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# Characterization of Iron(III) in Organic Soils Using Extended X-ray Absorption Fine Structure Spectroscopy

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The distribution of different iron (Fe) species in soils, sediments, and surface waters has a large influence on the mobility and availability of Fe, other nutrients, and potentially toxic trace elements. However, the knowledge about the specific forms of Fe that occurs in these systems is limited, especially regarding associations of Fe with natural organic matter (NOM). In this study, extended X-ray absorption fine structure (EXAFS) spectroscopy was used to characterize Fe(III) in organic soils (pH 4.6–6.0) with varying natural Fe content. The EXAFS data were subjected to wavelet transform analysis, to facilitate the identification of the nature of backscattering atoms, and to conventional EXAFS data fitting. The collective results showed the existence of two pools of iron: mononuclear Fe(III)-NOM complexes and precipitated Fe(III) (hydr)oxides. In the soil with lowest pH (4.6) and Fe content mononuclear organic complexes were the completely dominating fraction whereas in soils with higher pH and Fe content increasing amounts of Fe (hydr)oxides were detected. These results are of environmental importance, as the different iron pools most likely have markedly different reactivities.

## Introduction

Iron (Fe) is a micronutrient, essential to all organisms, and one of the most abundant metals in soils and sediments. The Fe chemistry has a large influence on the mobility and availability of Fe, other nutrients, and potentially toxic trace elements. However, there are still gaps in the knowledge about the specific forms of Fe that occur in these systems, especially regarding associations of Fe with natural organic matter (NOM). Past methods for speciation have mainly been

restricted to wet-chemical methods, which are time-consuming and destructive, and the different Fe species obtained in each fraction are operationally defined. A promising alternative for Fe speciation in natural materials are the recent developments in synchrotron-based X-ray absorption spectroscopy (XAS).

Much research has been devoted to XAS on pure crystalline or amorphous Fe-bearing phases, and the structures of these materials have been thoroughly characterized (1–3). Furthermore, XAS has been used in several studies to analyze the associations of anions and cations to these iron containing phases (4–6). However, there are relatively few studies where XAS have been used to determine the molecular structures of Fe in soils (7–9) and only a few specific EXAFS studies on the association of Fe with NOM. For instance, Gustafsson et al. (10) determined the binding of Fe(III) in organic soils at pH 4. They reported that Fe occurred either as Fe (hydr)oxides or organically complexed likely as a mixture of  $(\text{O}_5\text{Fe})_3\text{O}$  and  $(\text{O}_5\text{Fe})_2\text{O}$  complexes. Rose et al. (11) and Vilg -Ritter et al. (12) determined the speciation of Fe in NOM from natural freshwaters and found that Fe was poorly polymerized because of complexation of Fe by the organic matter. Van Schaik et al. (13) have studied the reaction between Fe and fulvic acids and found that Fe formed mononuclear complexes with fulvic acids in solution. In studies of Fe(III) associated to humic acids and ligneous material only first shell contributions have been reported, showing that Fe(III) is coordinated by 6 O atoms at a distance of approximately 2.0   (14, 15).

In order to separate between different Fe species a proper analysis of the second coordination shell is critical. However, in conventional analysis of EXAFS data it may prove difficult to separate different backscattering atoms in higher coordination shells present at similar bonding distances from the central iron atom. Recently a method based on wavelet transforms (WT) was introduced which facilitates the identification of the nature of backscattering atoms (16–18). Herein we apply this method for the first time to EXAFS data of Fe in organic soils and combine it with conventional EXAFS analysis in order to extend our knowledge on Fe speciation in the environment and especially its association to NOM.

We focused on organic soils with varying natural Fe contents and used both untreated and manipulated samples where Fe was displaced using either pyrophosphate or oxalate. Two forested soils with high Fe content and one peat soil with significantly lower amounts of Fe were selected. Organic soils with high Fe content are mainly found in groundwater discharge areas (19), and the Fe accumulation in these soils has large implications for the dynamics of phosphorus (20).

## Material and Methods

**Sites and Soils.** Soil samples were collected from two forested groundwater discharge areas in northern Sweden (Soil-1, Betsele [64 39'N, 18 30'E], and Soil-2, Flakastugan [64 25'N, 19 25'E]) and from a cultivated fen peat in southwestern Sweden (Soil-3, Majneg rden 58 0' N, 14 5' E). About seven to eight samples were sampled from the forest floor (O-horizon) in the two northern sites, bulked into one composite sample, sieved (2 mm mesh size), and gently homogenized. The homogenized bulk samples were stored in polyethylene bags in a freezer at –20  C. The sample from Majneg rden (Soil-3) was taken as a single bulk sample at a depth of 35–45 cm. It was sealed in double polyethylene bags and stored at 4  C until freeze-dried (Edwards Modulyo 4K Freeze-dryer) followed by homogenization by a tungsten carbide ball mill

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**TABLE 1. Chemical Composition of the Soils used for EXAFS Analysis<sup>a</sup>**

sample	pH	[Org-C] (g kg <sup>-1</sup> )	[Fe <sub>Pyr</sub> ] <sup>b</sup> (mmol kg <sup>-1</sup> )	[Fe <sub>Ox</sub> ] <sup>b</sup> (mmol kg <sup>-1</sup> )	[Fe <sub>CD</sub> ] <sup>b</sup> (mmol kg <sup>-1</sup> )	[Fe <sub>CuCl<sub>2</sub></sub> ] <sup>c</sup> (mmol kg <sup>-1</sup> )
Betsle (Soil-1)	6.0	290	161	351	364	
Flakastugan (Soil-2)	4.9	360	180	199	203	
Majnegården (Soil-3)	4.6	427				39

<sup>a</sup> Organic carbon (Org-C). <sup>b</sup> According to Buurman et al. (22), fresh soils were extracted with 0.1 M pyrophosphate (Pyr) for 18 h, 0.2 M ammonium oxalate (Ox) adjusted to pH 3.0 for 4 h, and a mixture of 0.6 M sodium citrate and 0.1 M sodium dithionite (CD) for 18 h, at a soil solution ratio of 1:40. <sup>c</sup> Extraction with 0.5 M CuCl<sub>2</sub> according to Skjllberg and Borggaard (23).

(Retsch, S2, Germany). Three reference samples were selected for comparison with our natural organic soil samples: synthetic goethite, a trisoxalatoiron(III) [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>] complex in solution (21), and a mixture consisting of 25% synthetic goethite and 75% ammonium trisoxalatoiron(III) trihydrate [(NH<sub>4</sub>)<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·3H<sub>2</sub>O]. The proportions in the mixture were based on the Fe(III) content. The synthetic goethite and the goethite/trisoxalatoiron(III) mixture was ground in a mortar and diluted 1:40 with boron nitride. Before EXAFS analysis the soil and reference samples were mounted in Teflon sample holders and sealed with Kapton tape (CHR-Furon).

Iron in the soil samples were determined by commonly used wet-chemical extraction methods (Table 1). Pyrophosphate and CuCl<sub>2</sub> is assumed to extract mainly organically complexed Fe; the oxalate extraction also includes amorphous Fe oxides, and the citrate-dithionite extraction also includes crystalline Fe (22, 23). From the Betsle site, the subsamples remaining after extraction with pyrophosphate (Soil-1\_Pyr) and oxalate (Soil-1\_Ox) were also analyzed by EXAFS. Chemical data for the soils are presented in Table 1.

**EXAFS Data Collection and Analysis.** Iron K-edge (7.112 keV) spectra were collected at the superconducting multipole wiggler beamline I811, at MAX-lab (Lund University, Sweden), with 1.5 GeV beam energy and 100–200 mA electron current. Data were collected at room temperature at ambient atmospheric pressure in fluorescence mode and the beam was monochromatized with a double crystal monochromator (Si [111]). EXAFS spectra were quantitatively analyzed using the programs WinXAS v3.1 (24) and Viper (25). From each averaged and energy calibrated (7.112 keV) spectrum, a polynomial pre-edge function was subtracted and the data were normalized. Above the absorption edge a cubic spline fit was used to remove the background and the data were *k*<sup>3</sup>-weighted to enhance the higher *k* values. These *k*<sup>3</sup>-weighted spectra were fitted in a nonlinear least-squares refinement procedure with theoretical phase and amplitude functions calculated by the *ab initio* code FEFF7 (26). The input structures used in the FEFF calculations were those of [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> and goethite (21, 27). During the fitting procedure the edge energy ( $\Delta E_0$ ) was varied but correlated to be the same for all shells in a sample. In all refinements the amplitude reduction factor (*S*<sub>0</sub><sup>2</sup>) was set to 0.78. This was based on the average obtained for the soil samples and for goethite (range 0.72–0.86), by setting the total coordination number in the first coordination shell to 6.

A qualitative analysis of the nature of backscattering atoms in higher coordination shells was conducted using the Morlet wavelet transform (WT) method as implemented in the Igor Pro script developed by Funke et al. (17). This method complements the conventional Fourier transform (FT) analysis and reveals the energies where back scattering takes place that give rise to the FT peaks. The WT modulus of the

organic soil samples was analyzed and compared with the WT modulus for reference samples with contribution from C and/or Fe backscattering in the second coordination shell. More details on the EXAFS data collection and analysis are given in the Supporting Information.

## Results and Discussion

**EXAFS Results for the First Coordination Shell.** The WT analysis showed similar first shell contributions for all soil samples with back-scattering maxima around 5 Å<sup>-1</sup>, and these are in agreement with the Fe–O scattering of goethite (Figure 1). This was further supported by the quantitative analysis of EXAFS data which showed that Fe(III) in the organic soils was coordinated by approximately 6 O/N atoms (O and N cannot be distinguished by means of EXAFS data fitting), in the first shell (Table 2). The mean Fe–O/N bond distance of 2.00 Å indicates that Fe occurs predominantly as Fe(III), as the Fe–O/N bonding distance for Fe(II) is substantially longer, 2.10 Å (28). This is also apparent in the first derivatives of the XANES region where the organic soil samples are similar to the reference samples containing Fe(III) (Figure S-1). The distances found in the first shell of the organic soil samples are in fair agreement with Fe–O distances reported for organic compounds, Fe (hydr)oxides, organic soils, humic acids, and ligneous materials (3, 10, 14, 15, 21).

**Wavelet Transform Analysis of the Higher Coordination Shells.** Both the overview and the high-resolution wavelets (Figures 1 and 2) of the goethite EXAFS spectrum reveal a strong feature corresponding to the second peak in the Fourier transform. This feature appears at significantly higher energy (ca. 8 Å<sup>-1</sup>) as compared the WT modulus of the first shell discussed above, indicating the presence of heavier back-scatterers in accordance with the second nearest Fe neighbors of the goethite structure (Table 2). Note however that not even the high-resolution plot (Figure 2) is able to resolve the individual Fe–Fe distances of goethite at 3.03, 3.26, and 3.43 Å. Most of the soil samples also display the Fe–Fe feature in their WT plots, but there is clear difference in intensity between the samples (Figure 2). The strong Fe–Fe contribution displayed in goethite is weaker or missing completely in the goethite/trisoxalatoiron(III) mixture and in the organic soils. An important result is that the Soil-3 sample, which is the organic soil with the lowest amount of Fe, lowest pH (4.6), and highest Org-C content (Table 1), shows no indications of Fe in the second shell (Figure 2). In turn, this indicates no or very little Fe hydrolysis and that the Fe speciation is dominated by mononuclear complexes. This is reasonable since the hydrolysis of Fe is expected to be suppressed by low Fe concentrations and pH.

The decrease of Fe back-scattering in the organic soils is accompanied by the appearance of a new feature at low energies (ca. 3.0–4.0 Å<sup>-1</sup>) in the high-resolution WT plots (Figure 2). This energy is lower than the first shell Fe–O contribution and coincides with features caused by C back-scattering in trisoxalatoiron(III) complexes and in the goethite/trisoxalatoiron(III) mixture. We therefore assign this feature to the presence of carbon atoms in the second coordination shell around iron. This assignment is corroborated by the quantitative results obtained from fitting the EXAFS spectra (see below). For the soil samples studied herein, the WT results thus show that the average composition of the second shell may range from predominately Fe to practically only C.

**Quantitative Results from the EXAFS Data Fitting.** The prior knowledge from the WT analysis was used as input to the quantitative modeling of the EXAFS spectra. Hence, second-shell paths from both C and Fe back-scattering were included in the model. In order to constrain the fits, literature values of Debye–Waller factors for Fe–Fe and Fe–C paths were used as fixed parameters (Table 2). Furthermore, the

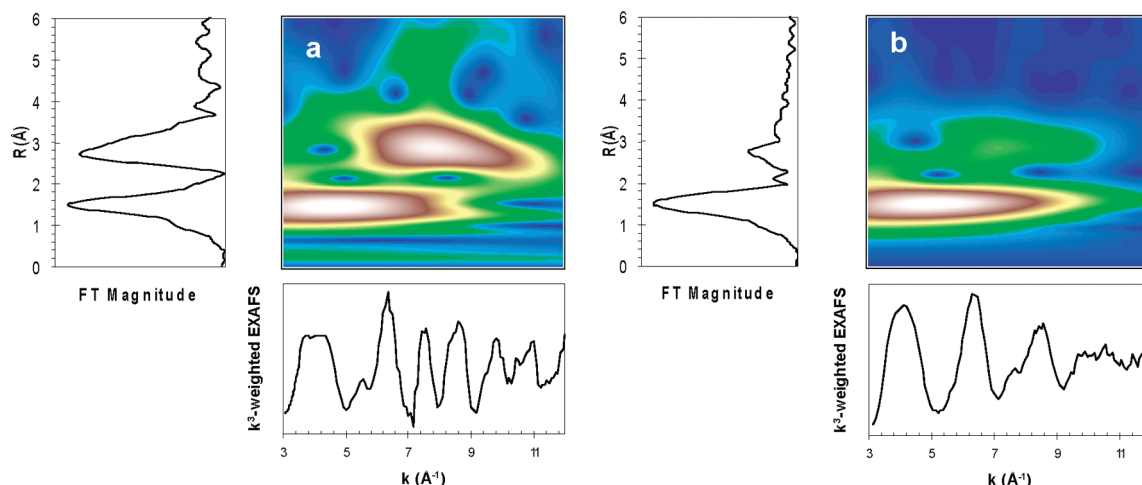


FIGURE 1. Overview of the Morlet WT modulus displaying the first and second coordination shell ( $\eta = 10$ ,  $\sigma = 1$ ) for (a) goethite and (b) the Soil-1 sample, plotted as a function of  $k$  ( $\text{\AA}^{-1}$ ) on the  $x$ -axis and  $R$  ( $\text{\AA}$ ) on the  $y$ -axis.

TABLE 2. Fits to Unfiltered EXAFS Data in  $k$ -Space for Goethite, the Untreated Organic Soil Samples (Soil-1–Soil-3), and the Pyrophosphate (Soil-1\_Pyr) and Oxalate (Soil-1\_Ox) Extracted Samples<sup>a</sup>

sample	Fe–O/N (SS)			Fe–Fe (SS) <sup>b</sup>		Fe–Fe (SS) <sup>c</sup>		Fe–C (SS) <sup>d</sup>		Fe–C–O/C (MS) <sup>e</sup>		$\Delta E_0$ (eV)
	CN	$R$ ( $\text{\AA}$ )	$\sigma^2$ ( $\text{\AA}^2$ )	CN	$R$ ( $\text{\AA}$ )	CN	$R$ ( $\text{\AA}$ )	CN	$R$ ( $\text{\AA}$ )	CN	$R$ ( $\text{\AA}$ )	
goethite	3 <sup>f</sup>	1.97	0.0039	1.9 <sup>g</sup>	3.03	3.8 <sup>g</sup>	3.43					–0.2
	3 <sup>f</sup>	2.12	0.0067	1.9 <sup>g</sup>	3.26							
Soil-1	6.7	1.99	0.0111	0.5 <sup>g</sup>	3.02	1.0 <sup>g</sup>	3.42	1.1 <sup>h</sup>	2.86	2.2 <sup>h</sup>	4.06	–3.2
Soil-1_Pyr	5.2	2.00	0.0083	0.6 <sup>g</sup>	2.98	1.2 <sup>g</sup>	3.47	1.3 <sup>h</sup>	2.72	2.6 <sup>h</sup>	3.93	–3.4
Soil-1_Ox	6.3	2.04	0.0137	0.6 <sup>g</sup>	3.06	1.2 <sup>g</sup>	3.47	0.9 <sup>h</sup>	2.83	1.8 <sup>h</sup>	3.97	0.0
Soil-2	5.4	1.97	0.0071	0.4 <sup>g</sup>	2.99	0.8 <sup>g</sup>	3.40	1.4 <sup>h</sup>	2.78	2.8 <sup>h</sup>	4.08	–3.6
Soil-3 <sup>i</sup>	5.8	1.99	0.0083	0.1 <sup>g</sup>	2.92	0.2 <sup>g</sup>	3.31	1.6 <sup>h</sup>	2.81	3.2 <sup>h</sup>	4.08	–1.5
Soil-3 <sup>i</sup>	5.9	2.00	0.0084					1.8 <sup>h</sup>	2.85	3.6 <sup>h</sup>	4.07	–1.2

<sup>a</sup> The amplitude reduction factor ( $S_0^2$ ) was set to 0.78, and coordination numbers (CN), bond distances ( $R$ ), Debye–Waller factors ( $\sigma^2$ ), and the edge energy ( $\Delta E_0$ ) were either varied, covaried, or fixed as specified in the table. <sup>b</sup> For goethite  $\sigma^2 = 0.0033$  and  $0.0104$ , respectively, and for the soil samples  $\sigma^2 = 0.0037$ , the average for goethite and ferrihydrite (3). <sup>c</sup> For goethite  $\sigma^2 = 0.0074$  and for the soil samples  $\sigma^2 = 0.0083$ , the average for goethite and ferrihydrite (3). <sup>d</sup>  $\sigma^2 = 0.0056$  (21). <sup>e</sup>  $\sigma^2 = 0.0061$  (21). <sup>f</sup> Fixed value. <sup>g</sup> The CN for the longer Fe–Fe path is correlated to be  $2 \times$  CN of the shorter ones in agreement with the goethite and ferrihydrite structures. <sup>h</sup> The CN for the Fe–C–O/C MS path is correlated to be  $2 \times$  CN of the Fe–C SS path in agreement with structures involving carboxylate or similar groups. <sup>i</sup> According to the F-test (29) it is only within 25% probability that the model with C and Fe is better than one with C back-scattering only.

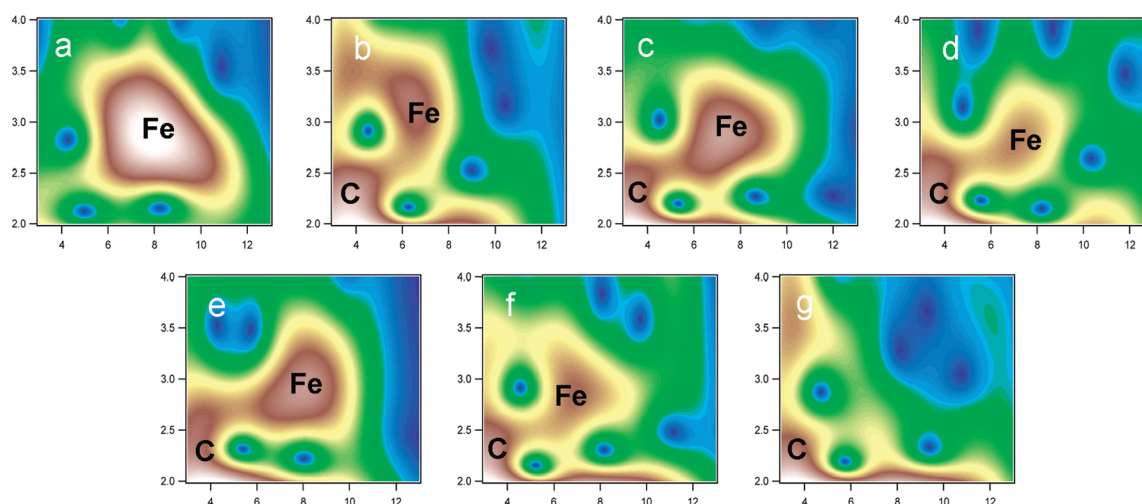
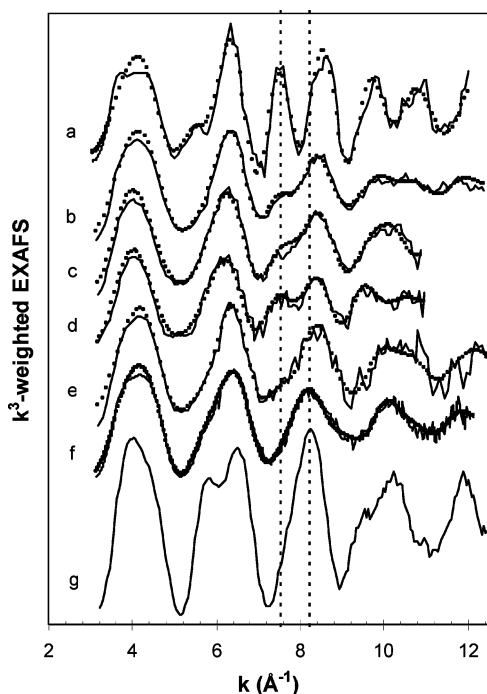


FIGURE 2. High resolution Morlet WT modulus displaying the second coordination shell ( $\eta = 4$ ,  $\sigma = 2$ ) for (a) goethite, (b) goethite/trisoxalatoiron(III) mixture, (c) Soil-1, (d) Soil-1\_Pyr, (e) Soil-1\_Ox, (f) Soil-2, and (g) Soil-3, plotted as a function of  $k$  ( $\text{\AA}^{-1}$ ) on the  $x$ -axis and  $R$  ( $\text{\AA}$ ) on the  $y$ -axis in the range 2.0–4.0 ( $\text{\AA}$ ).

coordination number (CN) for the longer Fe–Fe path was correlated to be  $2 \times$  CN of the shorter Fe–Fe path in agreement with the goethite and ferrihydrite structures, and

the CN of the Fe–C–O/C multiple scattering (MS) path was correlated  $2 \times$  CN of the Fe–C single scattering (SS) path in agreement with carboxylate coordination or similar structures





**FIGURE 3.**  $k^3$ -weighted EXAFS data for (a) goethite, (b) Soil-1, (c) Soil-1\_Pyr, (d) Soil-1\_Ox, (e) Soil-2, (f) Soil-3, and (g) trisoxalatoiron(III) complex in solution. Experimental data (solid lines) and data derived from fitting parameters (dotted lines; Table 2). The fit to the Soil-3 sample includes both C and Fe backscattering. All experimental spectra are unfiltered except for the Soil-1\_Pyr and Soil-1\_Ox samples, for which a smoothing function was applied to improve the visual appearance. Vertical dashed lines indicate the peak position for the third oscillations in goethite and trisoxalatoiron(III).

(Table 2). The number of independent points in the fits to the EXAFS spectra is according to the Nyquist theorem ( $N_{\max} = 2 \times \Delta k \times \Delta R / \pi$ , where  $\Delta k$  is the  $k$ -range of the EXAFS spectrum and  $\Delta R$  is the  $R$ -range of the Fourier transform considered) in the range 15–18. This clearly exceeds the maximum number of free variables in our fitting procedure, which is 10. Hence in no case is the EXAFS spectra overfitted.

Table 2 and Figure 3 present the fit results to the unfiltered EXAFS spectra of the soil samples, and the corresponding Fourier transforms and the first derivatives of the XANES region are illustrated in Figures S-1, S-2 and S-3. In agreement with the WT analysis, the quantitative EXAFS analysis shows that the average composition of the second shell varies between the soils; in the untreated samples the contribution from C decreases and the contribution from Fe increases in the order Soil-3, Soil-2, Soil-1 (Table 2). This trend is also seen in the first derivatives of the XANES region, where the Soil-3 sample is similar to trisoxalatoiron(III) while the Soil-1 sample is in better agreement with the goethite/trisoxalatoiron(III) mixture (Figure S-1). The Fe–C distances (2.78–2.86 Å) for the untreated soil samples and the Fe–Fe distances (2.99–3.02 and 3.40–3.42 Å) for the Soil-1 and Soil-2 samples are in agreement with those in complexes between Fe(III) and small organic ligands, 2.82–2.84 Å (21, 30), and in Fe(III) (hydr)oxides such as goethite and ferrihydrite, 3.03–3.04 Å and 3.42–3.43 Å (3), respectively.

Of particular importance are the results obtained for the Soil-3 sample, i.e., the soil with lowest pH and total iron concentration, which show a strong contribution from C atoms in the second shell (Table 2). The WT analysis indicated no second shell iron in this sample, and it is questionable whether the iron paths should be included in the model; according to the F-test (29) it is only within 25% probability

that the model including Fe is better than one with C backscattering only. The fits to unfiltered  $k$ -space data are visually very similar with and without Fe backscattering; however, a small difference is seen in the  $k$  region 8.2–9.4 Å<sup>−1</sup> where the fit including Fe is better (Figure S-4). Furthermore, the Fe–Fe distances obtained, which are very uncertain due to the weak contribution, differ from the distances obtained for the other organic soils (Table 2). Irrespectively, the fitting results show that the Fe speciation in Soil-3 is dominated by mononuclear Fe–NOM complexes. Thus, the apparently strong complexation to NOM functional groups prevents the iron hydrolysis otherwise expected at pH 4.6 and accordingly also prevents the formation of polynuclear complexes and/or Fe (hydr)oxide precipitates. The obtained single-scattering Fe–C and multiple-scattering Fe–C–O/C distances (Table 2) are very similar to those in the trisoxalatoiron(III) complex (Table S-1), indicating a similar coordination environment; the existence of the latter path is corroborated by the F-test, and with 95% probability a model including this path is better than one without. The similarity with the oxalate complex suggests the formation of a five-membered chelate ring structure. This is in line with the strong complexation and limited hydrolysis and furthermore also agrees with EXAFS-derived structures of Cu(II) in organic soils (31). Tipping et al. (32) showed that there is a significant competition between Fe(III) and Cu(II) for binding by NOM in freshwaters over a wide pH range (4–9); thus, it is likely that Fe and Cu competes for the same binding sites also in organic soils. However, because of the small difference in atomic number between C, N, and O, we cannot ascertain whether the multiple-scattering is caused by for instance Fe–C–C or Fe–C–O. Hence, several different types of functional groups may be involved in the complexation including carboxyls, hydroxyls, amines, and catecholic groups.

For the soils with higher pH and total Fe concentrations (Soil-1 and Soil-2), a significant contribution from Fe backscattering appears in the EXAFS spectra, which is asserted with >95% probability using the F-test. The presence of polynuclear Fe species does not, however, influence the single-scattering Fe–C and multiple-scattering Fe–C–O/C distances, indicating that a fraction of Fe in these samples is similar to the mononuclear complexes in Soil-3. Two Fe–Fe distances are detected at approximately 3.0 and 3.4 Å which correspond to octahedral edge-sharing and double-corner geometries, respectively (1). By comparison with distances in Fe minerals and complexes the identity of the Fe phase cannot be unambiguously determined, but the distances obtained are in good agreement with goethite and ferrihydrite (Table S-1). However, compared to these minerals the Fe–Fe path at ca. 3.26 Å is apparently missing in the soil samples. Attempts were made to also include this path, but the improvements of the fits were statistically insignificant. This may be a consequence of the comparatively high Debye–Waller factor reported (Table S-1) and hence the minor contribution of this scattering path. An important result is the detection of edge-sharing Fe–Fe at ca. 3.0 Å. In  $\mu$ -oxo complexes such as (O<sub>5</sub>Fe)<sub>2</sub>O and (O<sub>5</sub>Fe)<sub>3</sub>O the Fe–Fe distances are substantially longer (10, 33, 34), indicating that these complexes contribute very little or not at all to the Fe speciation in the studied samples. Furthermore, the practically invariant Fe–C and Fe–C–O/C distances suggest that other forms of small polynuclear Fe–NOM complexes are unlikely.

The collective information from the WT analysis and the quantitative EXAFS data fitting leads to the conclusion that Fe speciation in the investigated soils is dominated by two pools of iron: mononuclear Fe(III)-NOM complexes and Fe(III) (hydr)oxides. This is further supported by electron microscope images showing a heterogeneous distribution of Fe with clusters having increased Fe concentration,

especially in Soil-1 (Figure S-5 and S-6). These results are in line with XANES results reported by Prietzel et al. (8) for organic top soils from a forested watershed, and with studies of river-borne material from tropical systems, using electron paramagnetic resonance spectroscopy (35, 36), showing that Fe(III) mainly occurs as Fe bound to organic matter and as Fe oxides. Furthermore, Allard et al. (35) have shown that the amount of Fe bound to organic matter decreases with increasing pH in river water. The concentration of free  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  ions should be negligible at pH values above 4.5, as demonstrated by Weber et al. (37) for Fe in interaction with organic matter.

However, the coexistence of predominately mononuclear Fe–NOM complexes and Fe (hydr)oxides partly contrasts the results of Rose et al. (11), Vilg -Ritter et al. (12), and Gustafsson et al. (10), suggesting the predominance of hydrolyzed polynuclear Fe complexes in riverine NOM and in organic soils, respectively. These discrepancies may be caused by differences in chemical conditions, such as pH, the number of NOM functional groups with high Fe affinity, and total iron concentrations but may also be related to differences in data interpretation/modeling. The unambiguous identification of mononuclear Fe–NOM complexes and the complete or almost complete absence of polynuclear complexes/Fe (hydr)oxides in Soil-3 show that mononuclear species must be considered when analyzing Fe speciation in natural organic matrices. This poses a particular problem when the analysis is based on EXAFS data which provide information on the average coordination environment. Thus, it may prove difficult to distinguish between polynuclear complexes and a mixture between mononuclear complexes and Fe (hydr)oxides. In these cases traditional EXAFS data analysis preferably is complemented by other techniques or methods. One example is the complementary small-angle X-ray scattering (SAXS) measurements by Vilg -Ritter et al. (12) showing the initial predominance of trimeric complexes when Fe(III) is hydrolyzed in the presence of NOM, and another is the WT analysis presented herein.

The results from the EXAFS data fitting can be used to estimate of the distribution of Fe–NOM complexes and Fe (hydr)oxides in the organic soil samples. However, it should be noted that the determined CNs are subjected to a relatively large error ( $\pm 25\%$ ), which makes this estimation quite uncertain. As Soil-3 contains no or very little Fe (hydr)oxide and has a Fe–C coordination number of approximately 2, it is reasonable to assume that the second coordination shell in the Fe–NOM complexes on average includes two C atoms, in agreement with a mononuclear chelate structure. For the Fe (hydr)oxide phase our data suggest a coordination similar to ferrihydrite or goethite i.e. a CN of 2 for Fe at  $\approx 3.0 \text{ \AA}$ . These assumptions together with the EXAFS-derived CNs (Table 2) tentatively suggest that mononuclear Fe–NOM complexes dominate the speciation (55–90%) in the organics soils studied, especially in Soil-3. This is somewhat different to the distribution of Fe reported by Prietzel et al. (8) for organic top soils (Fe–NOM 33–53%, Fe (hydr)oxides 24–54%, and biotite 10–22% at pH 3.2–3.6), which may be due to different chemical conditions in the samples and/or methods used for analyzing the Fe speciation.

**Effects of Conventional Extraction Methods on the Fe Speciation.** In Soil-1 and Soil-2 pyrophosphate extracted 44% and 88% and oxalate 96% and 98%, respectively, of the Fe extracted by citrate-dithionite (Table 1). This indicates that a larger proportion of the Fe is organically complexed in Soil-2 and that all or most of the Fe (hydr)oxides in Soil-1 and Soil-2 are amorphous. However, the WT results (Figure 2) and the results from the quantitative EXAFS fitting (Table 2) for Soil-1 and the pyrophosphate (Soil-1\_Pyr) and oxalate (Soil-1\_Ox) extracted subsamples show that the average Fe speciation in these samples is similar. The WT of Soil-

1\_Pyr even shows a relative weakening of the Fe–Fe contribution which is contrary to what is expected from the presumed extraction specificity. The general results indicate that the distribution between mononuclear Fe–NOM complexes and Fe (hydr)oxide colloids is not dramatically altered by the extraction procedure and accordingly that the extractions are rather unspecific in the removal of different Fe species. Thus, the quantitative differences between the pyrophosphate and oxalate extractions of Soil-1 is not primarily due to the preferential removal of Fe–NOM complexes by pyrophosphate but instead must be caused by other factors.

**Environmental Implications.** Our combined wavelet transform analysis and quantitative refinement of the EXAFS data show that Fe(III) in organic soils can occur as a mixture of mononuclear Fe–NOM complexes and Fe (hydr)oxides at pH values of 4.6–6. Furthermore, our results also indicate that mononuclear Fe–NOM complexes may dominate the speciation in certain organic soils, and that the complexation by organic functional groups is sufficiently strong to play an important role in the hindrance of Fe hydrolysis, even at pH 6.0. This will likely increase the reactivity of Fe on a per atom basis in these soils and will thus have profound effects on soil sorption properties (20, 38). These findings are of importance not only for the understanding of the mobility and availability of Fe in soils but also for the speciation of other elements that interacts with these Fe species, including both nutrients and potentially toxic elements.

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## Supporting Information Available

More details on the EXAFS data collection and analysis, a material and methods section for the electron microscope images, first derivatives of the XANES region (Figure S-1), Fourier transforms and their imaginary parts for the organic soils and reference samples (Figure S-2 and S-3), fits with only C backscattering and with both C and Fe backscattering to  $k^3$ -weighted EXAFS data for the Soil-3 sample (Figure S-4), bond distances in well-defined Fe(III) compounds (Table S-1), and electron microscope images for the Soil-1 and Soil-2 samples (Figure S-5 and S-6). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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