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Comparison of multiple preservation and digestion methods for determination of tungsten concentrations in environmental media using ICP-MS

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ABSTRACT

Tungsten is an emerging environmental pollutant. However, a proved robust method for preserving and determining the concentrations of tungsten in environmental media is still lacking. This study examined and compared the suitability of classic methods and previously reported tungsten-oriented methods on preserving dissolved tungsten and recovering tungsten from soil/sediment matrix. Tungsten concentrations in the water samples and digestates were then determined by inductively coupled plasma mass spectrometry. Our data showed that the tungsten-oriented HF and alkaline preservatives indeed successfully maintained the stability of dissolved tungsten. Even when preserved using HNO_3 or HCl, dissolved tungsten concentrations did not notably change in most of our water samples over the course of ~4 months. Using glass containers for storing water samples also did not produce much difference from using high-density polyethylene containers. Our data further suggested that the addition of HF in digestion was important for tungsten solubilization from soil/sediment matrix. The digestion methods with HNO_3/HCl/HF and HNO_3/HF/NH_4OH/EDTA both yielded quantitative recoveries of tungsten from certified reference materials and known synthetic samples, while the other tested methods had limited recoveries. The methods validated by this study could be used to accurately determine tungsten concentrations in environmental media and thereby to assess the fate and potential risks of tungsten.

1. Introduction

Tungsten is a transition element in Group VIB of the Periodic Table. Although tungsten was long believed to be nontoxic, elevated tungsten concentration in groundwater was more recently found to be positively correlated with the occurrence of childhood leukemia and crowd diabetes [1,2]. Significant positive correlations were also observed between hematal and urinary tungsten levels and cardiovascular diseases such as spasms and stroke [3–5]. Tungsten is therefore classified as an emerging environmental pollutant [6]. Beside toxicity, tungsten is also found to be more soluble and mobile than previously recognized [7–9]. Due to its robust physical properties such as high density, hardness and melting point, tungsten has been widely used in the industrial and technological applications [10]. Accordingly, following the mining and smelting of tungsten ore, use of tungsten products, and disposal of tungsten-bearing wastes, tungsten and its compounds have been enriched in the natural environment [11,12]. At tungsten munitions impacted sites, dissolved tungsten levels in soil porewaters could reach hundreds of mg L^{-1}, and groundwater tungsten pollution has been also identified in the vicinity [7,13]. Obtaining accurate data on tungsten concentrations in soil and groundwater systems is essential for understanding the fate and transport of tungsten and for preventing and mitigating tungsten pollution. However, a proved robust method for preserving and determining the concentration of tungsten in environmental media is still lacking.

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To obtain an authentic level of tungsten in water and digestates, maintaining tungsten in soluble forms before analysis is critical. Hydrochloric acid (HCl) and nitric acid (HNO_3) are the most common preservation reagents for water samples, because they can effectively prevent the hydrolysis and precipitation of metal ions, prevent the adsorption of metal ions onto the container wall, and inhibit the activity of microorganisms [14–16]. Although HCl and HNO_3 are incapable of destructing silicate minerals, they are sufficient to extract many metal(loid)s that are typically bound to oxides and carbonates and therefore are often used individually or in combination for soil and sediment digestion [17]. Nevertheless, in the absence of a compound that can form stable soluble complexes with tungsten, tungstic acid ($H_2WO_4(s)$) would precipitate at low pH (see calculations in Supporting Information (SI) Fig. S1, Tables S1 and S2) [18,19]. Therefore, treating environmental samples with HCl and/or HNO_3 can potentially cause tungsten precipitation and compromise the determination of tungsten concentration.

Commercially available tungsten reference solutions, instead, use hydrofluoric acid (HF), sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH) as preservation reagents (Table S3). The use of HF can maintain tungsten in the form of soluble tungsten-fluorine complexes such as $H_3WO_4F_2^-$ even at pH < 1 (Tables S1 and S2) [18,20]. NaOH and NH_4OH can create alkaline condition to maintain tungsten in the form of soluble monomeric tungstate WO_4^{2-} (Tables S1 and S2). Since the addition of chelates can further complex free tungstate and therefore increase tungsten solubility, Clausen et al. [21], Sun and Bostick [22] and Bostick et al. [7] used a combination of NH_4OH and ethylenediaminetetraacetic acid (EDTA) for the preservation of tungsten-containing water samples and digestion of tungsten-containing soil samples. In addition, the presence of oxyanions such as phosphate can polymerize with tungstate and form soluble polymeric tungstates such as phosphotungstate $PW_{12}O_{40}^{3-}$ [23,24]. Therefore, Bednar et al. [25] added phosphoric acid (H_3PO_4) to the classic HNO_3/H_2O_2 digestion method to improve the recovery rate of tungsten from soils. At present, the jury is still out on which reagent can preserve and which digestion procedure can extract the true level of tungsten in environmental samples the most effectively [26]. Furthermore, there are also concerns regarding the container, because tungsten may form unrecoverable precipitate with silica glass under acidic conditions, although the exact chemical form of the precipitate has not yet been determined [13,25]. So far, the effect of the material of the container on tungsten preservation has not been properly investigated.

The main objective of this study was therefore to compare and evaluate the performances of different preservation and digestion methods for tungsten-bearing water and solid samples. Known water samples were prepared by dissolving sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) in both deionized water (DIW) and artificial groundwater (AGW). The effectiveness of preserving dissolved tungsten with two classic acid preservatives and four tungsten-oriented reagents was investigated and compared with thermodynamic modeling result. The effects of glass and high-density polyethylene (HDPE) containers were also studied. Known solid samples included not only certified reference materials but also synthetic samples that were prepared by mixing different forms of tungsten with quartz sand. The recovery rates of tungsten by three classic digestion methods from U.S. EPA and three tungsten-oriented digestion methods were compared. Tungsten concentrations in the water samples and digestates were then determined by inductively coupled plasma mass spectrometry (ICP-MS).

2. Methods and materials

2.1. Preparation of water samples

To represent typical tungsten concentration in aquatic systems [10], water samples with initial tungsten concentrations of 0.01, 0.1 and 1 mg L^{-1} were prepared. Tungsten was added from a freshly prepared stock solution containing 400 mg L^{-1} tungsten added as $Na_2WO_4 \cdot 2H_2O$. To investigate the effects of common co-existing ions on tungsten preservation, water samples were prepared in both DIW and AGW matrices and compared. Based on typical groundwater composition [27,28], AGW used in this study consisted of DIW amended with 0.5 mM $NaHCO_3$, 1 mM KCl, 0.4 mM $MgSO_4$, 0.4 mM $CaCl_2$ and 0.02 mM NH_4Cl, and was adjusted to pH 7 with 0.1 M HCl. Before use, the AGW was equilibrated with the atmosphere for >24 h. Tungsten-containing water samples were then prepared by diluting the stock solution with either DIW or AGW. The reagents used in this study were GR or AR grade (Table S4).

2.2. Water sample preservation

Six preservation reagents were selected for water samples in this study, including HCl, HNO_3, HF, NaOH, NH_4OH and NH_4OH/EDTA (Table 1). For each concentration (i.e., 0.01, 0.1 and 1 mg L^{-1}) of tungsten in either DIW or AGW, six samples treated individually with six preservation reagents as well as a blank without any preservative (i.e., tungsten in DIW or AGW only) were prepared in capped 250 mL HDPE containers in triplicate. Concentrated HCl (38 %) and HNO_3 (68 %) were added to the typical volume fractions, i.e., 1 % HCl [15,29] and 2 % HNO_3 [16], respectively. Based on Poehle et al. [30] and Oburger et al. [31], the volume fraction of concentrated HF (40 %) added in the water samples was 0.3 %. Based on the concentration of NaOH in commercially available tungsten reference solutions (Table S3), NaOH was added to 0.01 M. Consistent with Clausen et al. [21] and Bostick et al. [7], the concentrations of NH_4OH and NH_4OH/EDTA added were 0.2 % and 0.2 %/0.1 %, respectively. To identify the effect of container materials on tungsten preservation, a series of water samples containing 1 mg L^{-1} tungsten were also prepared in capped 250 mL glass bottles. Because HF corrodes glass container [32], water samples treated with HF were only stored in HDPE containers. These tungsten-bearing water samples were preserved at room temperature for up to 6 months, during which the bottles were opened for subsampling at desired time intervals with <2 min each time. During subsampling, a 10 mL aliquot of each solution was periodically removed and filtered to 0.22 μm using a polyethersulfone membrane syringe filter (Tianjin Jinteng Experimental Equipment Co., Ltd.) as a subsample. Dissolved tungsten concentrations in the subsamples were determined immediately after collection using ICP-MS.

2.3. Preparation of solid samples

Certified reference materials used in this study were from China National Center for Standard Materials, which included three soils -

Table 1
Preservative reagents for tungsten-bearing water samples and digestion methods for tungsten-bearing solid samples examined in this study.

Sample type	Classification	Procedure	Reference
Water	Traditional preservatives	HNO_3 HCl	[14]
	Tungsten-oriented preservatives	HF NaOH NH_4OH NH_4OH/EDTA	[18] [24] [7] [7]
Solid	Classic digestion methods	HNO_3/H_2O_2 Reverse aqua regia HNO_3/HCl/HF	[34] [35] [36]
	Tungsten-oriented digestion methods	$HNO_3/H_3PO_4/H_2O_2$ $HNO_3/H_2O_2/NH_4OH$/EDTA $HNO_3/HF/NH_4OH$/EDTA	[25] [7] [7]

GBW07941, GBW07980 and GBW(E) 070234, and three sediments - GBW07312, GBW07311 and GBW07307. Detailed information and elemental compositions of these references are given in Table S5. GBW07941 is an agricultural soil from Tongguan, Shanxi, containing 33.8 ± 2.9 mg kg^{-1} tungsten. GBW07980 is an alluvial and diluvial soil downstream of the tungsten-tin-molybdenum-bismuth mining area from Shizhuyuan, Chenzhou, Hunan, containing 164 ± 9 mg kg^{-1} tungsten. GBW(E) 070234 is a soil contaminated by the iron mining industry from Xuzhou, Jiangsu, containing 30.9 ± 2.0 mg kg^{-1} tungsten. GBW07312 is a stream sediment from copper-tungsten-tin mining area in Yangchun, Guangdong, containing 37 ± 2 mg kg^{-1} tungsten. GBW07311 is a stream sediment also from the tungsten-tin-molybdenum-bismuth mining area in Shizhuyuan, Chenzhou, Hunan, containing 126 ± 9 mg kg^{-1} tungsten. GBW07306 is a stream sediment from the copper mine (porphyry type) mining area in Zhaduo, Qinghai, containing 25 ± 2 mg kg^{-1} tungsten. Based on information on the certificates, tungsten concentrations in these reference materials were determined by multi-acid digestion followed by ICP-MS analysis, polarography and/or neutron activation analysis.

Five known synthetic samples were prepared by mixing metallic tungsten W^0 (99.99 %), $Na_2WO_4{\cdot}2H_2O$ (99.0–101.0 %), H_2WO_4(s) (99 %), scheelite $CaWO_4$(s) (72 % WO_3), and wolframite $(Fe,Mn)WO_4$(s) (70 % WO_3) with high purity quartz sand (Macleans, 200–250 mesh, ≥99.7 %). To represent tungsten concentration in contaminated soils and sediments [7,26,33], tungsten concentration in the synthetic samples were set at ~1000 mg kg^{-1}. Accordingly, 0.5000 g tungsten metal, 0.8971 g $Na_2WO_4{\cdot}2H_2O$, 0.6795 g H_2WO_4, 0.8756 g $CaWO_4$ or 0.9006 g $(Fe,Mn)WO_4$ was mixed into 500 g quartz sand. Each sample was homogenized through 3 sequential steps: (1) with horizontal shaker (SK–O330-Pro, Dalong Xingchuang Laboratory Instrument Co., Ltd.) for 3 h, (2) with disc spin mixer (MX-RD-Pro, Scilogex) for 6 h, and (3) with ball mill (GQM-4-5, Changsha Tianchuang Powder Technology Co., Ltd.) for 24 h. The ball mill used 72 corundum balls of various sizes (0.5–2.5 cm diameter) and corundum jars. To prevent cross-contamination, the ball mill was cleaned between samples by mixing pure quartz sand for 20 min and wiping with ethanol at least 3 times before and after quartz sand mix. To know the baseline, a 500 g quartz blank (without tungsten) was also prepared in a consistent fashion and digested as described below. X-ray fluorescence (XRF) spectrometer (Hitachi, XMET 8000) was used on multiple random mounts of each of the prepared synthetic materials, which showed tungsten was evenly distributed (Table S6).

2.4. Digestion procedures

Six digestion methods were used and compared, including three classic methods from U.S. EPA, i.e., (1) HNO_3/H_2O_2, (2) reverse aqua regia, and (3) $HNO_3/HCl/HF$, as well as three methods that were specifically designed for tungsten-bearing solid samples, i.e., (4) $HNO_3/H_3PO_4/H_2O_2$, (5) $HNO_3/H_2O_2/NH_4OH/EDTA$ and (6) $HNO_3/HF/NH_4OH/EDTA$ (Table 1). High-pressure digestion and a closed-vessel oven (Tianjin Taisite Instrument Co., Ltd., 202-3AB) heated system were used in this study. All the digestion procedures were performed in Teflon vessels. Each digestion batch included one reagent blank, one quartz blank, six certified references and five known synthetic samples. Dissolved tungsten concentrations in the digestates were determined using ICP-MS. All digestions were performed in triplicate, and the mean values were reported.

2.4.1. Classic digestion methods from U.S. EPA

HNO_3/H_2O_2 digestion was conducted following EPA Method 3050B [34]. The use of HNO_3 can dissolve organics, metal oxides, carbonates and sulfide minerals and liberate the associated trace metals. The use of H_2O_2 can enhance the oxidation of organics and improve metal recovery from organic matter enriched solid analytes. Reverse aqua regia digestion was conducted following EPA Method 3051A [35]. The co-use of HCl with HNO_3 can improve solubility and recovery of certain elements such as Ag, Ba, Pb and Sb. $HNO_3/HCl/HF$ digestion, which is a complete digestion method, was conducted following EPA Method 3052 [36]. The addition of HF can dissolve elements bound to recalcitrant silicate minerals. More detailed procedures of these three classic digestion methods are provided in Table S7.

2.4.2. Tungsten oriented digestion methods

$HNO_3/H_3PO_4/H_2O_2$ digestion was conducted based on Bednar et al. [25], except that the concentration of H_3PO_4 used was reduced from 14.63 M to 1 M. This modification was made based on Chen et al. [37], which found that concentrated H_3PO_4 would increase the viscosity of the digestates and compromise ICP-MS analysis, while 1 M H_3PO_4 (in combination with 2.5 M H_2SO_4) could guarantee recovery of tungsten from mineral tungstates. For each solid sample, a 0.05 g aliquot was heated in 3 mL concentrated HNO_3 and 1 mL 1 M H_3PO_4 at 140 °C for 16 h. Once complete, the suspensions were cooled to room temperature and evaporated to dryness at 120 °C on a hotplate (Nanjing Zhenghong Instrument Co., LTD, GS-1). Once dry, 3 mL 30 % H_2O_2 was added and heated at 140 °C for 2 h. The suspensions were again cooled to room temperature and evaporated to dryness at 120 °C on a hotplate. Then, 1 mL concentrated HNO_3 and 3 mL DIW were added, and the suspensions were heated at 140 °C for 9 h. Finally, the obtained suspensions were cooled to room temperature and centrifuged at 4000 rpm for 10 min. Each of the supernatants was filtered to 0.22 μm using a polyethersulfone membrane syringe filter (Tianjin Jinteng Experimental Equipment Co., Ltd.), and diluted to 50 mL with DIW before ICP-MS analysis.

$HNO_3/H_2O_2/NH_4OH/EDTA$ digestion was conducted based on Bostick et al. [7]. A 0.05 g aliquot of each sample was heated in 3 mL concentrated HNO_3 at 140 °C for 16 h, cooled to room temperature and evaporated to dryness at 120 °C on a hotplate. Once complete, 3 mL 30 % H_2O_2 was added and heated at 140 °C for 2 h. The suspensions were cooled to room temperature and evaporated to dryness at 120 °C on a hotplate. Once dry, 1 mL 20 % NH_4OH/10 % EDTA and 3 mL DIW were added. The suspensions were heated at 140 °C for 9 h, and then sonicated for 1 h to ensure mixing. Finally, the obtained suspensions were centrifuged at 4000 rpm for 10 min, filtered to 0.22 μm, and diluted to 50 mL with DIW before ICP-MS determination. $HNO_3/HF/NH_4OH/EDTA$ digestion was also conducted based on Bostick et al. [7], except that 1 mL concentrated HF (40 %), instead of 3 mL 30 % H_2O_2, was used to dissolve silicate minerals and the associated tungsten. All other steps remained consistent with the $HNO_3/H_2O_2/NH_4OH/EDTA$ digestion procedure described above.

2.5. Sample analysis

Dissolved tungsten concentrations in the water samples and solid digestates in this study were determined by ICP-MS. The analyses were carried out using an Agilent 7700X ICP-MS (G3281A) equipped with a PFA Inert Kit (G4912-68000), a Connector tube Insert Kit (G4912-80016) and a PFA MicroFlow Nebulizer (G3139-65100). Single-element internal standard solution of rhenium (^{103}Rh) was added inline through a tee valve to correct non-mass spectra interference. Because the presence of organics could lead to instability of plasma torch and carbon deposits in the interface cones for ICP-MS [38], the samples preserved in NH_4OH/EDTA were diluted 10 times with DIW immediately before entering the machine, while all the other samples were injected without dilution. 3 % HNO_3/3 % HF was used as the rinse solution to remove residual tungsten between samples during analysis. Quantification of tungsten concentration in the water samples was based on comparison to a six-point standard curve, either between 0 and 0.12 mg L^{-1} or between 0 and 1.2 mg L^{-1} depending on the concentration in the sample. Quantification of tungsten concentration in the digestates was based on comparison to a six-point standard curve between 0 and 0.2 mg L^{-1}. The standards were prepared freshly before each sample run by dilution of a single-element reference solution containing 100 mg L^{-1} tungsten in trace NaOH (Table S4). To avoid mutual influence between different matrices, the matrices of the standards (i.e., the solutions used for diluting the reference) were consistent with those of the determined samples. All standard curves were linear with correlation coefficients of >0.999. Three diluted tungsten reference solutions were also prepared in the respective matrix and inserted in each sample run as quality controls (QCs), which verified accuracy of the quantification. Each sample was run six times and averaged. The relative standard deviation between six runs was always better than 6 %, which verified precision of the quantification. In addition to tungsten, the concentrations of many other elements, including Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn,

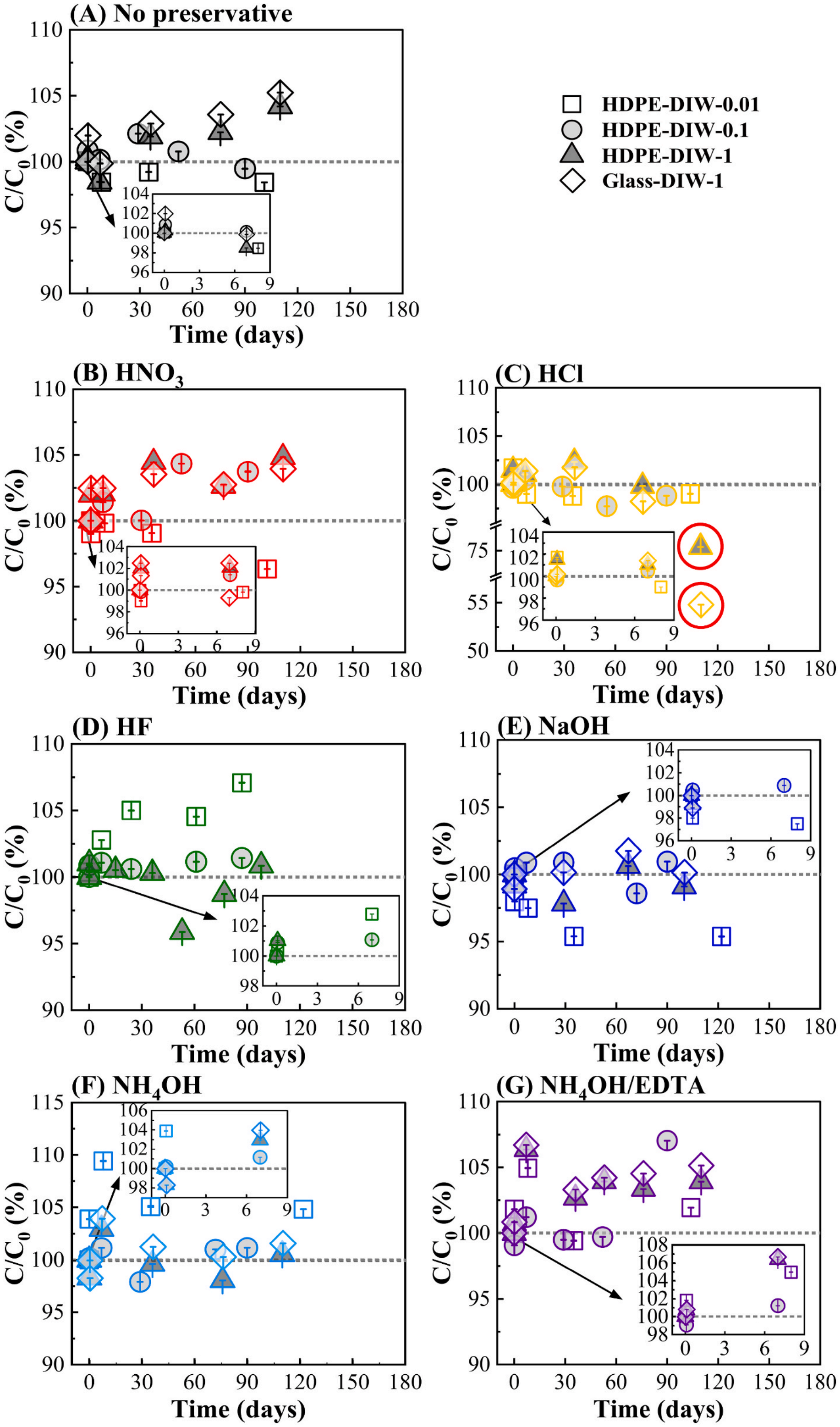

Fig. 1. Dissolved tungsten concentrations versus time in tungsten-bearing DIW samples without preservatives (Black) and with HNO_3 (Red), HCl (Yellow), HF (Green), NaOH (Blue), NH_4OH (Lake blue) and NH_4OH/EDTA (Purple). The grey dashed line in each subplot represents C/C_0 = 100 %.

Mo, Na, Ni, Pb, Sr and Zn, in digestate solutions were also determined (the detailed information on analysis is given in Text S1).

2.6. Thermodynamic calculation

Thermodynamic calculations were performed to estimate tungsten solid-solution speciation in the presences of different preservatives. The geochemical modeling software PHREEQC Interactive 3.3.12 was used for the calculation, in which the standard database *Amm. dat* was used and updated for tungsten [39]. Many of the tungsten related reactions and equilibrium constants were sourced from the database *thermo. vdb* in Visual MINTEQ, which contains data for HWO_4^-, $H_2W_6O_{22}^{6-}$, $HW_7O_{24}^{5-}$,

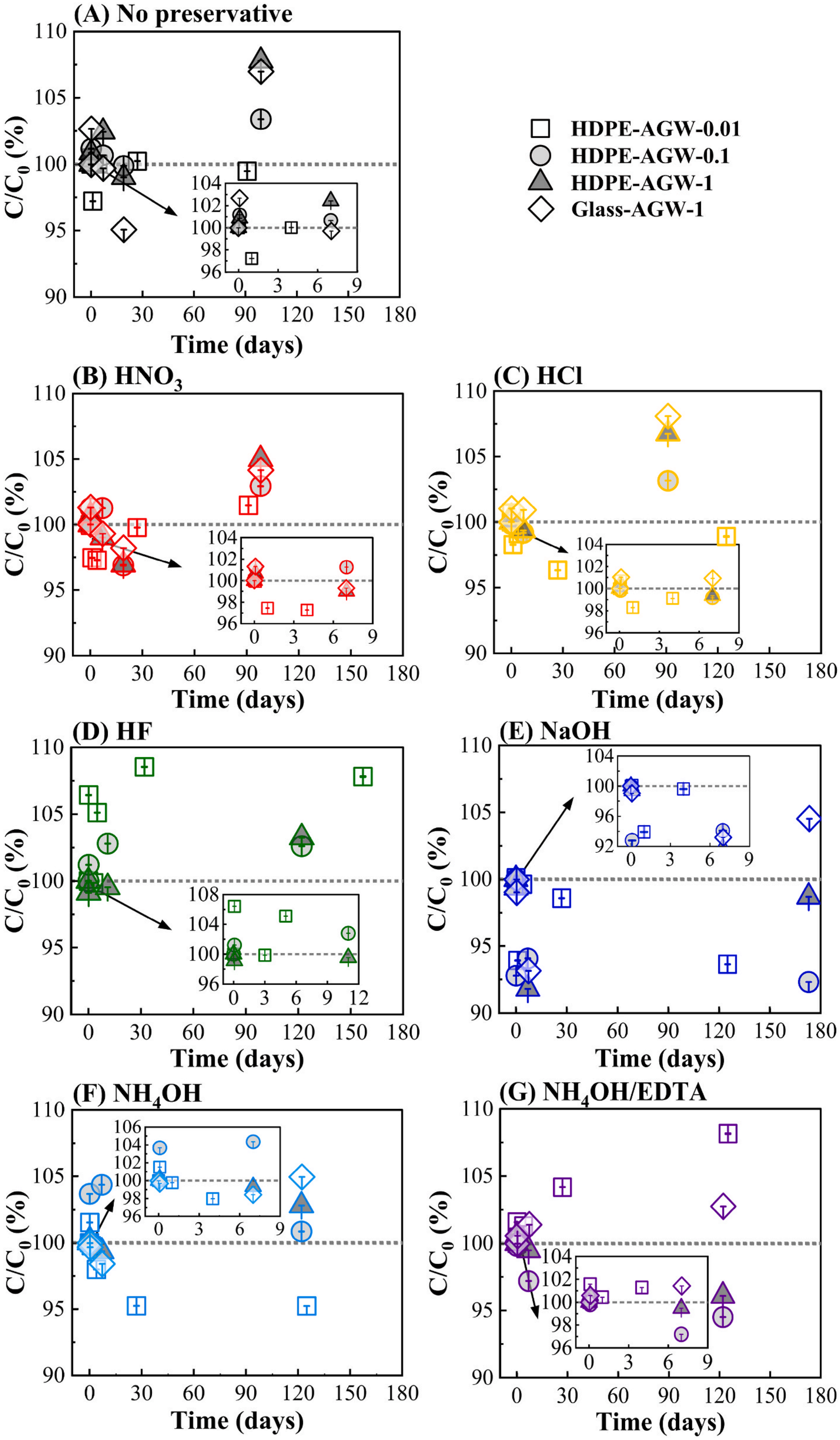

Fig. 2. Dissolved tungsten concentrations versus time in tungsten-bearing AGW samples without preservatives (Black) and with HNO_3 (Red), HCl (Yellow), HF (Green), NaOH (Blue), NH_4OH (Lake blue) and NH_4OH/EDTA (Purple). The grey dashed line in each subplot represents $C/C_0 = 100$ %.

$W_7O_{24}^{6-}$, $H_2W_{12}O_{42}^{10-}$, $WO_3(H_2O)_3$ (aq), $CaWO_4$(aq), $MgWO_4$(aq), H_2WO_4(s) and $CaWO_4$(s) [40]. The database was further updated with additional polytungstates $W_{10}O_{32}^{4-}$, $HW_6O_{21}^{5-}$, and $H_2W_{12}O_{40}^{6-}$ from Rozantsev and Sazonova [41], tungsten-fluorine complex $H_3WO_4F_2^-$ from Wang et al. [20], and tungsten-EDTA complexes from Zare et al. [42]. The relevant reactions, stoichiometries, and equilibrium constants are provided in Table S8. The effects of adding six different preservation reagents on tungsten solid-solution speciation with initial concentrations of 0.01, 0.1 and 1 mg L^{-1} in both DIW and AGW were calculated.

3. Results and discussion

3.1. Performance of different reagents on preserving dissolved tungsten

Without preservatives, dissolved tungsten concentrations changed by −1.57 %, −0.52 %, and +4.18 %, respectively, in DIW (Fig. 1A), and by −0.53 %, +3.37 %, and +7.78 %, respectively, in AGW (Fig. 2AA), relative to the initial values of 0.01, 0.1, and 1 mg L^{-1}, in HDPE containers. Consistent with the criteria used in many previously published studies [43–46], the relative difference (RD) between the added concentration (C_{added}) and the determined concentration ($C_{determined}$) by ICP-MS was calculated to assess the stability of the target element, i.e., tungsten:

$$RD = \frac{C_{determined} - C_{added}}{C_{added}} \times 100\% \tag{1}$$

The stability can be classified as "excellent" with $|RD| < 3$ %, "good" with $|RD| = 3$–7%, "acceptable" with $|RD| = 7$–10 % and "bad" with $|RD| > 10$ %. Accordingly, our data indicated that the stability of dissolved tungsten was at least acceptable in both DIW and AGW without preservatives (Table S9). Geochemical modeling further confirmed that tungsten would not precipitate at pH ≥ 6, and that typical concentrations of typical groundwater constituents would not affect dissolved tungsten level (Fig. S1). While most of the constituents in AGW do not react with tungsten, the co-existence of Ca^{2+} and tungstate can lead to the precipitation of scheelite $CaWO_4$(s) [47]. Nevertheless, based on thermodynamic calculations, $CaWO_4$(s) was always under saturated in our systems, and instead, the added Ca^{2+} would form ion pair $CaWO_4$(aq) with WO_4^{2-} in solution (Table S2).

When preserved within 2 % HNO_3, dissolved tungsten was stable in both DIW and AGW in HDPE containers, with RD ranging from −3.66 % to +5.23 % (Figs. 1B and 2B). In the presence of 1 % HCl, dissolved tungsten was also stable in most samples, with RD ranging from −1.18 % to +6.74 %, except for 1 mg L^{-1} tungsten in DIW, which changed by −24.6 % after 110 days (Figs. 1C and 2C). These data implied that 2 % HNO_3 could be used to preserve ≤1 mg L^{-1} tungsten at least within 4 months, whereas 1 % HCl was unsuitable for preserving ≥1 mg L^{-1} tungsten. However, based on known equilibria with common tungsten-bearing species as detailed above, in 1 % HCl and 2 % HNO_3, while 0.01 mg L^{-1} tungsten could maintain the dissolved form, 0.1 mg L^{-1} tungsten would already lose ~61 % and ~63 % of the dissolved form to precipitation of H_2WO_4(s), respectively, and 1 mg L^{-1} tungsten would almost entirely (~96 %) precipitate as H_2WO_4(s) (Fig. S1, Tables S1 and S2). Even though no significant change in the concentration of dissolved tungsten was observed in this study, H_2WO_4(s) might still exist. It is well known that monomeric tungstate WO_4^{2-} forms various polymeric tungstates under acidic conditions [48,49]:

$$mH^+ + nWO_4^{2-} = H_xW_nO_{4n-0.5(m-x)}^{(2n-m)-} + \frac{1}{2}(m-x)H_2O \tag{2}$$

H_2WO_4(s) starts to precipitate when $m/n \geq 2$, and the particle size of precipitated H_2WO_4(s) decreases with increasing m/n value [50]. At room temperature with a m/n value of 1.50, the size of H_2WO_4(s) is ~2 μm [50]. The m/n values of even 1 mg L^{-1} tungsten in 2 % HNO_3 and 1 % HCl in this study were already 64,000 and 24,000, respectively. Therefore, H_2WO_4(s), if present, might be small enough to pass through 0.22 μm pore size filters. Dissolved tungsten concentration in soil porewater impacted by tungsten munitions could reach several hundred mg L^{-1} [7,13], while the highest concentration of dissolved tungsten in the water samples prepared in the study was only 1 mg L^{-1}. Based on the negative correlation between the value of m/n and the particle size of H_2WO_4(s) (Reaction 2), it is possible that H_2WO_4(s) particles precipitated in tungsten-rich water samples treated with 2 % HNO_3 or 1 % HCl would be large enough to be filtered out. This possibility, however, still needs to be testified through further studies. The generation of H_2WO_4(s) at room temperature is a kinetically controlled, slow process [47], which could explain the inconsistency between observations and the thermodynamic modeling results. Nevertheless, water samples are commonly stored at low temperatures (for example, 4 °C) until analysis [14]. Previous studies pointed out that low temperature might promote the formation of H_2WO_4(s) in tungsten-containing water samples treated with acidic preservatives [18]. The suitable preservation temperature for dissolved tungsten, therefore, also needs to be further assessed. Furthermore, various polymeric tungstates and ion pairs could form in our systems and stabilize tungsten in solution, many of which do not have reported equilibrium constants in the literature and could not be properly considered in the thermodynamic calculations [7,49,51]. Metastable tungsten-bearing complexes, such as tungsten–chlorine complexes WO_3Cl^- and $(WO_3)_2Cl^-$ might also exist [52,53].

The four tungsten-oriented preservatives, including 0.3 % HF, 0.01 M NaOH, 0.2 % NH_4OH, and 0.2 % NH_4OH/0.1 % EDTA could maintain the stability of dissolved tungsten in DIW and AGW in HDPE containers, with RD ranging from −7.69 % to +8.15 % (Figs. 1 and 2). While thermodynamic modeling demonstrated broadly consistent results with observations, it showed that 1 mg L^{-1} tungsten would lose ~94 % of the dissolved form to precipitation of H_2WO_4(s) in 0.3 % HF (Fig. S1). Besides the aforementioned possible causes, the discrepancy between observations and the thermodynamic calculations might also partially result from the missing information on tungsten–fluorine equilibria. In addition to $H_3WO_4F_2^-$ that has known equilibrium constant, many other tungsten–fluorine solution complexes, such as WOF_5^-, $WO_2F_4^{2-}$, $WO_3F_3^{3-}$, WO_4F^{3-}, $WO_3F_3^{2-}$, WO_3F^-, and $WO_2F_3^-$ might also exist [52–54].

Previous studies suggested that tungsten might precipitate in silica glass containers under acidic conditions [13,25]. In this study, water samples containing 1 mg L^{-1} tungsten were also stored in glass containers and compared with the results from HDPE containers. Relative to initial concentration of 1 mg L^{-1}, dissolved tungsten concentrations changed between −6.83 % and +8.06 % in glass containers, except for the sample in DIW with 1 % HCl, which had a RD of −45.18 % (Figs. 1 and 2). Therefore, when switching from HDPE to glass, the stability of dissolved tungsten in most samples did not change, no matter in DIW or AGW, with preservatives or without. Nevertheless, in DIW with 1 % HCl, the concentration of dissolved tungsten decreased more in the glass container (Fig. 1C), which can be attributed to the adsorption of polytungstates on glass. The tungsten atoms in polytungstates that are present under acidic conditions can form weak p_π–d_π coordination bonds with the oxygen atoms of the Si–O groups of the silica glass [52,55]. Compared to DIW, the existence of metal cations in AGW could increase the degree of protonation of the Si–O groups and thereby weaken the adsorption of polytungstates onto the wall of the glass container [56, 57]. Accordingly, the concentration of dissolved tungsten in the AGW matrix did not decrease (Fig. 2).

3.2. Tungsten recovery from solid samples using different digestion procedures

The performances of three classic digestion methods from U.S. EPA were examined in this study on known tungsten-bearing solid samples (Table 1). Sizable differences in tungsten recovery were found between these three methods (Table 2 and Fig. 3). Tungsten recoveries obtained by the HNO_3/H_2O_2 procedure only ranged between 0.13 ± 0 % and 50 ± 2 % from reference materials and between 12 ± 1 % and 20 ± 3 %

Table 2

Tungsten recovery (%) from certified reference materials and known synthetic samples using six different digestion procedures. Each data represents the mean value of triplicates, and each error represents the standard deviation.

Sample		Classic digestion methods			Tungsten-oriented digestion methods		
		HNO_3/ H_2O_2	Reverse aqua regia	HNO_3/HCl/ HF	HNO_3/H_2O_2/ H_3PO_4	HNO_3/H_2O_2/NH_4OH/ EDTA	HNO_3/HF/NH_4OH/ EDTA
Reference materials	GBW07941	46 ± 7	90 ± 0	129 ± 1	68 ± 6	46 ± 1	44 ± 5
	GBW07980	33 ± 1	68 ± 1	113 ± 1	52 ± 1	26 ± 0	98 ± 2
	GBW(E) 070234	0.13 ± 0	1 ± 0	106 ± 1	29 ± 3	5 ± 0	70 ± 1
	GBW07312	31 ± 2	91 ± 4	122 ± 1	64 ± 2	32 ± 3	111 ± 4
	GBW07311	50 ± 2	79 ± 1	116 ± 4	54 ± 1	64 ± 1	96 ± 3
	GBW07306	1 ± 0	24 ± 1	113 ± 4	88 ± 2	34 ± 6	99 ± 0
Synthetic samples	W^0	20 ± 3	23 ± 0	85 ± 2	64 ± 1	98 ± 1	98 ± 1
	Na_2WO_4	14 ± 1	23 ± 0	78 ± 2	59 ± 1	97 ± 2	94 ± 1
	H_2WO_4	20 ± 1	23 ± 1	80 ± 3	57 ± 1	97 ± 0	98 ± 3
	$CaWO_4$	15 ± 1	22 ± 0	80 ± 5	50 ± 1	94 ± 1	100 ± 2
	$(Fe,Mn)WO_4$	12 ± 1	23 ± 1	81 ± 3	53 ± 1	94 ± 1	107 ± 3

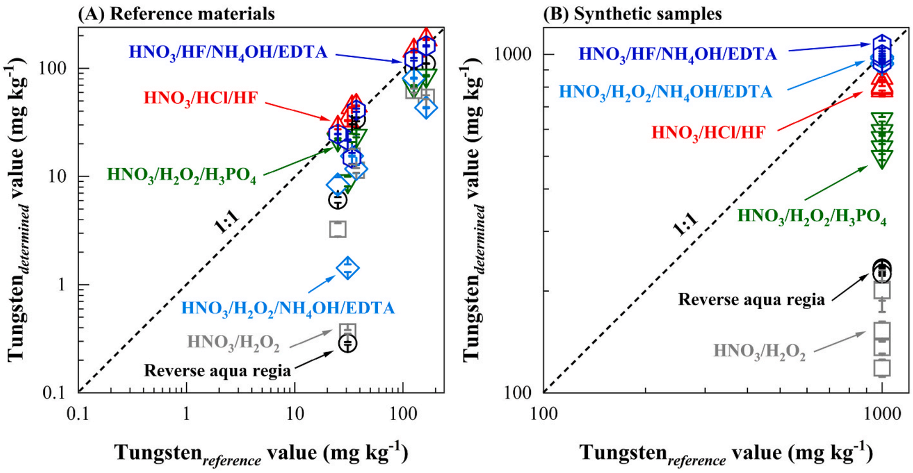

Fig. 3. Comparison between known tungsten concentrations and the concentrations determined by HNO_3/H_2O_2 (Light grey), reverse aqua regia (Black), HNO_3/HCl/HF (Red), $HNO_3/H_2O_2/H_3PO_4$ (Green), $HNO_3/H_2O_2/NH_4OH$/EDTA (Lake blue) and HNO_3/HF/NH_4OH/EDTA (Blue) digestions followed by analysis on ICP-MS. The black dashed line represents the 1-to-1 line.

from synthetic samples. These recovery rates were consistent with the reported recoveries (i.e., between 0.4 % and 47 %) by Bednar et al. [25], which also tested the same digestion procedure but used inductively coupled plasma atomic emission spectroscopy (ICP-AES) for analysis. Tungsten recoveries obtained by reverse aqua regia digestion increased to between 1 ± 0 % and 91 ± 4 % from reference materials but was still only between 22 ± 0 % and 23 ± 1 % from synthetic samples. When HF was added to the acid cocktail, tungsten recoveries substantially increased to between 106 ± 1 % and 129 ± 1 % from reference materials and between 78 ± 2 % to 85 ± 2 % from synthetic samples. In natural soils and sediments, tungsten usually exists as Fe/Mn oxide-bound and silicate-bound forms [8,26,33,58]. Unlike the total digestion procedure with HNO_3/HCl/HF, the two acid digestion methods can dissolve elements bound to Fe/Mn oxides but cannot dissolve those bound within silicate structure [34,35]. Limited leaching of Fe/Mn oxides by HNO_3 compared with reverse aqua regia could explain the lower tungsten recovery from HNO_3/H_2O_2 digestion. Furthermore, the use of concentrated HNO_3 in the final steps of the HNO_3/H_2O_2 and reverse aqua regia methods would convert liberated tungsten into H_2WO_4(s) [18,19]. The use of HF, on the other hand, could not only successfully decompose the soil/sediment matrix but also solubilize tungsten by forming tungsten–fluorine solution complexes [18,20]. Nevertheless, even the total digestion method did not fully extract tungsten from the synthetic samples in this study (Table 2 and Fig. 3).

The $HNO_3/H_2O_2/H_3PO_4$ procedure from Bednar et al. [25] was developed on the basis of U.S. EPA Method 3050B, i.e., the HNO_3/H_2O_2 method. Tungsten recoveries obtained by this $HNO_3/H_2O_2/H_3PO_4$ procedure ranged between 29 ± 3 % and 88 ± 2 % from reference materials and between 53 ± 1 % and 64 ± 1 % from synthetic samples in this study (Table 2 and Fig. 3). Therefore, compared to the HNO_3/H_2O_2 procedure, the addition of H_3PO_4 helped stabilize tungsten in soluble forms to some extent, most likely as (substituted) heteropolytungstates that are more stable than their corresponding conventional (homonuclear) polytungstate analogues [25,37]. Still, most recovery rates were markedly lower than the reported recoveries (i.e., between 76 % and 98 %) by Bednar et al. [25], in which the majority of sample analysis was conducted with ICP-AES. The reason was most likely be that to accommodate the requirement for ICP-MS analysis, the concentration of H_3PO_4 used in this study (i.e., 1 M) was substantially lower than what was used in Bednar et al. [25] (i.e., 14.63 M). Nevertheless, ICP-MS was in fact used in Bednar et al. [25] on analyzing the digestate of a certified reference material (SRM 2709), from which the reported tungsten recovery was only 25 %.

The $HNO_3/H_2O_2/NH_4OH$/EDTA procedure from our previous study, Bostick et al. [7], also initially followed U.S. EPA Method 3050B but then dissolved the digestates in alkaline matrix to prevent the generation of H_2WO_4(s). Tungsten recoveries using this procedure were between 5 ± 0 % and 64 ± 1 % from reference materials and between 94 ± 1 % and 98 ± 1 % from synthetic samples (Table 2 and Fig. 3). Therefore, the alkaline modification of the HNO_3/H_2O_2 procedure substantially increased tungsten recovery from synthetic samples, in which tungsten exists as metallic tungsten or mineral tungstates (i.e., $(Fe,Mn)WO_4$ and $CaWO_4$). Consistently, the method used in the literature to digest tungsten ores is also often the alkaline digestion with NaOH [26,47]. This $HNO_3/H_2O_2/NH_4OH/EDTA$ procedure, however, still could not fully decompose silicates [59]. As a result, the recovery of tungsten from reference materials, which are natural soils and sediments, remained quite low. In comparison, the addition of HF to this procedure further extracted the silicate-bound tungsten and thereby notably improved tungsten recovery from natural soils/sediments. Tungsten recoveries from reference materials and synthetic samples obtained by the $HNO_3/HF/NH_4OH/EDTA$ procedure were all better than 70 ± 1 %, except for GBW07941 (Table 2 and Fig. 3). While the recovery rates of Fe, Mn and many other elements through $HNO_3/HF/NH_4OH/EDTA$ were all acceptable for the six certified reference materials assessed in this study, the Al recoveries ranged only between 46 ± 1 % and 76 ± 4 % (Table S11). In addition to Fe/Mn oxides, Al oxides are also an important type of tungsten scavengers [26]. Therefore, the low tungsten recovery from GBW07941 by $HNO_3/HF/NH_4OH/EDTA$ was possibly due to tungsten sequestration by (re)precipitation of Al oxides following NH_4OH addition.

The digestion methods for biological samples, such as animal and plant tissues, are often similar to the methods for soils and sediments [60]. In fact, the digestion procedure developed by Bednar et al. [25] for tungsten in soils were used for digesting snail, cabbage and soybean that were exposed to tungsten, although no certified animal or plant reference material was used to verify the obtained results [61,62]. The methods validated by this study can potentially be used to digest biological samples. Nevertheless, future digestion study of biological analytes is required to confirm the validity.

4. Conclusions

This study examined the effects of different preservatives and container materials on the stability of tungsten in water, and the performances of different digestion procedures on recovering tungsten from soil and sediment matrices. This is a timely, important examination as tungsten is an emerging environmental pollutant and has been receiving increasing attention in recent years. Our results confirmed that the tungsten-oriented HF and alkaline preservatives could maintain tungsten in soluble forms. Although the use of HNO_3 and HCl would potentially cause precipitation of $H_2WO_4(s)$ based on thermodynamic calculations, the changes in dissolved tungsten concentrations were subtle in most of our samples over the course of ~4 months, no matter in the presence of typical groundwater constituents or not. The use of glass containers for storing water samples did not produce much difference from HDPE containers either. Our results further showed that the addition of HF in the digestion techniques greatly improved tungsten solubilization. Both $HNO_3/HCl/HF$ and $HNO_3/HF/NH_4OH/EDTA$ digestion methods yielded quantitative recoveries of tungsten from certified references and known synthetic samples, while all the other tested methods as conducted had limited recoveries. The preservation and digestion methods validated by this study can be used to accurately determine the concentrations of tungsten in environmental media, and therefore are of great significance to evaluate the fate of tungsten and the associated health and ecological risks.

CRediT authorship contribution statement

Lei Song: Writing – original draft, Validation, Methodology, Investigation. **Fei Yang:** Validation, Supervision, Methodology, Investigation. **Benjamin C. Bostick:** Writing – review & editing, Validation. **Huihui Du:** Writing – review & editing, Supervision. **Yu Dai:** Validation. **Chao Li:** Software, Validation. **Jing Sun:** Funding acquisition, Project administration, Supervision, Writing – review & editing. **Chengshuai Liu:** Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

[1] A. Menke, E. Guallar, C.C. Cowie, Metals in urine and diabetes in U.S. adults, Diabetes 65 (2016) 164–171, https://doi.org/10.2337/db15-0316.

[2] C.S. Rubin, A.K. Holmes, M.G. Belson, R.L. Jones, W.D. Flanders, S.M. Kieszak, J. Osterloh, G.E. Luber, B.C. Blount, D.B. Barr, Investigating childhood leukemia in Churchill county, Nevada, Environ. Health Perspect. 115 (2007) 151–157, https://doi.org/10.1289/ehp.9022.

[3] S. Agarwal, T. Zaman, E. Murat Tuzcu, S.R. Kapadia, Heavy metals and cardiovascular disease: results from the national health and nutrition examination survey (NHANES) 1999-2006, Angiology 62 (2011) 422–429, https://doi.org/10.1177/0003319710395562.

[4] J. Tyrrell, T.S. Galloway, G. Abo-Zaid, D. Melzer, M.H. Depledge, N.J. Osborne, High urinary tungsten concentration is associated with stroke in the National Health and Nutrition Examination Survey 1999–2010, PLoS One 8 (2013) e77546, https://doi.org/10.1371/journal.pone.0077546.

[5] R. Lemus, C.F. Venezia, An update to the toxicological profile for water-soluble and sparingly soluble tungsten substances, Crit. Rev. Toxicol. 45 (2015) 388–411, https://doi.org/10.3109/10408444.2014.1003422.

[6] U.S. Environmental Protection Agency, Emerging Contaminat-Tungsten. (2008) 1-4. Avaliable at https://nepis.epa.gov/Exe/ZyPDF.cgi/P1000L3K.PDF?Dockey=P1000L3K.PDF. (Accessed 17 January 2024).

[7] B.C. Bostick, J. Sun, J.D. Landis, J.L. Clausen, Tungsten speciation and solubility in munitions-impacted soils, Environ. Sci. Technol. 52 (2018) 1045–1053, https://doi.org/10.1021/acs.est.7b05406.

[8] C. Hobson, H.V. Kulkarni, K.H. Johannesson, A. Bednar, R. Tappero, T. J. Mohajerin, P.R. Sheppard, M.L. Witten, G.M. Hettiarachchi, S. Datta, Origin of tungsten and geochemical controls on its occurrence and mobilization in shallow sediments from Fallon, Nevada, USA, Chemosphere 260 (2020) 127577, https://doi.org/10.1016/j.chemosphere.2020.127577.

[9] O.A. Akintomide, S. Adebayo, J.D. Horn, R.P. Kelly, K.H. Johannesson, Geochemistry of the redox-sensitive trace elements molybdenum, tungsten, and rhenium in the euxinic porewaters and bottom sediments of the Pettaquamscutt River estuary, Rhode Island, Chem. Geol. 584 (2021) 120499, https://doi.org/10.1016/j.chemgeo.2021.120499.

[10] A. Koutsospyros, W. Braida, C. Christodoulatos, D. Dermatas, N. Strigul, A review of tungsten: from environmental obscurity to scrutiny, J. Hazard Mater. 136 (2006) 1–19, https://doi.org/10.1016/j.jhazmat.2005.11.007.

[11] C. Lin, R. Li, H. Cheng, J. Wang, X. Shao, Tungsten distribution in soil and rice in the vicinity of the world's largest and longest-operating tungsten mine in China, PLoS One 9 (2014) e91981, https://doi.org/10.1371/journal.pone.0091981.

[12] I. Timofeev, N. Kosheleva, N. Kasimov, Contamination of soils by potentially toxic elements in the impact zone of tungsten-molybdenum ore mine in the Baikal region: a survey and risk assessment, Science of the Total Environment 642 (2018) 63–76, https://doi.org/10.1016/j.scitotenv.2018.06.042.

[13] J.L. Clausen, N. Korte, Environmental fate of tungsten from military use, Sci. Total Environ. 407 (2009) 2887–2893, https://doi.org/10.1016/j.scitotenv.2009.01.029.

[14] M. Sliwka-Kaszyńska, A. Kot-Wasik, J. Namieśnik, Preservation and storage of water samples, Crit. Rev. Environ. Sci. Technol. 33 (2003) 31–44, https://doi.org/10.1080/10643380390814442.

[15] R. Dhar, Y. Zheng, J. Rubenstone, A. Van Geen, A rapid colorimetric method for measuring arsenic concentrations in groundwater, Anal. Chim. Acta 526 (2004) 203–209, https://doi.org/10.1016/j.aca.2004.09.045.

[16] C. Wang, X. Wang, Spatial distribution of dissolved Pb, Hg, Cd, Cu and as in the Bohai sea, J. Environ. Sci. 19 (2007) 1061–1066, https://doi.org/10.1016/S1001-0742(07)60173-9.

[17] H. Hödrejärv, A. Vaarmann, Pseudo-total analysis for metallic elements in siliceous soil by acid digestion and flame atomic absorption spectrometry, Anal. Chim. Acta 396 (1999) 293–301, https://doi.org/10.1016/S0003-2670(99)00480-8.

[18] E. Lassner, W.D. Schubert, Tungsten: Properties, Chemistry, Technology of the Elements, Alloys, and Chemical Compounds, Springer Science & Business Media, New York, 1999, pp. 85–132.

[19] J.L. Clausen, M.E. Ketterer, A.J. Bednar, M.R. Koenig, Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples, Int. J. Environ. Anal. Chem. 90 (2010) 773–783, https://doi.org/10.1080/03067310903267323.

[20] X. Wang, A. Williams-Jones, R. Hu, L. Shang, X. Bi, The role of fluorine in granite-related hydrothermal tungsten ore genesis: results of experiments and modeling, Geochem. Cosmochim. Acta 292 (2021) 170–187, https://doi.org/10.1016/j.gca.2020.09.032.

[21] J.L. Clausen, B.C. Bostick, A.J. Bednar, J. Sun, J.D. Landis, Tungsten speciation in firing range soils. https://erdc-library.erdc.dren.mil/jspui/handle/11681/8569, 2021. (Accessed 6 July 2021).

[22] J. Sun, B.C. Bostick, Effects of tungstate polymerization on tungsten (VI) adsorption on ferrihydrite, Chem. Geol. 417 (2015) 21–31, https://doi.org/10.1016/j.chemgeo.2015.09.015.

[23] A. Bednar, W. Jones, R. Boyd, D. Ringelberg, S. Larson, Geochemical parameters influencing tungsten mobility in soils, J. Environ. Qual. 37 (2008) 229–233, https://doi.org/10.2134/jeq2007.0305.

[24] Z. Zhu, R. Tain, C. Rhodes, A study of the decomposition behaviour of 12-tungstophosphate heteropolyacid in solution, Can. J. Chem. 81 (2003) 1044–1050, https://doi.org/10.1139/v03-129.

[25] A. Bednar, W. Jones, M. Chappell, D. Johnson, D. Ringelberg, A modified acid digestion procedure for extraction of tungsten from soil, Talanta 80 (2010) 1257–1263, https://doi.org/10.1016/j.talanta.2009.09.017.

[26] H. Song, Y. Cao, Z. Miao, H. Luo, Q. Guo, Characterization of tungsten distribution in tungsten-rich slag and sediment via leaching experiments, Environ. Earth Sci. 82 (2023) 52, https://doi.org/10.1007/s12665-022-10727-9.

[27] S.G. Benner, C.M. Hansel, B.W. Wielinga, T.M. Barber, S. Fendorf, Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions, Environ. Sci. Technol. 36 (2002) 1705–1711, https://doi.org/10.1021/es0156441.

[28] J. Sun, B.C. Bostick, B.J. Mailloux, J.M. Ross, S.N. Chillrud, Effect of oxalic acid treatment on sediment arsenic concentrations and lability under reducing conditions, J. Hazard Mater. 311 (2016) 125–133, https://doi.org/10.1016/j.jhazmat.2016.02.060.

[29] J. Sun, S.N. Chillrud, B.J. Mailloux, B.C. Bostick, In situ magnetite formation and long-term arsenic immobilization under advective flow conditions, Environ. Sci. Technol. 50 (2016) 10162–10171, https://doi.org/10.1021/acs.est.6b02362.

[30] S. Poehle, K. Schmidt, A. Koschinsky, Determination of Ti, Zr, Nb, V, W and Mo in seawater by a new online-preconcentration method and subsequent ICP–MS analysis, Deep Sea Res. Oceanogr. Res. Pap. 98 (2015) 83–93, https://doi.org/10.1016/j.dsr.2014.11.014.

[31] E. Oburger, C. Vergara Cid, J. Preiner, J. Hu, S. Hann, W. Wanek, A. Richter, pH-dependent bioavailability, speciation, and phytotoxicity of tungsten (W) in soil affect growth and molybdoenzyme activity of nodulated soybeans, Environ. Sci. Technol. 52 (2018) 6146–6156, https://doi.org/10.1021/acs.est.7b06500.

[32] J.S. Judge, A study of the dissolution of SiO_2 in acidic fluoride solutions, J. Electrochem. Soc. 118 (1971) 1772, https://doi.org/10.1149/1.2407835.

[33] H. Du, Y. Li, D. Wan, C. Sun, J. Sun, Tungsten distribution and vertical migration in soils near a typical abandoned tungsten smelter, J. Hazard Mater. 429 (2022) 128292, https://doi.org/10.1016/j.jhazmat.2022.128292.

[34] U.S. Environmental Protection Agency, Method 3050B: Acid digestion of sediments, sludges, and soils, 1996. Available at https://www.epa.gov/hw-sw846/sw-846-test-method-3050b-acid-digestion-sediments-sludges-and-soils. (Accessed 17 January 2024).

[35] U.S. Environmental Protection Agency, Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils, 2007. Available at https://www.epa.gov/esam/us-epa-method-3051a-microwave-assisted-acid-digestion-sediments-sludges-and-oils. (Accessed 17 January 2024).

[36] U.S. Environmental Protection Agency, Method 3052: Microwave assisted acid digestion of siliceous and organically based matrices, 1996. Available at https://www.epa.gov/hw-sw846/sw-846-test-method-3052-microwave-assisted-acid-digestion-siliceous-and-organically-based. (Accessed 17 January 2024).

[37] X. Chen, F. Guo, Q. Chen, X. Liu, Z. Zhao, Leaching tungsten and rare earth elements from scheelite through H_2SO_4–H_3PO_4 mixed acid decomposition, Miner. Eng. 156 (2020) 106526, https://doi.org/10.1016/j.mineng.2020.106526.

[38] Z. Yu, J. Sun, M. Jing, X. Cao, F. Lee, X. Wang, Determination of total tin and organotin compounds in shellfish by ICP-MS, Food Chem. 119 (2010) 364–367, https://doi.org/10.1016/j.foodchem.2009.05.079.

[39] D.L. Parkhurst, C. Appelo, Description of input and examples for PHREEQC version 3—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, Denver, 2013, pp. 1-497. Available only at https://pubs.usgs.gov/tm/06/a43/. (Accessed 17 January 2024).

[40] J.P. Gustafsson, Visual MINTEQ 4.0 user guide, 2022. Available at https://vminteq.com/download/. (Accessed 17 January 2024).

[41] G. Rozantsev, O. Sazonova, Thermodynamic parameters of interconversions of isopolyanions in solutions of tungsten (VI), Russ. J. Coord. Chem. 31 (2005) 552–558, https://doi.org/10.1007/s11173-005-0135-x.

[42] K. Zare, P. Lagrange, J. Lagrange, Determination and comparison of stability constants of vanadium (V), molybdenum (VI), and tungsten (VI) aminocarboxylate complexes, J. Chem. Soc., Dalton Trans. (1979) 1372–1376, https://doi.org/10.1039/DT9790001372.

[43] R. Thomas, Practical Guide to ICP-MS: a Tutorial for Beginners, second ed., CRC Press, Boca Raton, 2008, pp. 115–150.

[44] H.J. Van de Wiel, Determination of elements by ICP-AES and ICP-MS, Horozontal. (2004) 1-19. Available at https://horizontal.ecn.nl/docs/society/horizontal/hor_desk_19_icp.pdf. (Accessed 17 January 2024).

[45] G. Jenner, H. Longerich, S. Jackson, B. Fryer, ICP-MS—a powerful tool for high-precision trace-element analysis in Earth sciences: evidence from analysis of selected USGS reference samples, Chem. Geol. 83 (1990) 133–148, https://doi.org/10.1016/0009-2541(90)90145-W.

[46] F. Vanhaecke, H. Vanhoe, R. Dams, C. Vandecasteele, The use of internal standards in ICP-MS, Talanta 39 (1992) 737–742, https://doi.org/10.1016/0039-9140(92)80088-U.

[47] H. Li, J. Yang, K. Li, Tungsten Metallurgy, Central South University Press, Changsha, 2010.

[48] J.P. Launay, Reduction de l'ion metatungstate: Stades eleves de reduction de $H_2W_{12}O_{40}^{6-}$, derives de l'ion $HW_{12}O_{40}^{7-}$ et discussion generale, J. Inorg. Nucl. Chem. 38 (1976) 807–816, https://doi.org/10.1016/0022-1902(76)80361-2.

[49] N.I. Gumerova, A. Rompel, Polyoxometalates in solution: speciation under spotlight, Chem. Soc. Rev. 49 (2020) 7568–7601, https://doi.org/10.1039/D0CS00392A.

[50] J. Martins, F. Delmas, H. Casquinha, S. Costa, The influence of particle size of raw materials on the final WO_3 grain size, Hydrometallurgy 67 (2002) 117–123, https://doi.org/10.1016/S0304-386X(02)00162-7.

[51] Q. Guo, B. Planer-Friedrich, K. Yan, Tungstate thiolation promoting the formation of high-tungsten geothermal waters and its environmental implications, J. Hydrol. 603 (2021) 127016, https://doi.org/10.1016/j.jhydrol.2021.127016.

[52] D.A. Manning, P. Henderson, The behaviour of tungsten in granitic melt-vapour systems, Contrib. Mineral. Petrol. 86 (1984) 286–293, https://doi.org/10.1007/BF00373674.

[53] M. Pichavant, D. Manning, Petrogenesis of tourmaline granites and topaz granites; the contribution of experimental data, Phys. Earth Planet. In. 35 (1984) 31–50, https://doi.org/10.1016/0031-9201(84)90032-3.

[54] H. Jung, J. Hwang, H. Chun, B. Han, Elucidation of hydrolysis reaction mechanism of tungsten hexafluoride (WF_6) using first-principles calculations, J. Ind. Eng. Chem. 70 (2019) 99–102, https://doi.org/10.1016/j.jiec.2018.10.024.

[55] H. Wang, P. Liu, X. Chen, X. Liu, A. Chen, J. Li, L. He, F. Sun, Z. Zhao, Efficient dissolution of tungstic acid by isopolytungstate solution based on the polymerization theory of tungsten, Hydrometallurgy 209 (2022) 105835, https://doi.org/10.1016/j.hydromet.2022.105835.

[56] V. Sydorchuk, V. Zazhigalov, S. Khalameida, J. Skubiszewska-Zięba, B. Charmas, R. Leboda, Deposition of tungsten heteropolycompounds on activated silica surface, Colloids Surf. A Physicochem. Eng. Asp. 341 (2009) 53–59, https://doi.org/10.1016/j.colsurfa.2009.03.038.

[57] G.S. Frankel, J.D. Vienna, J. Lian, J.R. Scully, S. Gin, J.V. Ryan, J. Wang, S.H. Kim, W. Windl, J. Du, A comparative review of the aqueous corrosion of glasses, crystalline ceramics, and metals, npj Mater. Degrad. 2 (2018) 15, https://doi.org/10.1038/s41529-018-0037-2.

[58] M. Cui, M. Gomes, Impacts of manganese oxides on molybdenum and tungsten speciation and implications for their geochemistry in aquatic environments, Geochem. Cosmochim. Acta 312 (2021) 217–234, https://doi.org/10.1016/j.gca.2021.07.009.

[59] S. Rakshit, B. Sallman, A. Davantés, G. Lefèvre, Tungstate (VI) sorption on hematite: an in situ ATR-FTIR probe on the mechanism, Chemosphere 168 (2017) 685–691, https://doi.org/10.1016/j.chemosphere.2016.11.007.

[60] K.J. Lamble, S.J. Hill, Microwave digestion procedures for environmental matrices, Analyst 123 (7) (1998) 103–133, https://doi.org/10.1039/A800776D.

[61] A.J. Kennedy, D.R. Johnson, J.M. Seiter, J.H. Lindsay, R.E. Boyd, A.J. Bednar, P. G. Allison, Tungsten toxicity, bioaccumulation, and compartmentalization into organisms representing two trophic levels, Environ. Sci. Technol. 46 (17) (2012) 9646–9652, https://doi.org/10.1021/es300606x.

[62] J.H. Lindsay, A.J. Kennedy, J.M. Seiter-Moser, A.J. Bednar, R.E. Boyd, D. R. Johnson, P. Allison, R.V. Tappero, Uptake kinetics and trophic transfer of tungsten from cabbage to a herbivorous animal model, Environ. Sci. Technol. 51 (23) (2017) 13755–13762, https://doi.org/10.1021/acs.est.7b04376.