MOBILITY, GEOCHEMISTRY, AND SPECIATION OF TUNGSTEN

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ABSTRACT

Tungsten metal is used in many industrial, military, and consumer applications, and interest in its biogeochemistry is increasing partially due to its potential mobility and biological effects. Recent studies have investigated the geochemistry of tungsten from the laboratory to field scale, to determine its mobility and toxicity. Tungsten exists in most environmental matrices as the soluble and mobile tungstate anion, although polymerization to form poly- and heteropoly- tungstates has been shown to occur. The current study investigates tungsten speciation in soil using size exclusion chromatography (SEC) interfaced to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to separate and quantify monomeric and polymeric tungsten species. Direct infusion Electrospray Ionization Mass Spectrometry (ESI-MS) is also used to identify the specific polymeric species present in the soil. Finally, solid phase speciation has been conducted using XANES and XAFS spectroscopy utilizing specialized synchrotron techniques. Poly- and heteropolytungstate species have been identified in environmental matrices using these techniques, and the variable speciation observed directly affects biogeochemical processes, such as mobility, sorption, and toxicity.

1. INTRODUCTION

Recently, interest in tungsten geochemistry and occurrence in groundwater has increased. Sources of tungsten to the environment include natural deposits of ore and anthropogenic use of tungsten in industrial (e.g. tungsten carbide tools), civilian recreational (e.g. lead shotshell replacement), and military (e.g. kinetic penetrators and small arms ammunition) activities (Seiler, Stollenwerk, and Garbarino, 2005; Koutsospyros, et al., 2006; Strigul, et al., 2005). The potential impact to human health has made the Centers for Disease Control and Prevention (CDC) investigate the link of tungsten to human health in impacted areas, although no direct link to tungsten exposure has yet been shown (U.S. CDC, 2003; Seiler, Stollenwerk, and Garbarino, 2005; Sheppard et al., 2006).

Other anthropogenic activities, such as agriculture and mining, can increase the concentration of tungsten in soils through direct application or atmospheric deposition onto soil (Senesi et al., 1999; Pyatt and Pyatt, 2004; Sheppard et al., 2007). Tungsten uptake by agricultural crops is of concern because of the potential for tungsten getting into the food supply. Tungsten concentrations have been demonstrated to be highest (approximately 1.5 mg/kg) in phosphate fertilizers (Senesi et al., 1999). As a result, tungsten has been detected in fertilized agriculture soils in Europe, USA, and New Zealand at concentrations ranging from 0.5-83, 0-2, and 1.9-21.4 mg/kg, respectively (Quin and Brooks, 1972; Fu and Tabatabai, 1988; Senesi et al., 1999).

Zero valent tungsten is not found in nature, however oxyanion species of tungsten are found in a variety of minerals, which can dissolve to yield the tungstate in most common environmental matrices (Seiler, Stollenwerk, and Garbarino, 2005; Koutsospyros, et al., 2006; Strigul, et al., 2005). Tungstate is thermodynamically stable under most environmental relevant conditions (Seiler, et al., 2005; Strigul, et al., 2005; Koutsospyros, et al., 2006), although tungsten chemistry is not limited to the soluble monomeric species, since polymerization with other common oxyanions (e.g. molybdate, phosphate, and silicate), can yield a variety of ill-defined poly-species with variable

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biogeochemical properties (Feigl, 1958; Seiler, et al., 2005; Koutsospyros, et al., 2006).

Speciation of tungsten is important in toxicological and geochemical studies. Additionally, the ability to simultaneously determine concomitant analytes that may play a role in tungsten chemistry is crucial to forming a complete understanding of tungsten interactions in the environment, such as the polymerization with phosphate, which may affect sorption and mobility in soils as well as biological uptake of tungsten species. Tungstate may polymerize with phosphate *in vivo*, disrupting biological processes dependent on phosphates, such as energy production and cell signaling. Toxicological effects on sunflower growth have been shown previously, at soil concentrations of 2600 mg/kg (Johnson et al., 2008).

In recent years, High Performance Liquid Chromatography (HPLC) coupled to element specific detectors, such as Inductively Coupled Plasma Mass Spectrometry (ICP–MS), has proven valuable as a method for determining elemental speciation at μg/L and sub-μg/L levels in environmental samples (Bednar et al., 2004, 2008; Guerin et al., 1997; Sarzanini and Mentasti, 1997). Methods involving other mass spectrometric detection techniques have also been employed, but have not been used as extensively as ICP–MS. However, due to the polymeric nature of these tungsten compounds, and the relatively low resolution of Size Exclusion Chromatography (SEC), the present work also utilized Electrospray Ionization Mass Spectrometry (ESI–MS) for confirmation and identification of polymeric tungstate species.

The methods have been used to investigate tungsten speciation in a variety of soil samples. Specifically, deionized water leaches of tungsten-containing soils and lysimeter samples collected in the field. The results indicate that polymeric species predominate in many soil extract samples, and phosphotungstates represent a significant fraction in some matrices. Additionally, a variety of polymeric species are observed, indicating that a distribution of species is formed in such systems.

2. EXPERIMENTAL

2.1 Reagents

All chemicals used were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.3 MΩ · cm. Sodium carbonate, sodium polytungstate, and sodium tungstate dihydrate was purchased from Sigma Aldrich (St. Louis, MO) and Alfa Aesar (Ward Hill, MA). Single element and mixed analyte standards were purchased from SPEX CertiPrep (Metuchen, NJ) and PlasmaCal (Champlain, NY).

2.2 Sample Collection and Preparation

All liquid samples were processed through a 0.45-μm pore-size syringe filter to obtain classically defined 'dissolved' constituents. Samples for dissolved tungsten analysis were diluted in 1% nitric acid and samples for speciation were diluted in deionized water, as needed.

A tungsten-containing soil was created by adding metallic tungsten (<1 μm particles) to a Grenada Loring soil, mixing, and allowing it to age for over one year at ambient outside conditions. The geochemistry of this soil and its use in other experiments has been described previously (Inouye et al., 2006; Bednar et al., 2008). Additionally, soil samples and lysimeter water samples were collected from military firing ranges where tungsten ammunition had been used previously (Clausen et al., 2007).

2.3 Instrumentation

Dissolved tungsten concentrations were analyzed directly using nebulization Inductively Coupled Plasma Atomic Emission Spectroscopy or Mass Spectrometry (ICP–AES or ICP–MS) as appropriate for the concentration ranges observed (Following modifications of EPA Methods 6010B and 6020, US EPA, 1996), using a Perkin Elmer (Wellesley, MA) Optima 5300DV or Elan DRC II, respectively. Speciation samples were analyzed using an Agilent (Palo Alto, CA) 1100 HPLC interfaced to the Perkin Elmer Elan DRC II ICP–MS with a MiraMist pneumatic nebulizer. Details of the HPLC, chromatographic conditions, sample introduction system, and ICP–MS are listed in Table 1. Retention time and chromatographic peak width determined the ICP–MS dwell time and number of readings per replicate and were selected so that data were collected for the entire length of the chromatogram.

The HPLC analytical column, mobile-phase composition, flow rate, and typical injection volume are also listed in Table 1. Chromatographic separation of tungstate and polytungstates was attained isocratically with a 1-mM sodium carbonate mobile phase at a flow rate of 1.0 mL/min. A Dionex (Sunnyvale, CA) AMMS-III conductivity suppressor was used to remove sodium from the column effluent prior to introduction into the ICP–MS to prevent salt buildup on the interface cones. The suppressor used 18 mM sulfuric acid pumped at a flow rate of approximately 1.4 mL/min. The 100 mM sodium carbonate mobile phase concentrate was prepared by dissolving 10.6 g of sodium carbonate pellets into 1 L of deionized water. The molarity of the carbonate mobile phase was adjusted on- line with deionized water by using the proportioning valves of the HPLC.

Table 1: Instrumental Operating Conditions for the HPLC-ICP-MS System.

HPLC	
Agilent 1100 system with quaternary pump	
SEC column	Shodex KW-803 300 x 8 mm
Autosampler and Column temperatures	10 °C and 25 °C, respectively
Elution program and mobile phase	Isocratic, 1 mM sodium carbonate
Mobile phase flow rate	1.0 mL/min
Dionex AMMS-III Suppressor Regenerant and flow rate	18 mM sulfuric acid at 1.4 mL/min
Typical injection volume	25 µL
Total chromatogram time	10 min
ICP–MS Instrument	
PE Sciex Elan DRC–II ICP–MS	
MiraMist nebulizer argon flow rate	0.85 L/min
Plasma Power	1,200 W
Typical Tungsten dwell time	300 ms
Typical Phosphorus dwell time	500 ms
Masses monitored	31 & 182 m/z
ESI–MS Instrument	
Bruker Esquire 6000 ESI–MS	
Carrier Nitrogen flow rate	9 L/min
Capillary Voltage	3500 V
Capillary Temperature	623 K
Skimmer Voltage	-80 V
Masses monitored	100–2000 m/z

2.4 Calibration

Graphical Analysis™ software (Vernier Software & Technology, Beaverton, OR) was used to integrate the chromatographic peaks generated by the ICP–MS. Linear regression analysis established the response function from the reagent blank and the series of at least three standard solutions (range 2 to 100 µg/L) with typical correlation coefficients (R^2) greater than 0.999. The linear dynamic range extends to at least 1,000 µg/L when using a 25 µL sample injection and pulse-counting detection mode on the ICP–MS (~ 4 orders of magnitude). Method detection limits for the SEC–ICP–MS were less than 1 µg/L. Because the ESI–MS was only used for species identification, only single concentration species standards were analyzed. However, ion intensities for standards ranging from 50 to 5000 µg/L tungsten (as tungstate or polytungstate) also gave linear relationships.

2.5 Solid Phase Speciation Using XAFS

XAFS spectra for solid phase speciation were obtained at the DND-CAT beamline, Advanced Photon Source (APS), Argonne National Laboratory, Chicago, IL. Air-dried soils were passed through 75 mm sieve, spread evenly between two pieces of clear tape, and placed in the beam path at a 45° angle. The sample was scanned along the absorption energy of the tungsten LIII band (10,207 eV) and data collected in fluorescence mode. Multiple sample scans were aligned, merged, and analyzed by statistical linear combination fits of the derivative normalized spectra using a set of XAFS spectra from standards, also collected at APS.

3. RESULTS AND DISCUSSION

3.1 SEC-ICP-MS Method

Typical SEC–ICP–MS chromatograms for reagent water containing 5 µg/L of tungsten as tungstate, 3 µg/L tungsten as polytungstate, 100 µg/L phosphorus as phosphate, and 15 µg/L phosphorus as tripolyphosphate are shown in figure 1. Detection of analytes by ICP–MS can be influenced by molecular interferences from isobaric oxides and isotopes, however, the tungsten isotope 182 used for this work is generally free of interferences (only minor polyatomics from rare earth element oxides are observed). Because phosphorus is monoisotopic (31 AMU), there are no alternative isotopes, and therefore a slightly elevated background is always observed due to polyatomic ions formed in the plasma, such as $^{15}N^{16}O$ and $^{14}N^{17}O$.

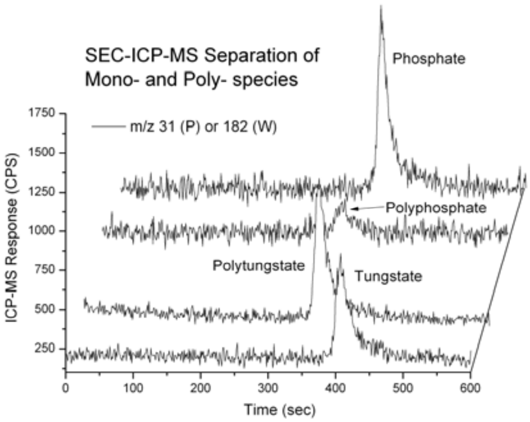

Figure 1. A typical SEC–ICP–MS chromatogram of monomeric and polymeric forms of tungsten and phosphorus showing chromatographic separation of monomeric and polymeric species.

3.2 ESI-MS Analysis of Tungstate Species

ESI–MS mass spectra of tungstate and polytungstate standards are shown in figures 2A and 2B. The tungstate standard in figure 2A clearly shows the tungsten natural abundance isotope ratio (tungsten isotopes of 180, 182, 183, 184, and 186 AMU yield tungstate ions at 245, 247, 248, 249, and 251 m/z, respectively) with good agreement compared to the theoretical isotope ratio values (figure 2A). The polymeric species shown in figure 2B indicate that the commercially available standards have multiple forms that are collectively referred to as polytungstate, i.e. the standards are polydisperse.

3.3 Speciation in Spiked Soils

Deionized water extractions of the Grenada Loring soil produced dissolved tungsten concentrations in excess of 125 mg/L, as previously reported (Bednar et al., 2007). These solutions were then subjected to speciation by the SEC-ICP-MS method described above, as shown in figure 3.

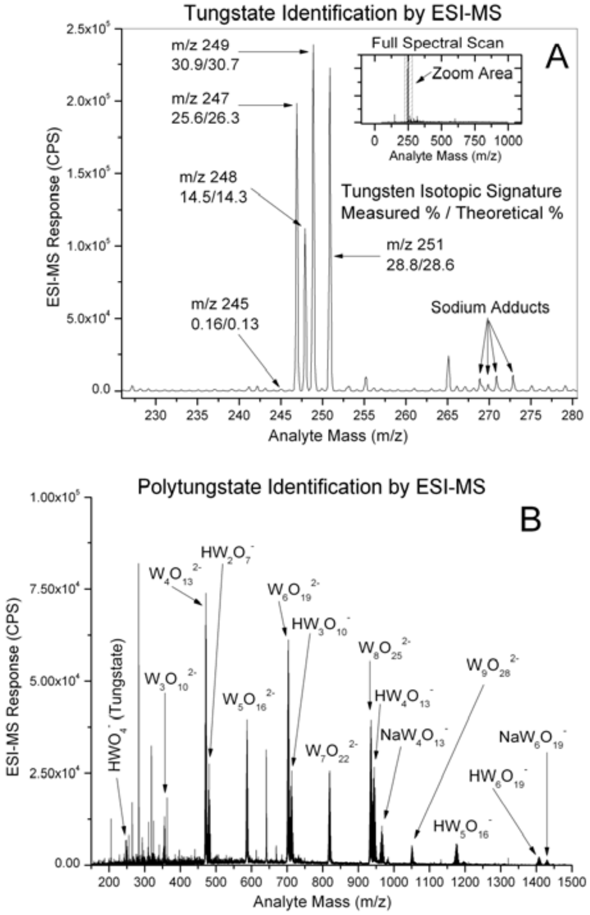

Figure 2. ESI–MS of (A) tungstate and (B) polytungstate standards showing identification of several polymeric forms. The measured natural isotopic abundance of tungsten agrees well with the theoretical ratios in the monomeric tungstate standard.

This soil extract was also analyzed by ESI–MS, as shown in figure 4, where the presence of several polytungstates and phosphotungstates (due to the natural phosphate present in the soil) is confirmed. A trace amount of monomeric tungstate is also identified by ESI–MS, which further suggests the shoulder of the peak observed in figure 3 is due to smaller tungstate species.

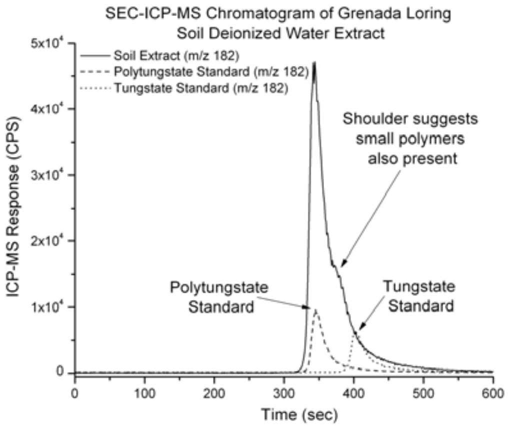

Figure 3. SEC–ICP–MS chromatogram of the soil deionized water extract from tungsten-spiked Grenada Loring soil. The peak is predominantly polymeric species, although the shoulder indicates monomeric or very small polymers (e.g. dimers) are present.

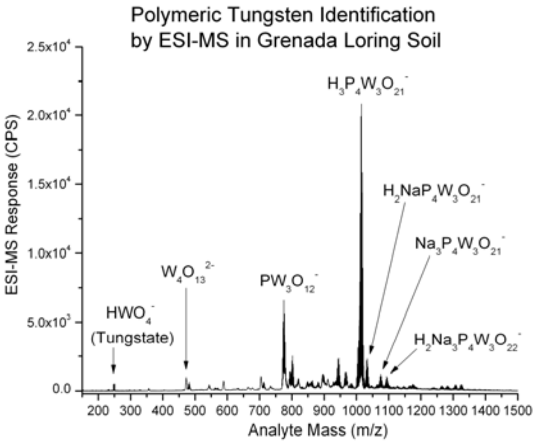

Figure 4: ESI–MS of the soil deionized water extract from tungsten-spiked soil with several polytungstates and phosphotungstates identified.

3.4 Speciation in Field Samples

SEC-ICP-MS analysis of deionized water extractions of the field collected soils is shown in figure 5. The dissolved tungsten concentration in this sample was approximately 30 mg/L, as determined by direct nebulization ICP-MS. The SEC-ICP-MS chromatogram clearly shows the presence of monomeric and polymeric tungsten species. The distribution of tungsten species is apparently greater in the field soil than in the spiked Grenada Loring sample (figure 3), as two distinct peaks are observed (even though they are not baseline resolved).

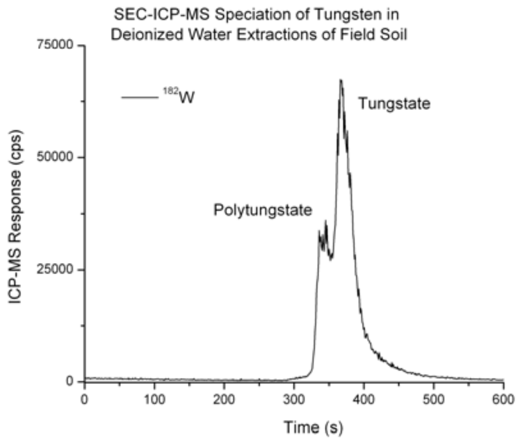

Figure 5: SEC–ICP–MS chromatogram of the deionized water extraction sample from a field collected soil showing the presence of monomeric and polymeric tungsten species.

Analysis of this same field soil water extraction sample by ESI-MS, as shown in figure 6, indicates that there are again several tungsten polymer compounds present in this sample. Some of these compounds are also observed in the Grenada Loring soil (figure 4), although each soil has some unique species detected. To date, not all of the peaks in either soil sample have been positively identified, however, there are suggestions that there are silico-tungsten and phosphor-tungsten compounds present, indicating that tungsten is polymerizing with the matrix components of the soils.

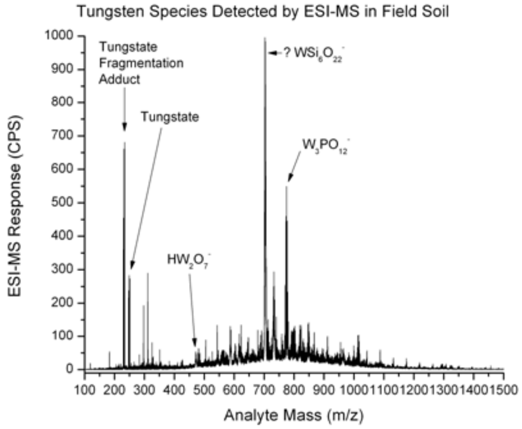

Figure 6: ESI–MS of the deionized water extract from field soil with monomeric and polymeric tungstate species identified.

To address the question of whether or not these species are present in the field environment, figure 7 shows an SEC-ICP-MS chromatogram of three water samples collected from the training range field site using a lysimeter at three different time points. The SEC separation further demonstrates that not only are tungstate and polytungstates present in the system, but the distribution changes over time. This temporal speciation change suggests that dynamic geochemical parameters can influence tungsten speciation in soil systems.

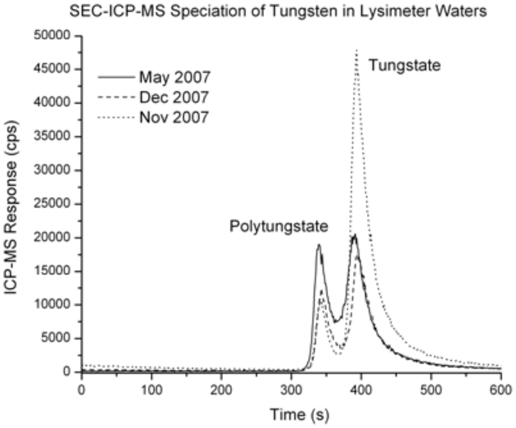

Figure 7: SEC–ICP–MS chromatogram of the lysimeter water samples collected from a training range, showing the presence of monomeric and polymeric tungsten species.

3.5 Solid Phase Speciation

The solid phase speciation data collected using the XAFS technique (figure 8) shows that soil tungsten species are estimated to be overwhelmingly in the +6 oxidized state, with major complexes estimated to be predominantly PWO_4 type species, with minor mixtures of mono-and polymerized-tungstate species in the spiked Grenada Loring soil. This supports the previous findings using aqueous leach experiments that identified the presence of monomeric and polymeric species in the Grenada Loring soil.

Determination of the complete tungsten complexation environment in this soil is not currently possible because the crystallographic database used for modeling tungsten compounds is extremely limited. Further experimentation is currently underway to increase the tungsten speciation database to more accurately fit the XAFS data and refine the tungsten speciation fit.

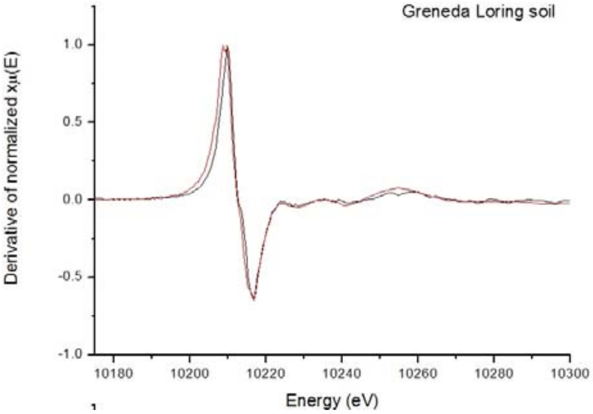

Figure 8: XAFS spectra of the Grenada Loring soil used to determine solid phase speciation of tungsten. Actual transformed data is shown in black, linear combination fit data is shown in red.

4. CONCLUSIONS

Methods for the determination of tungsten polymeric species is described. Poly- and heteropoly-tungstates, as are determined as a group by size exclusion chromatography coupled to ICP-MS as an elemental specific and selective detector. The exact tungsten species are then identified by Electrospray Ionization Mass Spectrometry. Detection limits for the SEC-ICP-MS instrument are less than 1 μg/L. Deionized water extractions of tungsten-containing soil have been shown to contain various tungsten species, which has implications for sorption, mobility, toxicity, and bioavailability. Additionally, solid phase speciation using advanced XAFS techniques further support the aqueous speciation information obtained on the presence of polymeric species.

Application of the methods to laboratory deionized water extractions of tungsten spiked soils and soils collected from training ranges where tungsten munitions were used indicate that both monomeric and polymeric species are present. Additionally, analysis of field collected lysimeter water samples also indicate the presence of monomeric and polymeric species, in agreement with the laboratory studies. The speciation observed is quite complex, and not all polymeric species have been identified, therefore work continues to further identify poly- and heteropolytungstates present in these systems.

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