



Exploring the ability of cations to facilitate binding between inorganic oxyanions and humic acid



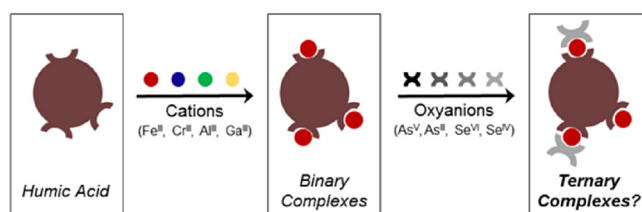
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HIGHLIGHTS

- Formation of ternary complexes between humic acid, metal cations (Fe, Cr, Al, Ga), and metal oxyanions (As, Se) was examined.
- Size exclusion chromatography coupled to ICP-MS was used to observe metals complexed with humic acid.
- Fe^{III} and Cr^{III} facilitated ternary complex formation with As^V and Se^{IV} while Al^{III} and Ga^{III} did not form any such complexes.
- Only Fe^{III} formed ternary complexes with humic acid and As^{III}.
- Transition metal character appears to be crucial to the formation of ternary complexes, but other factors are also important.

GRAPHICAL ABSTRACT



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ABSTRACT

The mobility and fate of inorganic oxyanions in the environment can be greatly influenced by interactions with natural organic matter (NOM). There is increasing evidence that this interaction between two anionic species is facilitated by cationic bridges, but detailed mechanistic studies into this system are challenging due to the heterogeneous nature of NOM. This work examines the ability of cations (Fe^{III}, Cr^{III}, Al^{III}, or Ga^{III}) to form ternary complexes with Suwannee River humic acid (SRHA) and the oxyanions of As (As^{III} and As^V) and Se (Se^{IV} and Se^{VI}). Complexes were characterized by separating SRHA from unbound species using size exclusion chromatography coupled to ICP-MS to determine its metal content. Unlike Cr^{III} and Fe^{III}, the post-transition metal ions Al^{III} and Ga^{III} proved ineffective at forming ternary complexes with any of the oxyanions, although minor complexation was observed with Ga^{III}, suggesting that electrostatic interactions are not the primary driving force behind the stabilization of these ternary complexes. The results also show differences in the behavior of Fe^{III} and Cr^{III} that may indicate that the two cations stabilize the ternary complexes by different mechanisms.

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1. Introduction

Inorganic contamination is of great concern due to both the high toxicity of this class of materials as well as their environmental persistence (Wuana and Okieimen, 2011). Inorganic contamination

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can arise from a variety of anthropogenic sources including mining, farming, and industrial processes and can pose a significant threat to human health and the environment. Accurate predictions of the fate and transport of inorganic species in the environment are critical to both remediation and risk assessment; the behavior of inorganic ions in the environment, however, is dependent on a number of interdependent processes including dissolution/precipitation, oxidation/reduction, biotransformation, and sorption to components of the environmental matrix that can be difficult to model (Violante et al., 2010).

Complexation of inorganic ions by natural organic matter (NOM) is one factor that can have a significant impact on their speciation and transport in soil and water systems. Since NOM contains a large number of electron donor groups (e.g. CO₂H, OH, NH₂) (Chen et al., 2002), it can readily bind cationic metal species and these interactions have been relatively well-studied (Marx and Heumann, 1999; Tipping et al., 2002; Hagvall et al., 2014; Piana and Zahir, 2000; Pandey et al., 2000; Weng et al., 2002; Gustafsson et al., 2014; Sutheimer and Cabaniss, 1997). Despite being an anionic species itself, NOM has also been observed to bind inorganic oxyanions, such as those of arsenic (As^V as AsO₄³⁻ and As^{III} as AsO₃³⁻) (Buschmann et al., 2006; Anwar et al., 2003; Liu et al., 2011; Ritter et al., 2006) and selenium (Se^{VI} as SeO₄²⁻ and Se^{IV} as SeO₃²⁻) (Kamei-Ishikawa et al., 2008; Gustafsson and Johnsson, 1994; Bruggeman et al., 2007; Kamei-Ishikawa et al., 2007; Johnsson and Gustafsson, 1994). Recently, evidence has been accumulating that the interactions between the two anionic species are mediated by bridging cations, particularly Fe^{III} (Sharma et al., 2010; Hoffmann et al., 2013; Mikutta and Kretzschmar, 2011; Sundman et al., 2014). This binding mechanism is not limited to inorganic oxyanions; similar ternary complexes have been shown to form between NOM and organic tetracyclines (MacKay and Canterbury, 2005).

The objective of this study was to gain insight into the coordination chemistry that governs the formation of ternary complexes between NOM, metal cations, and oxyanions. The ability of trivalent cations to facilitate the formation of ternary complexes between Suwannee River humic acid (SRHA) and the oxyanions of As and Se was determined by using size exclusion chromatography to separate the NOM from ions free in solution interfaced to ICP-MS for element-specific analysis. The ability of SRHA loaded with different metals (Fe^{III}, Cr^{III}, Al^{III}, and Ga^{III}, which carry a similar charge but vary in their chemical properties) to bind inorganic oxyanions can provide insight into how these cations facilitate the formation of ternary complexes between NOM and oxyanions; this information can provide a valuable complement to direct spectroscopic methods to more accurately describe the binding mechanisms governing these systems.

2. Materials and methods

2.1. Materials

Chemicals (reagent grade or higher purity) were obtained from commercial sources and used without further purification. Suwannee River humic acid (1.04% ash content; a more complete description of the material can be found in the Supplementary Information) was obtained from the International Humic Substances Society and used without further purification. All aqueous solutions were prepared using deionized (18.2 MΩ cm) water.

2.2. Sample preparation

Stock solutions of humic acid (1 g/L) were prepared in HPLC mobile phase while those for metal salts (100 mg/L) were prepared

in water. The salts used for this study were FeCl₃, Cr(NO₃)₃, AlK(SO₄)₂, Ga(NO₃)₃, Na₂HAsO₄, NaAsO₂, Na₂SeO₄, and Na₂SeO₃. Samples (1 mL) were prepared by the addition of metal stock solutions into mobile phase containing 25 mg/L humic acid and allowed to incubate overnight. Samples were centrifuged (15 min at 10,000 RPM) prior to analysis to remove any precipitated species. Although precipitate was visible in the Fe^{III} and Al^{III} trials, analysis of the total organic carbon in the supernatant indicated that the concentration of SRHA had not decreased significantly (<5%); separate analysis showed that roughly 50% of the Fe^{III} and all of the other metals remained in solution following the incubation period. The final nominal cation concentrations, which correspond to roughly 0.3 equivalents relative to the carboxylic acid content of the SRHA, were 1 mg/L for Fe^{III}, Cr^{III}, and Ga^{III} and 0.5 mg/L for Al^{III}. The final oxyanion concentrations were 0.25 mg/L for As^V and 1 mg/L for As^{III}, Se^{VI}, and Se^{IV}. No significant differences were observed in the data when the SRHA was incubated with cations to allow formation of binary complexes prior to the addition of oxyanions.

2.3. Size exclusion chromatography

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) running a mobile phase of 10 mM sodium acetate (pH 7.0, adjusted with HNO₃) with 1% methanol and a flow rate of 0.75 mL/min. Polystyrenesulfonate standards were used to correlate elution time and molecular weight (Fig. S1). Real-time metals detection of the eluent was obtained by interfacing the HPLC system with a Perkin Elmer Elan DRC II ICP-MS using a MiraMist pneumatic nebulizer. Since background signal was not a concern, the ICP-MS was operated in standard mode with the plasma operated at 1300 W and a nebulizer flow rate of 0.9 mL/min. Data were background-subtracted using Origin software.

3. Results and discussion

3.1. Binary complex formation

Although the complexes between SRHA and the metal cations used in this study have been previously described in the literature (Marx and Heumann, 1999; Tipping et al., 2002; Hagvall et al., 2014; Piana and Zahir, 2000; Pandey et al., 2000; Weng et al., 2002; Gustafsson et al., 2014; Sutheimer and Cabaniss, 1997), initial experiments were performed to verify their formation under the current conditions. SRHA was incubated overnight with increasing concentrations of Fe^{III}, Cr^{III}, Al^{III}, and Ga^{III} and centrifuged prior to analysis to remove any precipitated species. Size exclusion chromatography was used to separate the SRHA from free metal ions in solution and the metal content of the eluent monitored by ICP-MS. Metal ions that coelute with the SRHA (as indicated by its UV absorbance) are assumed to be bound by it; control experiments were performed in the absence of SRHA to verify no colloidal species that may elute at a time similar to that of SRHA were formed. It should be noted that the Fe content of the as-received SRHA was found to be roughly 50 nmol/mg (as determined by direct analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy) and SEC-ICP-MS analysis shows that this Fe is complexed with the SRHA (Fig. S2). When the SRHA is incubated with increasing concentrations of the cations, its secondary structure begins to change and, if the cation concentration is sufficiently high, it precipitates from solution (Fig. S3); all subsequent experiments were performed at concentrations that maximized the cation loading but did not result in significant changes to the SRHA

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