Extraction and characterization of ternary complexes between natural organic matter, cations, and oxyanions from a natural soil

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HIGHLIGHTS

- Humic acid from a natural soil and its ternary complexes were characterized by SEC-ICP-MS.
- Intact ternary complexes were extracted directly from the soil and characterized.
- Complexes in the soil extract were similar to those of the purified humic acid.
- The amount of As observed bound in these complexes is relatively small but merits further study.

GRAPHICAL ABSTRACT
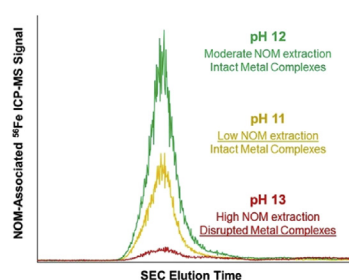
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ABSTRACT

Natural organic matter (NOM) can have a significant influence on the mobility and fate of inorganic oxyanions, such as arsenic and selenium, in the environment. There is evidence to suggest that interactions between NOM and these oxyanions are facilitated by bridging cations (primarily Fe^{3+}) through the formation of ternary complexes. Building on previous work characterizing ternary complexes formed in the laboratory using purified NOM, this study describes the extraction and characterization of intact ternary complexes directly from a soil matrix. The complexes are stable to the basic extraction conditions (pH 12) and do not appear to change when the pH of the extract is adjusted back to neutral. The results suggest that ternary complexes between NOM, cations, and inorganic oxyanions exist in natural soils and could play a role in the speciation of inorganic oxyanions in environmental matrices.

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1. Introduction

Heavy metals and other inorganic species contamination pose a problem due to their high toxicity and their long residence time in soil (Wuana and Okieimen, 2011). While these species occur naturally and exist in soils at low levels, they can accumulate due to anthropogenic activities including: industrialization and mining; application of fertilizers, pesticides, sewage sludge, or manures; petrochemical or high metal waste spills; or atmospheric deposition. Because the fate and transport of metals can be influenced by changes in their speciation (e.g. oxidation state or coordination environment), understanding their chemistry in the environment is critical to remediation and risk assessment efforts (Violante et al., 2010). This behavior is governed by many interdependent factors such as redox reactions, biotransformation, solubility, and sorption or complexation of metals to other components of the soil matrix.

Table 1
Characterization of soils used in this study.

Sample	Metals Content by ICP-AES and ICP-MS (mg/kg)							TOC (mg/kg)
	Na	Al	Cr	Fe	Cu	As	Se	
Site 1, Sample 1	3870	24,900	15.4	43,200	33.3	11.3	0.60	9200
Site 1, Sample 2	4210	24,600	15.5	42,500	32.6	11.2	0.67	9300
Site 2, Sample 1	4630	25,000	15.3	43,200	33.7	10.3	0.59	8700
Site 2, Sample 2	3840	24,100	15.3	40,700	34.4	10.3	0.55	8500
Site 3, Sample 1	4310	25,700	15.3	43,600	33.7	12	0.59	7700
Site 3, Sample 2	4060	24,300	15.5	41,800	33.8	10.2	0.56	7600

Complexation with NOM, such as humic acids (HA), is one factor that can affect the behavior of metal ions by acting as carriers in soil solution, reducing their bioavailability, or changing their solubility (Aiken et al., 2011). Given the large number of electron donor groups in NOM, it can act as a complexing agent and bind cationic metal species (Chen et al., 2002; Violante et al., 2010), an interaction that has been studied in great detail (Donisa et al., 2003; Fujii et al., 2014; Pandey et al., 2000; Weng et al., 2002). In addition to this binary interaction, the bound cations (e.g. Fe^{III} and Cr^{III}) have been proposed to have the ability to act as a bridge to form ternary complexes with NOM and anionic species (Liu et al., 2011; Mikutta and Kretzschmar, 2011; Sharma et al., 2010).

Arsenic, which is classified and monitored as one of eight heavy metals under the Resource Conservation and Recovery Act (RCRA), has been found in the literature to form ternary complexes with purified humic acids using Fe^{III} as a bridging cation (Buschmann et al., 2006; Liu et al., 2011; Ritter et al., 2006). In previous work by the authors (Martin et al., 2017), ternary complexes between a purified humic acid, cations (Fe^{III} and Cr^{III}), and oxyanionic metals (As and Se) were characterized by size exclusion chromatography interfaced to ICP-MS; this study aimed to build on that work by isolating such complexes directly from a soil matrix. An extraction procedure was developed to maximize extraction efficiency while not disrupting the metal coordination interactions, and the intact ternary complexes were then characterized using size-exclusion chromatography interfaced to ICP-MS. The characteristics of these complexes are compared to those made by the HA fraction purified from the same soils to ensure that the observed signals are in fact NOM-metal complexes rather than artifacts of the extraction procedure.

2. Materials and methods

2.1. Soil samples

Soil samples were collected from Eagle River Flats, AK (Lawson et al., 1995), and were chosen due to the presence of significant amounts of all the species necessary for ternary complexes to form. In addition to substantial organic content in the soil (determined by EPA Method 9060), which is consistent with the site being a salt marsh, elemental analysis showed high levels of Fe and As (selected analytes shown in Table 1). Three separate sites were sampled, with duplicate samples taken at each location to increase the number of subsamples available for investigation. The pH of the soil samples was between 6.0 and 6.9.

2.2. Extraction and purification of humic acid

The NOM fractions of the soil were extracted and purified using slight modifications of previously reported procedures (Malcolm, 1976; Swift, 1996) in order to provide an analytical comparison for the extracts. A slurry of 10 g of dried soil in 100 mL of 0.1 M NaOH was shaken overnight, then the slurry was centrifuged

($3000 \times g$, 15 min), decanted, and filtered (0.45 μm). The pH of the filtrate was adjusted to ~2.5 using 5 M HCl and refiltered. The solid from the filter was combined with the centrifuged pellet and the extraction procedure repeated, but with a 20% (w/v) slurry. The two filtrates were combined and acidified (pH 1) to precipitate the HA fraction. Following centrifugation ($3000 \times g$, 15 min), the resulting supernatant (containing the fulvic acid fraction) was decanted, while the HA pellet was redissolved in a minimal amount of 0.1 M NaOH. To remove any residual fulvic acids, the dissolved HA was precipitated again with a second addition of HCl and centrifuged ($3000 \times g$, 15 min). The final HA pellet was dissolved in a minimal amount of 0.1 M NaOH for use in subsequent experiments.

2.3. Extraction of ternary complexes

In order to optimize the extraction of humic substances in a manner that would preserve the humic-metal-anion ternary complexes, modifications to the extraction procedure described above were explored. Samples of soil (1 g) were slurried in 5 mL of DI water. The samples were then adjusted to the desired pH (11, 12 or 13) with 1 M NaOH before dilution to a final volume of 10 mL. Samples were then incubated (4 h) either at room temperature with constant shaking or at 65 °C with intermittent shaking. The samples were centrifuged ($10,400 \times g$, 45 min) to remove the debris and the supernatant was analyzed without further purification by SEC-ICP-MS as described below.

2.4. Size exclusion chromatography — ICP-MS

Separation of a 50 μL injection was performed using an Agilent 1100 High Performance Liquid Chromatography (HPLC) system with a Shodex OH pak SB803 HQ column (analytical range 1–100 kDa; exclusion limit 100 kDa). The column effluent was fed

Table 2
Instrumentation and operating conditions for the SEC-ICP-MS system.

HPLC	
Agilent 1100 with quaternary pump	
Analytical size exclusion column	Shodex OH pak SB830 HQ 300 × 8 mm
Autosampler and column temperatures	10 °C and 25 °C, respectively
Mobile phase	10 mM sodium acetate, 1% methanol, pH 7.0
Mobile phase flow rate	0.6 mL min⁻¹
Typical injection volume	50 μL
UV wavelength monitored for organic moieties	254 nm
Total chromatogram time	Approximately 25 min
ICP-MS	
Perkin Elmer Elan DRC II	
MiraMist nebulizer argon flow rate	0.9 L min⁻¹
Plasma Power	1300 W
Typical dwell time (per isotope)	200 ms
Masses monitored in reaction cell mode	^{27}Al, ^{52}Cr, ^{56}Fe, ^{78}Se, ^{91}AsO
Reaction cell gas and flow rate	Ultrapure oxygen, 0.5 mL min⁻¹
Rp_q reaction cell parameter	0.75 for all except 0.55 for ^{91}AsO