C-1s NEXAFS Spectroscopy Reveals Chemical Fractionation of Humic Acid by Cation-Induced Coagulation

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The influence of cation-induced coagulation on the chemical composition of dissolved and coagulated fractions of humic acid was investigated in batch coagulation experiments for additions of aluminum at pH 4 and 5, iron at pH 4, and calcium and lead at pH 6. The partitioning of organic carbon and metals was determined by analyzing total organic carbon and total metal contents of the dissolved phase. Both the dissolved and the coagulated humic acid fractions were characterized using synchrotron scanning transmission X-ray microscopy (STXM) and C-1s near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Intensities of π* transitions of carboxyl carbon and o* transitions of alkyl, O-alkyl, and carboxyl carbon decreased with increasing metal concentration for the dissolved humic acid fractions. This decrease was accompanied by an increase of the respective intensities in the coagulated fraction as shown for lead. Intensities of aromatic and phenolic carbon were affected to a larger extent only by aluminum and iron additions. The changes observed in the C-1s NEXAFS spectra coincided with an increasing removal of organic carbon from the dissolved phase with increasing total metal concentrations. We conclude that humic acid was chemically fractionated by cation-induced coagulation, which preferentially removed functional groups involved in metal-cation binding from solution.

Introduction

Humic acids are natural polyelectrolytes with a large variety of reactive functional groups, which bind protons and metal cations. Due to their ability to form complexes with metal cations and to bind to mineral surfaces, humic acids can either enhance or reduce metal cation migration in soils by forming dissolved and mineral-bound metal-organic complexes, respectively (1). In addition, cation-induced coagulation, i.e., the mere interaction of humic acids with cations can strongly alter the migration behavior of metal-organic complexes. Defined by the water-solubility in alkaline solutions and insolubility under strong acidic conditions, the stability of humic acid in aqueous phases is governed by the extent of proton and metal cation binding influencing the charge of the organic molecules (2). Consequently, the transport of metal cation-humic acid complexes also depends on the coagulation behavior of humic acids.

Furthermore, the composition of humic acid itself may be affected by sorption and coagulation processes. Humic acids are thought to represent a polydisperse mixture of organic compounds that may widely differ in the physicochemical properties of the individual compounds (3). Any reaction leading to a partitioning of humic acid into two different phases such as, e.g., the aqueous phase and the solid phase during adsorption processes, may also cause a chemical fractionation of the original humic acid pool due to the differences in the reactivity of the individual compounds. For different natural organic matter (NOM) samples, including terrestrial and aquatic humic and fulvic acids, size fractionation phenomena were observed during NOM adsorption to mineral phases (4–6). Concurrently, NOM may be fractionated with respect to its metal cation affinity as shown for fulvic acid binding to kaolinite (4). Differences in the coagulation behavior were reported for size fractions of a peat humic acid (7) indicating that the smaller size fractions exhibited more negative charge and thus a higher stability than the large size fractions. This result implies that, in addition to surface sorption, coagulation of humic substances may lead to a fractionation with respect to its metal cation binding affinity.

Synchrotron-based C-1s near edge X-ray absorption fine structure (NEXAFS) spectromicroscopy offers a novel tool to investigate NOM. The high spatial resolution of about 30 nm facilitates obtaining information on the distribution of carbon on a submicron scale. Concurrently, information on the chemical bonding environment of the carbon atoms in NOM can be obtained. The possibility of investigating dry sample materials as well as aqueous samples makes the technique very attractive for research on environmental samples which are often characterized by a high spatial and chemical heterogeneity of organic compounds (8–10). Due to its technical merits, C-1s NEXAFS spectromicroscopy represents a technique of high potential to study fractionation of humic acids induced by cation binding and sorption processes. Despite all advantages C-1s NEXAFS spectromicroscopy offers today, the quantitative interpretation of the C-1s NEXAFS spectra still remains an unresolved challenge especially for NOM samples. Several discrete peak positions were identified using model substances (11–14). Strong absorbances were observed for C-1s → π* transition of aromatic carbon (π*C=c) and carboxyl carbon (π*C=O), while C–H/π* and Rydberg resonances and C-1s → o* transitions of alkyl C–C, O-alkyl C–O, aromatic C=C, as well as carboxyl and carboxyl C=O bonds appear to be comparably weak with respect to their intensities (15). Substitution of aromatic carbon by F, O, N, Cl, B, and I was shown to result in a distinct peak shift in an order corresponding to the electronegativity of the substituent atom (16). Neighboring phenolic groups as well as neighboring carboxyl groups as were observed to cause peak shifts and peak broadening (16). Due to uncertainties in absolute intensity response of electron transitions, strongly overlapping resonance ranges of electron transitions, effects of π* and π* bond–bond interactions, and bond-dependent positions of ionization potentials (15), an absolute quantification of C-1s NEXAFS spectra has not been achieved for complex mixtures of organic compounds such as humic acids. However, semiquantitative approaches (17–20) may provide valuable information if applied to quantify spectra of materials which are similar to those used for calibration.

Recent studies on humic acid-actinide interactions showed that signals of π*C=O transitions assigned to carboxyl carbon decreased for Aldrich humic acid when saturated with europium(III), thorium(IV), and uranium(VI) (14, 16). However, it remains unclear whether the proposed effect of cation binding to C-1s NEXAFS signals is cation-specific and...
depending on the cation loading. To elucidate this, we studied metal cation–humic acid interactions by C-1s NEXAFS spectroscopy at various pH and metal loading conditions. Following the predominant pH and cation conditions in many natural soils, we chose to study the interactions with iron at pH 4, with aluminum at pH 4 and 5, and with calcium at pH 6. In addition, interactions of humic acid with lead were studied at pH 6. To obtain a comprehensive view on metal cation–humic acid interaction, both the dissolved fractions of the humic acids and the coagulated fractions were investigated.

**Experimental Section**

**Sample Material and Coagulation Experiments.** A well characterized, purified humic acid extracted from a humic Gleyisol in northern Switzerland was used for this study (21). Series of 10 mL batch samples were prepared in glass tubes. All batch samples contained 0.5 g/L humic acid and 0.01 M NaNO₃ (Merck, p.a.). Prior to metal cation additions, the pH values of the humic acid solutions were adjusted to 4.0 (Fe and Al series), 5.0 (Al series), and 6.0 (Pb and Ca series) by addition of HNO₃ and NaOH, respectively. Then, solutions containing iron, aluminum, or calcium nitrates (Merck, p.a.) were added to the humic solutions to cause coagulation of the dissolved humic acid. Total metal concentrations of the batch samples ranged from 0.2 to 0.5 mM for the iron and aluminum series and from 1 to 5 mM for the calcium series. In addition, one sample containing 10 mM calcium without NaNO₃ background and one sample containing 0.7 mM lead with a 0.01 M NaNO₃ background were prepared at pH 6.0. All samples were shaken vigorously for 10 s after metal addition. The pH values of the humic acid solutions were readjusted twice, 1 h and 24 h after metal addition. Coagulated humic acid was allowed to settle for 10 days at room temperature in the dark. The transparent supernatants were filtered through a 0.45 μm nylon membrane filter (OPTIMA, Flow, Wicom) and stored in glass vials in the dark until analysis. Total organic carbon (TOC) and total metal concentrations were measured in subsamples of the supernatants using a TOC analyzer (Shimadzu TOC-5000) and a flame AAS instrument (SpectraAA 220, Varian).

**C-1s NEXAFS Spectroscopy.** C-1s NEXAFS spectra were measured using the Stony Brook Scanning Transmission X-ray Microscope (STXM) at beamline X-1A, National Synchrotron Light Source (NSLS), Upton, NY. The STXM is located inside a helium-purged enclosure at room temperature and atmospheric pressure. Details on the instrument are given by Jacobsen et al. (22). Air-dried specimens of selected supernatant solutions from coagulation experiments were prepared by placing 2 μL droplets onto a X-ray transparent Si₃N₄ window (Silson Ltd., Northampton, UK). At 15 different spots exhibiting an appropriate sample thickness (17), spectra were recorded for each dry film specimen from 280 to 310 eV in steps of 0.1 eV using a dwell time of 120 ms. In addition, five spectra were recorded at spots outside the sample area. The energy-dependent absorbance \( A(E) \) of each specimen was calculated as \( A(E) = -\ln[I(E)/I_0(E)] \), where \( I(E) \) denotes the average of the energy-dependent transmitted intensity measured at the 15 specimen spots and \( I_0(E) \) represents the average of the energy-dependent intensity of the clean Si₃N₄ window. The energy-dependent standard errors of absorbances were less than ±0.1. The absorbance \( A(E) \) was background-corrected by subtracting a linear preedge function fitted to the absorbance between 280 and 283 eV and normalized to the absorbance at 310 eV. As carboxyl and phenolic groups are to represent the major part of metal cation binding groups in humic acids, we also analyzed 1 mM solutions of benzoic acid, phthalic acid, pyrocatechol, and salicylic acid (Fluka, Buchs/Switzerland) adjusted to pH 5.0 by NaOH or HNO₃ additions. For the selected aromatic low molecular weight compounds, the preparation of dry film samples and the analysis of the C-1s NEXAFS data were the same as for the humic samples described above.

In addition, selected solutions containing coagulated humic acid were analyzed by C-1s NEXAFS spectroscopy using a wet cell consisting of two adjacent Si₃N₄ windows. Details on the preparation of wet cell specimens are given by Neuhausler et al. (23). Stacks of images were collected as a function of the incident photon energy \( E \) for selected sample regions. At energies ranging from 280 to 282.5 eV and from 290 to 315 eV, images were recorded in 0.5 eV steps at a dwell time of 3 ms. In the energy range from 282.5 to 290 eV, the energy was varied in 0.1 eV steps using a dwell time of 9 ms. For the analysis of the image stacks of wet cell specimens, the IDL routines, stack, analyze and pdb_gui, written by the research group of Chris Jacobsen (24, 25) were used to derive average intensity spectra \( I(E) \) for the coagulates. A coagulate-free sample area was chosen to extract an average \( I_0 \)-spectrum for each specimen. Background correction and normalization of the absorbance spectra \( A(E) \) were conducted as for the dry film spectra.

**Results and Discussion**

**Effect of Metal Cation Addition on Concentrations of Dissolved Humic Acid.** The addition of the metal cations Fe³⁺, Fe⁷⁺, and Ca²⁺ decreased the concentrations of dissolved humic acid within the chosen concentration range of total metal concentrations as indicated by the DOC measurements (Figure 1A). The DOC concentrations decreased with increasing metal cation concentration for all experimental series investigated, i.e., aluminum at pH 4 and 5, iron at pH 4 and calcium at pH 6. In all experiments, the total humic acid

![FIGURE 1. Effects of iron, aluminum, and calcium additions on concentrations of dissolved humic acid and dissolved metal cations in a 0.01 M NaNO₃ background at various pH values. Total humic acid concentrations amounted to 0.5 g/L, equivalent to 226 mg C/L (TOC). Experimental data are plotted using the following symbols: △ represent the iron series at pH 4, □ represent the aluminum series at pH 4, ■ represent the aluminum series at pH 5, and ○ represent the calcium series at pH 6. (A) Dissolved organic carbon (DOC) shown as percentage of TOC present in solution. (B) Dissolved metal cation concentrations given as percentages of total amounts of metal cations added.](image-url)
concentration was 0.5 g/L, which is equivalent to 226 mg C/L and a total proton-reactive charge of 2.9 mmol c/L (26). For the removal of 90% of TOC from solution, a total metal concentration of 0.4 mM Al was required at pH 4, 0.5 mM Al at pH 5, and 0.5 mM Fe at pH 4. In the case of calcium addition at pH 6, only 84% of TOC was removed at a total calcium concentration of 5 mM. This observation indicates that in all cases, the chosen metal cation addition caused a cation-induced coagulation leading to a decrease of DOC concentrations. Concurrently, the percentage of dissolved metal concentrations was diminished due to metal cation binding to the coagulated humic acid (Figure 1B). The differences in cation-induced coagulation for the investigated series are mainly caused by the pH-dependent binding of proton and metal cations affecting the charge of the humic molecules. The negative charge of humic acid increases with increasing pH (26). On the other hand, the negative charge can be compensated by metal cation binding, which strongly increases with increasing pH and increasing metal cation activity in solution (27). The effect of pH can be seen clearly when comparing the aluminum series for pH 4 and 5 (Figure 1A). Less humic acid was removed at a given total aluminum concentration at pH 5 than at pH 4. The similar amounts of organic carbon removed by iron and aluminum at pH 4 indicate that the humic acid exhibits a similar binding affinity for both metal cations at pH 4. The increased negative charge of humic acid at pH 6 compared to pH 4 and the weaker binding of calcium to humic acid, as compared to iron and aluminum (28), agree well with the observation that much less organic carbon was removed from the solution at a given total metal concentration in the calcium series as compared to the iron and aluminum series. To obtain more detailed information on the effect of cation-induced coagulation on the composition of the dissolved and coagulated humic acid fraction, we recorded C-1s NEXAFS spectra for selected samples of our coagulation batch experiments, which will be shown in the following section.

**C-1s NEXAFS Spectra of Humic Acid and Aromatic Low Molecular Weight Compounds.** The C-1s NEXAFS spectra of the humic acid samples studied are characterized by broad resonance features (Figure 2). Below the ionization potential of carbon (~290 eV, K-edge), three peaks positioned at 285.1, 286.5, and 288.4 eV can be identified. Above the carbon K-edge, the spectrum appears to be rather featureless. The pattern of the humic acid spectra is very similar to spectra of humic and fulvic acids provided by the International Humic Substances Society (17). Compared to the spectra of benzoic acid, phthalic acid, pyrocatechol, and salicylic acid, the preedge resonances of the humic acid coincide fairly well with the C-1s → π* resonance ranges of H and C-substituted aromatic carbon (π* C=C, 285.1 eV), O-substituted aromatic carbon (π* C=O, 286.5 eV), and carbonyl carbon (π* C=O, 288.4 eV) as labeled in Figure 2 with the characters a, b, and c. In addition, C–H*/Rydberg transitions, as well as π* C=O transitions of amide carbon and 2π* transitions of aromatic carbon may contribute to the overall absorbance spectrum in the preedge region. The apparent broad resonance bands in the postedge region are mainly due to overlapping resonances of π* transitions observed for alkyl, O-alkyl, carbonyl and carbonyl, H and C-substituted aromatic, as well as phenolic carbon (15).

**Effect of pH on C-1s NEXAFS Spectra of Humic Acid.** Investigation of pH-effects on C-1s NEXAFS spectra of glycine showed that C-1s NEXAFS spectra are sensitive to the protonation state of carbonyl and amine groups (13). For humic acid, the variation of pH-values from 4.0 to 6.0 significantly changed the C-1s NEXAFS spectrum (Figure 2). Below 288 eV, the intensities were lower at pH 6 than at pH 4. However, at photon energies above 288 eV, stronger absorbances were observed at pH 6 than at pH 4. Similarly as for humic acid, a significant increase of carboxyl carbon intensities (288.4 eV) with increasing pH was also observed for dry film specimen of poly(acrylic acid) solutions (not shown). Calculating the charge of the humic acid using the NICA-Donnan model based on acid–base titration data published previously (26) reveals that the negative charge of the humic acid increases from 0.54 mmol/L to 1.25 mmol/L when increasing the pH-value from 4 to 6. This increase in negative charge is mainly due to the deprotonation of carboxylic-like acidic functional groups. Phenolic-like functional groups may also be affected by the pH-shift from 4 to 6, but to a much lower extent. NICA-Donnan model calculations show that phenolic-like groups are present in the protonated state by 96% at pH 4 and by 91% at pH 6. It is noteworthy that the whole C1-s NEXAFS spectrum was affected by the pH-variation. This result indicates that for the humic acid, not only intensities assigned to π* C=O and σ* C=O transitions of carbonyl carbon were affected by the pH variation, but also intensities of humic moieties which are only slightly or even not at all involved in protonation–deprotonation reactions. Therefore, the metal-free humic acid spectra at the corresponding pH-value have to be used as a reference for the coagulation experiments shown in the following section.

**Effect of Metal Cation Additions on C-1s NEXAFS Spectra of Dissolved Humic Acid.** Addition of aluminum, iron, and calcium nitrates to humic acid solutions resulted in strong and systematic changes in the C-1s NEXAFS spectra of the humic acid remaining in solution (Figure 3). At pH 4, the C-1s NEXAFS intensity of the humic acid significantly decreased within the photon energy range of 283–305 eV when the total aluminum concentration was increased up to 0.25 mM. A further increase of the total aluminum
concentration did not further decrease the C-1s NEXAFS signal, although the dissolved humic acid concentration was further diminished. At pH 4, the addition of aluminum significantly decreased the C-1s NEXAFS intensity of the humic acid from 283 to 305 eV compared to the humic acid spectrum in the absence of aluminum (Figure 3A). The decrease of resonance intensity was even more pronounced at a total aluminum concentration of 0.25 mM. At pH 5, the presence of aluminum affected the intensities below energies of ~288 eV less than at pH 4. Above ~288 eV, increasing total aluminum concentrations evoked at pH 5 similar spectral changes as observed at pH 4 (Figure 3A and B). For iron additions at pH 4 (Figure 3C), spectral changes resembled the effects caused by aluminum at pH 4. The strong reduction of $\pi^*$ resonances (286.5 eV) at 0.40 mM Fe compared to 0.30 mM Fe may additionally result from a beginning formation of solid microstructures with a high affinity for binding of phenolic moieties at 0.40 mM Fe according to model calculations using the generic NICA-Donnan parameters for humic acid (28). Calcium additions also led to a decrease of intensities of the postedge resonances and the peaks at 288.4 eV at pH 6 (Figure 3D). The decrease of intensities caused by the presence of calcium increased with calcium concentrations increasing from 1 to 5 mM. Compared to iron and aluminum additions, calcium additions affected $\pi^*$ resonances (286.5 eV) intensities of phenolic moieties less strongly.

Comparison of the C-1s NEXAFS spectra at highest total metal concentrations investigated (red lines in Figure 3A-D) reveals that all spectra are very similar at energies above ~288 eV regardless of the type of metal added. At photon energies between 282 and 287 eV differences between the metal series can be identified. This observation implies that the interaction of cations with aromatic and phenolic moieties was rather cation-specific. However, all investigated metal cations strongly interacted with carboxyl groups of the humic acid indicated by a strong intensity decrease of the $\pi^*$ transitions at 288.4 eV. Consequently, intensities of $\sigma^*$ transitions are typically found at energies ranging from 296 to 297 eV and from 301 to 304 eV, respectively (29, 30), the decrease of resonance band intensities above ~294 eV is in agreement with the decrease of the $\pi^*$ intensity. For organo-metallic compounds containing 3d transition metals such as Mn, Fe, Co, and Ni, a pronounced decrease of C-1s $\rightarrow$ $\pi^*$ transitions of alkyl carbon, and $\sigma^*$ transitions of O-alkyl and carboxyl carbon are labeled with the characters a, b, c, d, and e, respectively. (A) effect of aluminum addition at pH 4, (B) effect of aluminum addition at pH 5, (C) effect of iron addition at pH 4, and (D) effect of calcium addition at pH 6.

**FIGURE 3.** Effect of metal cation addition on C-1s NEXAFS spectra of dissolved humic acid. All spectra were collected from dry film samples and represent average spectra of 15 single scans. A 0.01 M NaNO$_3$ background electrolyte was used for all experiments. Prior to metal cation additions, all samples contained 0.5 g/L dissolved humic acid, equivalent to 100% of TOC. The amounts of dissolved organic carbon after metal addition are given as percentages of TOC. Metal cation concentrations refer to total metal concentrations added as nitrate salts. Photon energy ranges exhibiting spectral features of $\sigma^*$ transitions of H- and C-substituted aromatic carbon, $\pi^*$ transitions of phenolic carbon, $\pi^*$ transitions of carboxyl carbon, $\sigma^*$ transitions of alkyl carbon, and $\sigma^*$ transitions of O-alkyl and carboxyl carbon are labeled with the characters a, b, c, d, and e, respectively. (A) effect of aluminum addition at pH 4, (B) effect of aluminum addition at pH 5, (C) effect of iron addition at pH 4, and (D) effect of calcium addition at pH 6.
acid concentrations as indicated by the percentage of TOC present in solution. As humic acid represents a mixture of a multitude of organic compounds exhibiting different metal cation binding affinities, a fractionation of humic acid in chemically different dissolved and coagulated compounds is likely to occur when metal cations are added at levels causing humic acid coagulation. Consequently, the C-1s NEXAFS spectra reflect the effect of a cation-induced coagulation of humic acid. This implies that, in all series investigated, carboxyl and alkyl C was preferentially removed from the solution by coagulation. In contrast to calcium additions at pH 6, aluminum or iron additions significantly led to a preferential removal of aromatic moieties from the dissolved phase at pH 4. This finding is in agreement with model calculations based on NICA-Donnan parameters published by Milne et al. (28) showing that, under the experimental conditions, calcium-binding to humic acid was mainly due to interactions with carboxylic-like functional groups, while in the case of aluminum and iron, significant amounts of metal cations were also bound to phenolic-like functional groups.

C-1s NEXAFS Spectra of Coagulated Huminic Acid. In addition to the spectra of the dissolved humic acid fractions, C-1s NEXAFS spectra were also collected for selected humic acid coagulates from wet cell specimens. The analysis of wet cell specimens was limited to coagulated humic acid samples in which most of the total carbon (>90%) was fixed in the coagulates with corresponding maximum background absorbances below 0.2 as determined from dry film specimens of a microliter droplet of the filtered supernatant solutions. To analyze the corresponding dissolved fraction, we successively dried up to three one-microliter droplets of the filtered supernatants onto a Si$_3$N$_4$ window to increase the total amount of carbon in the dry film. Because the successive drying greatly enhances the risk of Si$_3$N$_4$ window breakage and lower quality of data due to the consequent accumulation of background salts, we were able to collect high-quality spectra of corresponding dissolved and coagulated humic acid fractions for one sample only.

In the following, we show the results for humic acid coagulated by calcium and lead at pH 6 (Figure 4). The spectrum of the Ca-coagulate exhibits strong intensities of $\pi^*$ transitions for carboxyl carbon (288.4 eV) and $\sigma^*$ transitions in the postedge region. The Ca-coagulate spectrum is fairly similar to the spectrum of dissolved humic acid in the absence of calcium (Figure 4) and clearly differs from the spectra of dissolved humic acid in the presence of 3 and 5 mM total calcium (Figure 3D) in the energy region above ~280 eV. The similarity of the Ca-coagulate and the dissolved humic acid in the absence of calcium agrees well with the fact that the Ca-coagulate contained 91% of TOC. The spectral similarity also indicates that the C-1s NEXAFS spectrum of humic acid is virtually unaffected by calcium bound to carboxyl functional groups of the humic acid. This finding confirms that the spectra shown for the dissolved humic acid samples in the presence of calcium (Figure 3D) reflect the chemical fractionation of humic acid caused by the cation-induced coagulation.

As a second example, the effect of lead addition on C-1s NEXAFS spectra of humic acid is shown for pH 6. Here, C-1s NEXAFS spectra were collected for the coagulated and the dissolved fraction of the humic acid in the presence of 0.7 mM lead in a 0.01 M NaNO$_3$ background (Figure 4). Above 288 eV, the coagulated lead-humate exhibited stronger absorption intensities than the dissolved humic acid fraction in the presence of lead. The intensities of the lead-coagulates even exceeded the intensities of dissolved humic acid in the absence of lead above 288 eV. This result clearly indicates that the lead-induced coagulation of humic acid led to a preferential removal of carboxyl and alkyl carbon from solution. Our results further demonstrate that the fractionation effect of lead and calcium additions was fairly similar. However, more calcium had to be added to cause similar effects as observed for lead, a fact that reflects the higher affinity of humic acids for lead binding compared to calcium binding (28).

Previous C-1s NEXAFS studies on Aldrich humic acid coagulated by europium(III), thorium(IV), and uranium(VI) revealed that absorption intensities of $\pi^*$ transitions were decreased compared to the C-1s NEXAFS spectrum of Aldrich humic in the absence of these metals (14, 16). A similar effect was reported for the polyacrylic acid in the presence of europium (14) providing evidence for an electron interaction between europium and C=O bonds of carboxyl carbon. Contrary to these results, increased $\pi^*$ transitions of phenolic carbon, $\sigma^*$ transitions of carboxyl carbon, $\sigma^*$ transitions of alkyl carbon, and $\sigma^*$ transitions of O-alkyl and carboxyl carbon were labeled with the characters a, b, c, d, and e, respectively.

![FIGURE 4. C-1s NEXAFS spectra of coagulated calcium-humates (red line), coagulated lead-humates (blue line), and dissolved lead-humates (green line) at pH 6.0. The total humic acid concentration was 0.5 g/L. Total calcium and lead concentrations were 10 mM and 0.7 mM, respectively. Lead-humate samples contained a 0.01 M NaNO$_3$ background electrolyte. The calcium-coagulates contained 91% of TOC and 38% of total calcium. The lead-coagulates contained 92% of TOC and 96% of total lead. The coagulated and dissolved lead-humates originated from the same batch experiment. For comparison, the spectrum of dissolved humic acid at pH 6 in a 0.01 M NaNO$_3$ background is plotted with a black solid line.](image_url)
is not hampered by the presence of major soil cations such as calcium and contaminants such as lead.

Acknowledgments

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