recorded and later used for subtraction of the water and organic material contributions in the sample spectra. The concentration of free H_2PO_4^- in solution was evaluated by calculating the ratios between the height of the 1158 and 939 cm^{-1} phosphate bands and the height of the water bend vibration around 1600 cm^{-1} in the pH region 3-6 where H_2PO_4^- predominates. In order to isolate these phosphate bands, the spectral contributions from the organic material and $\text{FePO}_4(\text{s})$ were subtracted prior to baseline correction and evaluation of peak heights. The ratio between the phosphate bands and the water band accounts for differences in H_2PO_4^- peak intensities caused by different water content in the samples and thus isolates true concentration effects. A calibration curve was obtained by plotting this ratio for H_2PO_4^- standard solutions against H_2PO_4^- concentration (Fig. S1, SM). The concentration of free H_2PO_4^- in the P(V)-Fe(III)-OM samples were evaluated from this

calibration-curve. The concentrations reported were from the average of evaluations based on the 1158 and 939 cm⁻¹ peak heights.

2.3. Chemical equilibrium modelling

The speciation and the stable solid phases in the ternary P(V)-Fe(III)-OM system were obtained via chemical equilibrium modelling in WinSGW (Karlsson and Lindgren, 2006). The model was evaluated from measured pH values and total concentrations of the reacting species as well as on information from the XAS and IR samples (Tables 1, S3 and S4 in SM). This modeling approach was similar to Sundman et al. (2014b), where models for the analogous ternary As(V)-Fe(III)-OM systems were obtained. Carboxyls are the dominating functional group in SRN and these are characterized by the pKa values 2.9 and 5.7 (I= 0.27 M) (Karlsson and Persson, 2012). The fraction of SRN carboxyl groups involved in the interaction with iron was estimated to 20 % of the total concentration and the remaining carboxyls were assumed unreactive towards Fe(III) (Fujii et al., 2014; Hagvall et al., 2014; Sundman et al., 2014b). The composition and stability constants of the two Fe(III)-OM complexes (FeSRNH₁ and FeSRNH₂) were assumed to be identical to the Fe(III)-OM complexes previously determined (Sundman et al., 2014b). The formation constants of FePO₄(s) and Fe(OH)_{1.5}(PO₄)_{0.5}(s) were adjusted to find the best agreement between the model predictions and the spectroscopic observations. A compilation of chemical species and equilibrium constants is presented in Table 2.

The Davies equation (1) (Davies, 1962) was used to account for changes of the activity coefficients as a function of ionic strength (I).

$$\text{Log}\gamma_i = -0.509z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (1)$$

185 γ_i is the activity coefficient for the i^{th} species, z_i is the charge of the species and I is the ionic
186 strength in molar. In the calculation of I , contributions from high and low reactivity sites were
187 considered and I was found to vary from 0.3 to 1.2 M.

188

189 **Table 2.** Composition matrix with species defined according to the general equilibrium:

190 $\text{pH}^+ + \text{qFe}^{3+} + \text{rH}_3\text{PO}_4 + \text{sH}_2\text{SRN} \rightleftharpoons (\text{H}^+)^{\text{p}}(\text{Fe}^{3+})^{\text{q}}(\text{H}_3\text{PO}_4)^{\text{r}}(\text{H}_2\text{SRN})^{\text{s}}; \beta_{\text{p,q,r,s}}$. All log $\beta_{\text{p,q,r,s}}$

191 values are valid at $I=0$ M.

Species/ solids	log	p	q	r	s
	β_{pqrs}				
H^+	0	1	0	0	0
Fe^{3+}	0	0	1	0	0
H_3PO_4	0	0	0	1	0
H_2SRN	0	0	0	0	1
OH^-	-14.00 ^a	-1	0	0	0
FeOH^{2+}	-2.19 ^a	-1	1	0	0
$\text{Fe}(\text{OH})_2^+$	-5.67 ^a	-2	1	0	0
$\text{Fe}_2(\text{OH})_2^{4+}$	-2.95 ^a	-2	2	0	0
$\text{Fe}_3(\text{OH})_4^{5+}$	-6.3 ^a	-4	3	0	0
H_2PO_4^-	-2.14 ^b	-1	0	1	0
HPO_4^{2-}	-9.35 ^b	-2	0	1	0
PO_4^{3-}	-21.7 ^b	-3	0	1	0
$\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$	1.86 ^c	-1	1	1	0
$\text{Fe}(\text{HPO}_4)^+$	0.65 ^c	-2	1	1	0

Fe(PO ₄)(aq)	-1.8 ^c	-3	1	1	0
HSRN ⁻	-3.2 ^d	-1	0	0	1
SRN ²⁻	-9.5 ^d	-2	0	0	1
FeSRNH ₁	-0.39 ^e	-3	1	0	1
FeSRNH ₂ ⁻	-6.65 ^e	-4	1	0	1
Fe(OH) ₃ (s)	-4.1 ^f	-3	1	0	0
FePO ₄ (s)	2.9 ^g	-3	1	1	0
Fe(OH) _{1.5} (PO ₄) _{0.5} (s)	-0.27 ^g	-3	1	0.5	0

^aBaes and Mesmer (1976).

^bSmith and Martell (1976).

^cCiavatta et al. (1992).

^dKarlsson and Persson (2012).

^eSundman et al. (2014b).

^fLiu and Millero (1999).

^gThis work.

The equilibrium models were evaluated by means of the computer code WinSGW, (Karlsson and Lindgren, 2006), which is based on the SOLGASWATER algorithm (Eriksson, 1979). WinSGW minimizes the total residual sum of squares (U), calculated from experimental input data. Besides the measured pH-values of the solutions, the total concentrations [Fe(III)]_{tot}, [P(V)]_{tot}, [H₂SRN]_{tot} were known for each experimental point. Furthermore, interpretations of the XAS data contained information about the Fe(III)-OM speciation as well as the presence of Fe-P interactions indicating the presence of phosphate-containing polymerized Fe(III) phases, e.g. Fe(OH)_{1.5}(PO₄)_{0.5}(s) and/ or FePO₄(s). In some of the samples (c.f. Table S4, SM) no solid phases

were observed implying that the total concentration of Fe(III) in solution, $[\text{Fe(III)}]_{\text{tot.sln.}}$, was known and equal to $[\text{Fe(III)}]_{\text{tot}}$. Solid phases were treated as present (with activity $a_i = 1$) or absent (in amounts $n_i = 0 \text{ moles dm}^{-3}$). The quantification of total soluble H_2PO_4^- concentrations ($[\text{P(V)}]_{\text{tot.sln.exp}}$) obtained by the IR spectroscopy measurements provided information about the interplay between formed Fe(III)-OM complexes and the formation of phosphate-containing solids. The total residual sum of squares (U (2)) is expressed as:

$$U_{\text{tot}} = \sum ([\text{Fe}^{3+}]_{\text{tot.sln.calc.}} - [\text{Fe}^{3+}]_{\text{tot.sln.exp}})^2 + \sum ([\text{P(V)}]_{\text{tot.sln.calc.}} - [\text{P(V)}]_{\text{tot.sln.exp}})^2 + \sum (\sum (n_i(s_j)_{\text{calc.}} - n_i(s_j)_{\text{exp}})^2) + \sum (\sum (a_i(s_j)_{\text{calc.}} - a_i(s_j)_{\text{exp}})^2) \quad (2)$$

where (s_j) is the j different solid phases.

3. Results and discussion

3.1. IR spectroscopic results

The focus of the IR experiments was the P-O(H) vibrations between $1200\text{-}850 \text{ cm}^{-1}$ (Persson et al., 1996). These bands partly overlap with those of protonated and deprotonated SRN and therefore these latter contributions were subtracted from the spectra presented in Fig. 1. The ternary P(V)-Fe(III)-OM samples displayed one, predominant broad band overlaid with some sharper features that coincided with the spectrum of aqueous H_2PO_4^- (Fig. 1a). Removing the contribution from aqueous H_2PO_4^- via spectral subtraction showed that the broad feature was in agreement with the spectrum of precipitated $\text{FePO}_4(\text{s})$ (Fig. 1). We did not observe any additional contributions from phosphate surface complexes as those formed on goethite (Fig. 1n). Nor did the IR spectra indicate the formation of ternary P(V)-Fe(III)-OM complexes as P(V)-Me(III)-organic ligand complexes have been shown to display IR active P-O bands distinct from the broad features of $\text{FePO}_4(\text{s})$ (Lincoln and Stranks, 1968). Thus, the IR spectra of the ternary P(V)-Fe(III)-OM samples were composed of two main components, precipitated $\text{FePO}_4(\text{s})$ and aqueous

H_2PO_4^- . The isolation of the H_2PO_4^- peaks confirmed that their positions were identical with those of the aqueous H_2PO_4^- (Fig. S2, SM), which is the dominant phosphate species in the investigated pH-range. Based on the P-O(H) stretches, from H_2PO_4^- , at 939 and 1158 cm^{-1} , the fraction of bonded H_2PO_4^- in the 22 918 ppm Fe P(V)-Fe(III)-OM samples with Fe(III)/P(V)=1 ratios at pH 3.5-5.9 was estimated at 74-86 %, and no clear pH trend was observed (Fig. 2). These values were higher, but in the same range as reported for bonded H_2AsO_4^- in the corresponding ternary As(V) system (Sundman et al., 2014b). Hence, in the presence of Fe(III)-OM complexes, Fe(III) and P(V) or As(V) containing phases precipitated to similar extent. Furthermore, the existence of free, aqueous H_2PO_4^- indicated that Fe(III)-OM complexes may prevent the formation of a solid P(V) phase.

Fig1. IR spectra a) aqueous H_2PO_4^- , b) SRN IR1 (pH 3.5), c) SRN IR2 (pH 4.1), d) SRN IR3 (pH 4.6), e) SRN IR4 (pH 5.2), f) SRN IR6 (pH 5.9), g) SRN IR7 (pH 6.5), h) amorphous $\text{FePO}_4(\text{s})$, i) SRN IR1 (pH 3.5), j) SRN IR2 (pH 4.1), k) SRN IR3 (pH 4.6), l) SRN IR4 (pH 5.2), m) SRN IR6 (pH 5.9) and n) $2.2 \mu\text{mol}/\text{m}^2 \text{PO}_4^{3-}$ on goethite at pH 5.2. Spectra b-g were obtained by subtracting contributions of water and SRN, and from spectra i-m contributions from water, SRN and aqueous H_2PO_4^- have been subtracted.

Fig2. Estimated bound concentrations (in %) of P(V) in the samples containing 22 918 ppm Fe(III) at pH 3.5-5.9 (i.e. SRN IR1-6). The standard deviation is $\pm 4.1\%$.

3.2. Qualitative analysis of the XAS spectra

The first derivative Fe XANES spectra analysis indicated no shift to lower energies as compared to the Fe(III) model compounds and thus no significant reduction of Fe(III) to Fe(II) (Fig. S3, SM). The wavelet transform (WT) contour plots contained features caused by the presence of mononuclear Fe(III)-OM complexes and to some extent precipitated Fe(III) (hydr)oxides, in accordance with a previous study of the binary Fe(III)-OM system (Karlsson and Persson 2012). The precipitated Fe(III) (hydr)oxides displayed a characteristic Fe-Fe feature at ca. $7 \text{ \AA}^{-1}$, $2.5 \text{ \AA}$; c.f. ferrihydrite (Fig. 3a). In a few of the binary Fe(III)-OM reference samples and perhaps only one of the ternary P(V)-Fe(III)-OM samples (e.g. Fig. 3e, f and o) weak features caused by Fe(III) (hydr)oxides were detected. The WT characteristics of mononuclear Fe(III)-OM complexes at ca. $(3 \text{ \AA}^{-1}, 2.3 \text{ \AA})$ and $(3 \text{ \AA}^{-1}, 3.5 \text{ \AA})$ caused by Fe-C/O scattering (Karlsson and Persson, 2012) overlapped with those of precipitated $\text{FePO}_4(\text{s})$, displaying strong features at ca. $(3 \text{ \AA}^{-1}, 2.7 \text{ \AA})$ and $(3 \text{ \AA}^{-1}, 3\text{-}4 \text{ \AA})$ (Fig. 3b and c) caused by Fe-P single scattering and multiple scattering, respectively. Accordingly, it was difficult to resolve Fe(III)-SRN from $\text{FePO}_4(\text{s})$ in the WT plots. However the elongated feature at ca. $2.7 \text{ \AA}$ extending to ca. $6 \text{ \AA}^{-1}$ seemed to be unique to $\text{FePO}_4(\text{s})$ and this shape was present in a majority of the P(V)-Fe(III)-OM spectra, except for those at 6500 ppm Fe or less, i.e. SRN 1-6 (Fig. 3m and Fig. S4d-i, SM). Hence, at the lowest concentrations, Fe(III)-OM complexation seemed to be favored over precipitation of $\text{FePO}_4(\text{s})$ whereas at increased concentrations, constant pH and Fe:P ratio, the WT contour plots indicated the formation of $\text{FePO}_4(\text{s})$ (Fig. 3m-o). Only minor effects were observed when pH and the Fe:P ratios were varied (Fig. 3g-l).

Fig3. High resolution Fe WT modulus ($\eta=4$, $\sigma=2$) of a) 6L-ferrihydrite, b) amorphous $\text{FePO}_4(\text{s})$, c) Fe(III)-SRN at 6489 ppm Fe and pH 5, d) Fe(III)-SRN at 22 818 ppm Fe and pH 4.2, e) Fe(III)-SRN at 22 879 ppm Fe and pH 5.0, f) Fe(III)-SRN at 22 818 ppm Fe and pH 6.2, g) pH

2.9, SRN12, h) pH 5.0, SRN13, i) pH 7.0, SRN14, j) SRN10 with Fe/P ratio 2.0, k) SRN13 with Fe/P ratio 1.0, l) SRN16 with Fe/P ratio 0.5, m), SRN5 with 6504 ppm Fe, n) SRN8 with 11 971 ppm Fe and o) SRN18 with 50 000 ppm Fe. The wave vector, k , in $\text{\AA}^{-1}$ is plotted on the x-axis and the scattering distance, R (uncorrected for phase shift), in $\text{\AA}$ is displayed on the y-axis.

The Fourier transform (FT) second and third shell peaks, indicated by the WT plots to be caused by single scattering from C, Fe, and P, and possible multiple scattering effects, varied as a function of pH, concentration and Fe(III) to P(V) ratio (illustrative FTs are presented in Fig. 4, 5 and 6). The FTs of the low concentration samples (i.e. 5000-6504 ppm Fe, SRN1-6) were similar to the binary Fe(III)-SRN results presented by Karlsson and Persson (2012), and these were invariant in the pH range 2.9-6.5 (Fig. 4a-c and Fig. S5, SM). Hence, under these conditions formation of Fe(III)-OM complexes made Fe(III) inaccessible to phosphate which remained as free phosphate in solution. At higher concentrations (e.g. 11 971 ppm Fe), the weak FT peaks were modified by addition of phosphate indicating changes in Fe speciation (Fig. 4d-f). These changes were consistent with the WT results that suggested contributions from Fe-P scattering (Fig. 3n and Fig. S4j-l, SM). Further increase in concentration resulted in additional changes of the FT peaks between 2-4 $\text{\AA}$ (Fig. 5b-f). More specifically, the peak amplitudes at ca. 2.4 and 3.5 $\text{\AA}$ (uncorrected for phase shift) decreased while a new peak at ca. 2.6 $\text{\AA}$ (uncorrected for phase shift) became more pronounced. At the highest Fe concentration investigated the overall EXAFS and FT features were very similar to those of $\text{FePO}_4(\text{s})$ (Fig. 5f, g). Thus, these qualitative changes, primarily as a function of Fe concentration, were most likely caused by differences in relative concentrations of Fe(III)-OM complexes and $\text{FePO}_4(\text{s})$. In contrast to the WT analysis, discrimination between Fe and P backscatters was not possible merely by visual inspection of the FT magnitudes, and do not rule out minor contributions from Fe-Fe scattering. The real part of

the FT, however, supported the interpretation that all samples were dominated by Fe(III)-OM complexes and $\text{FePO}_4(\text{s})$ as ferrihydrite displayed a different beat pattern as compared to SRN1-SRN18 (Figure S5, SM). Finally, changes in the Fe(III) to P(V) ratio also resulted in minor changes in the FTs (Fig. 6a-c). Notably, these results displaying the partitioning between the different phases only reflected the situation from the perspective of the Fe core and the Fe speciation. To summarize, the interplay between Fe(III)-SRN complexes, precipitated $\text{FePO}_4(\text{s})$ and Fe(III) (hydr)oxides was controlled by the prevalent chemical conditions such as pH, concentration and the properties of OM.

3.3. Quantitative fits of the EXAFS spectra

The shell-by-shell EXAFS data fittings suffered from strong correlations between the coordination numbers (CN) and distances (R) of the Fe-C, Fe-Fe and Fe-P scattering paths. These correlations were in the range 0.6-1.0, and affected the reliability of the obtained CNs and distances of all second and third shell paths in Table 3. Nonetheless, the EXAFS fit results were in line with the previously presented IR and qualitative WT and FT analyses. All EXAFS spectra included contributions from scattering within Fe(III)-OM structures, and the obtained Fe-C and the corresponding Fe-C-O parameters were in general agreement with values reported for chelate-ring structures (Persson and Axe, 2005; Karlsson and Persson, 2010, 2012). In accordance with the failure to detect Fe-Fe scattering in the WT contour plots, the EXAFS spectra were satisfactorily fit with contributions from Fe(III)-OM and $\text{FePO}_4(\text{s})$ only. The Fe-P interactions detected could either originate from $\text{FePO}_4(\text{s})$ or a solid solution consisting of ferrihydrite with phosphate incorporated in the structure; based on the present data we cannot make this distinction. Note that Fe-P from a ternary P(V)-Fe(III)-OM complex is unlikely as no Fe-P interaction was detected at low total concentrations (samples SRN1-6). Thus, at conditions

where the Fe(III)-OM complexes completely predominated ternary complexes were not detected and consequently the formation of these complexes were not thermodynamically favored. At higher total concentration IR spectra were in agreement with the formation of FePO₄ (s). Overall, the coordination numbers of Fe-C and Fe-P paths followed the trends already discussed i.e. Fe-C decreased and Fe-P increased with increasing total concentrations, Table 3. This corroborated the interpretation that a fraction of the Fe(III)-OM was unreactive towards phosphate but at higher concentrations some of these complexes were converted into FePO₄(s) upon addition of P(V). The mechanism proposed is supported by previous results (Karlsson and Persson, 2012) showing that Fe-Fe interactions, and thus Fe (hydr)oxides, are absent under most conditions investigated in the present study in the absence of phosphate. Therefore, addition of P(V) and the concomitant appearance of Fe-P interactions indicated that a fraction of the Fe(III)-OM complexes was consumed at the formation of FePO₄ (s). This follows from the coupled equilibria describing the formation of Fe(III)-OM complexes and FePO₄ (s), respectively.

Fig4. I) k^3 -weighted and II) Fourier Transformed Fe-EXAFS for representative samples displaying the effect of pH at constant Fe and P(V) concentration, i.e. 6504 ppm (a-c) and 11 971 ppm (d-f) with a Fe/P ratio of 1 for a) SRN4 at pH 2.9, b) SRN5 at pH 5.0, c) SRN6 at pH 6.5, d) SRN7 at pH 3.2, e) SRN8 at pH 5.2 and f) SRN9 at pH 6.9. Black lines represent experimental data and red lines fit results. The vertical dashed lines are for visual guidance.

Fig5. I) k^3 -weighted and II) Fourier Transformed Fe-EXAFS for representative samples displaying the effect of concentration at pH 5 and $\text{Fe/P}=1.0\text{-}1.2$ for a) Fe(III)-SRN reference at 6489 ppm Fe and pH 5.0 previously published (Karlsson and Persson, 2012), b) 5000 ppm Fe in SRN (i.e. SRN1) c) 6504 ppm Fe in SRN (i.e. SRN5), d) 11 971 ppm Fe in SRN (i.e. SRN8), e) 22 916 ppm Fe in SRN (i.e. SRN13), f) 50 000 ppm Fe in SRN (i.e. SRN18), and g) amorphous $\text{FePO}_4(\text{s})$. Black lines represent experimental data and red lines fit results. The vertical dashed lines are for visual guidance.

Fig6. I) k^3 -weighted and II) Fourier Transformed Fe-EXAFS for representative samples displaying the effect of the Fe(III) to P(V) ratio at 22 916 ppm Fe in SRN at pH 4.9-5.0 for a) SRN16 with Fe(III)/P(V) ratio of 0.5, b) SRN13 with Fe(III)/P(V) ratio of 1.0, and c) SRN10 with Fe(III)/P(V) ratio of 2:1. Black lines represent experimental data and red lines fit results. The vertical dashed lines are for visual guidance.

365 Table 3. k^3 -weighted Fe K-edge EXAFS fit results of ternary P(V)-Fe(III)-OM samples.

Sample	Fe-O				Fe-C ^b		Fe-P ^c		Fe-C-O# ^d			F _i ^f
	CN	$\sigma^2(\text{\AA}^2)$	R($\text{\AA}$)	ΔE_0^a	CN	R($\text{\AA}$)	CN	R($\text{\AA}$)	CN ^e	R($\text{\AA}$)	ΔE_0^a	
Fe(III)-SRN ^g	5.3	0.0048	2.02	6.6	2.9	2.90			5.8	4.20	6.6	3.4
SRN1	5.9	0.0078	2.00	2.9	3.0	2.90			6.1	4.17	2.6	1.82
SRN2	5.8	0.0101	2.00	1.3	1.9	2.91			3.9	4.17	3.7	0.72
SRN3	5.9	0.0082	2.00	1.9	2.4	2.89			4.7	4.17	3.5	0.77
SRN4	5.9	0.0092	2.00	1.8	2.2	2.91			4.5	4.15	3.8	0.72
SRN5	5.9	0.0082	2.00	2.2	2.5	2.88			4.9	4.16	3.7	0.67
SRN6	5.8	0.0080	2.00	2.0	2.6	2.87			5.2	4.16	3.5	0.65
SRN7	6.1	0.0086	1.99	1.2	2.3	2.94	0.4	3.26	4.7	4.20	3.1	1.13
SRN8	6.2	0.0073	1.99	1.7	2.5	2.88	0.9	3.26	5.1	4.16	0.8	0.99
SRN9	6.1	0.0090	2.00	3.0	2.4	2.83	0.8	3.21	4.7	4.12	-1.4	1.01
SRN10	5.7	0.0093	1.99	2.6	2.3	2.93	0.9	3.26	4.7	4.19	2.6	0.85
SRN11	5.5	0.0078	1.99	2.5	2.3	2.86	1.4	3.23	4.7	4.13	-1.1	1.68
SRN12	6.4	0.0079	1.98	1.2	2.3	2.91	0.9	3.24	4.6	4.13	-0.4	1.01
SRN13	5.8	0.0085	1.99	0.1	1.8	2.95	1.0	3.27	3.7	4.17	0.2	1.11
SRN14	5.7	0.0082	1.99	2.0	1.6	2.85	1.5	3.22	3.2	4.09	-2.1	0.83
SRN15	5.9	0.0087	1.99	0.6	1.3	2.81	1.5	3.19	2.6	3.86	-7.6	1.56
SRN16	5.9	0.0090	1.99	2.4	0.7	2.80	1.5	3.20	1.4	4.03	-3.2	1.23
SRN17	6.0	0.0086	1.99	2.5	1.4	2.86	1.4	3.22	2.7	4.13	-2.5	1.14
SRN18	6.0	0.0088	1.99	1.4	1.4	2.86	2.3	3.22	2.8	4.10	-5.0	1.14

FePO ₄ (s)	6.0	0.0085	1.97	-0.1			2.0	3.19			-6.7	1.96
amorphous												

The amplitude reduction factor (S_0^2) was set to 0.85, # MS paths. The following abbreviations are used: coordination number (CN), bond distance (R), energy shift (ΔE_0) and Debye-Waller factor (σ^2). Conservative confidence limits on obtained distances and coordination numbers were estimated by varying each parameter in a step-wise fashion away from its optimal value, while varying all other parameters until $\Delta\chi^2$ increased 1.0 above its minimum value. This resulted in the following confidence limits: CN_{Fe-O}: ± 0.5 ; CN_{Fe-C}: ± 0.6 ; CN_{Fe-P}: ± 0.4 ; R_{Fe-O}: ± 0.01 ; R_{Fe-C}: ± 0.05 ; R_{Fe-P}: ± 0.05 .

^a ΔE_0 was assumed to be identical for the coordination shells beyond the first.

^bThe $\sigma^2(\text{\AA}^2)$ for the Fe-C was fixed to 0.0075 according to Sundman et al. (2014b).

^cThe $\sigma^2(\text{\AA}^2)$ for the Fe-P path was fixed to 0.0085 obtained from fitting the FePO₄(s) amorphous sample.

^dThe $\sigma^2(\text{\AA}^2)$ for the Fe-C-O# was fixed according to $2\sigma^2$ for Fe-C.

^eThe CN of the Fe-C-O# path was correlated to be 2CN of Fe-C according to carboxylic like structures.

^fF_i is defined as $((\sum(k^3 \chi_{\text{exp}} - k^3 \chi_{\text{fit}})^2 / \sum(k^3 \chi_{\text{exp}})^2)) \times 100$, where $k^3 \chi_{\text{exp}}$ and $k^3 \chi_{\text{fit}}$ represent experimental and fitted data points, respectively

^gBinary Fe(III)-SRN reference at 6489 ppm Fe and pH 5 from Karlsson and Persson, 2012.

3.4. Chemical equilibrium modeling

Using the modeling approach described under 2.3 the formation constants for the two solid phases FePO₄(s) and Fe(OH)_{1.5}(PO₄)_{0.5}(s) were determined to: $\log\beta_{-3,1,1,0}(\text{Fe}^{3+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{FePO}_4(\text{s}) + 3\text{H}^+) = 2.91$ and $\log\beta_{-3,1,0.5,0}(\text{Fe}^{3+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{Fe}(\text{OH})_{1.5}(\text{PO}_4)_{0.5}(\text{s}) + 3\text{H}^+) = -0.27$. The

model obtained, describing interactions in the ternary P(V)-Fe(III)-OM system, was in general agreement with the EXAFS observations. In total 18 EXAFS spectra were analyzed with respect to Fe(III)-OM and Fe(III)-P(V) interactions, which corresponded to 36 points of information (Table S4, SM). Comparison between the spectroscopic information and the modeling results showed that the agreement was better than 94 % (Table S4, SM). The model predicted the formation of $\text{FePO}_4(\text{s})$ in samples SRN7, 10-13 and 15-18 while $\text{Fe}(\text{OH})_{1.5}(\text{PO}_4)_{0.5}(\text{s})$ was formed only at the highest pH values (SRN 9, 11, 14 and 17). This finding was neither corroborated nor in contrast to the EXAFS results as these were not able to discriminate between $\text{FePO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{PO}_4)_{0.5}(\text{s})$, see discussion above. The disagreement between the model and the EXAFS results were observed in two lower concentration samples with pH values between 3 and 5, i.e. within the narrow experimental regime where Fe(III)-OM starts precipitating as $\text{FePO}_4(\text{s})$ upon P(V) addition. Reports on the stability of amorphous $\text{FePO}_4(\text{s})$ are scarce; the IUPAC Stability Constant database (Pettit and Powell, 2003) lists only one solubility study (Ciavatta et al., 1992; $\log\beta_{-3,1,1,0}(\text{Fe}^{3+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{FePO}_4(\text{s}) + 3\text{H}^+) = 4.0$). This value is higher than the one obtained in the present study. One possible explanation is that small $\text{FePO}_4(\text{s})$ particles were formed in the presence of OM, and such particles have been shown to have higher solubility than more coarse ones (Schindler, 1967).

According to Thibault et al. (2009), $\text{Fe}(\text{OH})_{1.5}(\text{PO}_4)_{0.5}(\text{s})$ is the end member of the solid solution series $\text{Fe}(\text{OH})_{3-3x}(\text{PO}_4)_x$, which forms in colloidal Fe(III)-P(V) systems. Previously, Sundman et al. (2014b) have determined the formation constant of the analogous $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ to $\log\beta_{-3,1,0.5,0}(\text{Fe}^{3+} + \text{H}_3\text{AsO}_4 \rightleftharpoons \text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s}) + 3\text{H}^+) = 0.20$, thus slightly higher than the phosphate phase. At present there is no literature value for the stability of this compound so additional comparisons were not possible. The model was also evaluated with respect to phosphate concentrations in solution (samples SRN IR1-6) yielding the following

results with respect to calculated and experimental values: 15.1, 8.6; 16.3, 11.7; 16.5, 8.3; 16.4, 11.8; 16.2, 7.1; 15.9, 7.0 mM (Table S3, SM). The model slightly overestimated the concentrations of phosphate in solution; however, given the difficulties in determining free phosphate concentrations in these samples, we find the discrepancies acceptable.

The equilibrium model was applied to conditions in natural stream waters using concentrations of Fe, P(V) and dicarboxylic acids from Jansson et al. (2012) and Neubauer et al. (2013). The predicted predominance of Fe-OM complexes at low pH and increasing contribution of precipitated $\text{Fe}(\text{OH})_3(\text{s})$ with increasing pH (Fig. 7) were in good agreement with previous XAS spectroscopic data collected on samples from the same stream waters (Sundman et al., 2013; Sundman et al., 2014a). The concentrations of soluble Fe-P complexes are negligible under these conditions and no precipitated P(V)-containing phases exist. In order to evaluate the environmental importance of precipitated P(V)-containing phases, the speciation of Fe was calculated under “natural” conditions where pH, dicarboxylic acid and Fe concentrations were kept constant at 4.9, 17.5 μM and 22.4 μM , respectively and the phosphate concentration was stepwise increased to 30 μM . Furthermore, the Fe was assumed to be in its trivalent state and not subject to microbially mediated Fe redox cycling. Previous studies have shown a predominance of trivalent Fe in these waters (Neubauer et al., 2013, Sundman et al., 2013, Sundman et al., 2014a), whereas the inability of the model to account for microbial Fe cycling is indeed a weakness of the model. The solid solution, $\text{Fe}(\text{OH})_{1.5}(\text{PO}_4)_{0.5}(\text{s})$, existed within a limited concentration range, 18-19 μM P(V), suggesting a minor contribution from this phase. The instability of the solid solution at higher P(V) concentrations is due to the formation of $\text{FePO}_4(\text{aq})$, which is formed to 20-22% of total soluble Fe. Results from the corresponding As(V) system (Sundman et al., 2014b) indicate that the $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ phase is slightly more

Fig. 7. Distribution diagram displaying the Fe speciation in an environment containing 22.4 μM Fe, 0.14 μM P(V) and 17.5 μM active dicarboxylic acid groups, calculated from stability constants and solubility products presented above.

4. Conclusion

We have shown that Fe and P speciation in the ternary P(V)-Fe(III)-OM system was strongly linked to the total concentrations of the elements, the Fe:OM and Fe:P ratios as well as to pH. Our collective spectroscopic and equilibrium modeling results highlighted the substantial effects exerted by Fe(III)-OM complexes on the speciation of phosphate. Over a wide range of experimental conditions the Fe(III)-OM complexes were sufficiently strong to suppress formation of ternary P(V)-Fe(III)-OM complexes, FePO₄(s) precipitates and/or Fe(III) (hydr)oxides. Thus, the strong complexation with OM resulted in a fraction of Fe(III) that was unreactive towards

phosphate. We acknowledge that our results were obtained at concentrations typically not present in natural environments. At lower concentrations the presence of stable Fe(III)-OM complexes will prevent reaction with phosphate, as shown by the chemical equilibrium model. This implies that phosphate will mainly be sequestered as surface complexes on Fe(III) (hydr)oxides present, and the balance between the formation of Fe(III)-OM complexes and Fe(III) (hydr)oxides will play a decisive role for phosphate. Moreover, the organic matter may compete with phosphate for binding sites at the Fe(III) (hydrox)oxide surfaces. A main conclusion from this study was therefore that increased input of OM can lead to redistribution of Fe from solid phases to Fe(III)-OM complexes, and the results offer a mechanistic and thermodynamic consistent explanation to why increased input of organic matter decrease the sorption of phosphate and contribute to elevated concentrations of soluble P and thereby to increased bioavailability of phosphorus in soils and waters.

Acknowledgements

This manuscript was significantly improved by the helpful comments and suggestions provided by two anonymous reviewers. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393) and the National Center for Research Resources (P41RR001209). The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of NIGMS,

474 NCRR or NIH. The vibrational spectroscopy platform run at the Chemical Biological Center at
475 Umeå University is acknowledged for use of the Bruker Vertex 80 instrument for IR
476 measurements. This project was supported by the Swedish Research council.

477

478 Conflict of Interest: The authors declare that they have no conflict of interest.

479

480 Supplementary material

481 Calibration curve for IR spectroscopy determination of aqueous H_2PO_4^- concentrations,
482 representative IR spectra showing the phosphate bands in SRN samples, chemical data for SRN,
483 detailed information about sample preparation, XANES spectra for SRN1-18, comparison
484 between spectroscopy observations and model predictions, and WT for the full SRN sample
485 series are found in the supplementary material.

486

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