1 **Effects of Tungstate Polymerization on Tungsten(VI) Adsorption on**
2 **Ferrihydrite**

3
4 Jing Sun ^{1,#} and Benjamín C. Bostick ^{2,*}

5
6 ¹ *Dept of Earth Sciences, Dartmouth College, HB 6105 Fairchild, Hanover, NH 03755*

7 ² *Lamont-Doherty Earth Observatory, PO Box 1000, 61 Route 9W, Palisades, NY 10964*

8
9 * Corresponding Author.

10 *Phone: (845) 365-8659; Fax: (845) 365-8155; Email: bostick@ldeo.columbia.edu.*

11
12 [#] Current Address.

13 *Dept of Earth and Environmental Sciences, Columbia University, Mail Code 5505, New York, NY 10027*

ABSTRACT

Tungsten (W) is expected to adsorb to soil minerals, but does not appear to do so in many environments. To explain this behavior, adsorption experiments were performed over a variety of W(VI) solution compositions with different extents of W polymerization, on ferrihydrite. Tungsten adsorption was more extensive at circumneutral pHs and in systems with lower W(VI) concentrations, conditions under which tungstate rather than polytungstate was stable or the transformation to polytungstates was inhibited. Polytungstates are not as particle-reactive as tungstate monomers. Silicate and phosphate suppressed W(VI) adsorption. At high pHs, their impact resulted from competitive adsorption; at pH 4 – 7, suppressed adsorption was attributed to incorporation of tungstate into persistent polyoxometalates (POMs). Systems containing phosphotungstate (a model POM) exhibited limited adsorption initially, but adsorption increased over time as phosphotungstate depolymerized. The structure of adsorbed W(VI) was examined using X-ray absorption spectroscopy, which suggested that tungstates often represented the bulk of adsorbed W(VI), even when POMs were the primary species in solution. Many polytungstates and POMs are metastable; the slow transformations between POMs and tungstate could affect adsorption over extended periods. Adsorption kinetics data confirmed that W(VI) adsorption could take more than 2 months to reach equilibrium. The results suggest that tungstate polymerization can significantly decrease W adsorption, and thereby potentially mobilize it in the environment.

KEYWORDS

Tungsten solubility; Solution speciation; Tungstates; Polytungstates; POMs; Adsorption on ferrihydrite

1. INTRODUCTION

Tungsten (W) based products have been widely used in various industrial and technological applications since its discovery (Dermatas et al., 2004; Koutsospyros et al., 2006; Lassner and Schubert, 1999; Petkewich, 2009). It also has been used in munitions for more than 50 years as a “green” alternative to lead or depleted uranium (Clausen and Korte, 2009; Dermatas et al., 2004). The demand for W has been expanding, partially because of the general assumption that W was neither toxic nor soluble (Dermatas et al., 2004; Koutsospyros et al., 2006). However, trace levels of W in drinking water were implicated as a possible cause of childhood leukemia in Fallon, Nevada (Seiler et al., 2005), and a number of subsequent investigations have demonstrated that W might be toxic to various organisms (Babula et al., 2008; Inouye et al., 2006; Johnson et al., 2010; Kelly et al., 2012; Lemus and Venezia, 2015; Tyrrell et al., 2013). Recent studies also have suggested that W is more soluble and therefore probably more mobile than previously recognized (e.g., Bednar et al., 2009; Bostick et al., Submitted.; Dermatas et al., 2004; Sen Tuna et al., 2012). Despite of the growing concerns, the existing information regarding the processes that regulate W solid-solution partitioning is limited, and in some cases, might be inconsistent with environmental data (Koutsospyros et al., 2006; Petkewich, 2009).

Tungsten is a metallic transition element and easily oxidized (Bostick et al., Submitted.; Dermatas et al., 2004). Tungsten often exists in natural environments as hexavalent W(VI) (Baes and Mesmer, 1986; Koutsospyros et al., 2006), which commonly forms polyoxometalates (POMs) and thus has complex solution chemistry (Lassner and Schubert, 1999; Pope and Muller, 1991). In concentrated neutral and acidic solutions, tungstate tetrahedra (WO_4^{2-}) can condense to a variety of (homonuclear) polytungstates, having variable chemical and toxicological properties (Baes and Mesmer, 1986; Karakonstantis et al., 1996; Lassner and Schubert, 1999; Pope and Muller, 1991; Strigul, 2010; Strigul et al., 2009; Strigul et al., 2010). Although some polytungstates are thermodynamically unstable species, others are long-lived intermediates that persist for kinetic reasons, including $\text{W}_4\text{O}_{12}(\text{OH})_4^{4-}$, $\text{HW}_6\text{O}_{20}^{3-}$, $\text{W}_6\text{O}_{20}(\text{OH})^{5-}$ and $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ (Baes and Mesmer, 1986; Lassner and Schubert, 1999). Tungsten(VI) solution speciation is further complicated by formation of (substituted) heteropolytungstates, called polyoxometalates (Pope and Muller, 1991), including Keggin clusters such as phosphotungstate $\text{PW}_{12}\text{O}_{40}^{3-}$ and silicotungstate $\text{SiW}_{12}\text{O}_{40}^{4-}$. Tungsten POMs can be produced from the mixture of (poly)tungstates and common oxyanions, such as phosphate, silicate and arsenate (Bednar et al., 2008; Chen et al., 2004; Himeno et al., 2005; Johnson et al., 2010; Keggin, 1934). Although their formation has long been recognized, most POMs lack well-established equilibrium constants describing their formation. Under comparable conditions, POMs are presumed to be more stable than their corresponding polytungstate analogues

72 (“conventional” polytungstates with the same number of W atoms) (Chen et al., 2004; Keggin, 1934;
73 Lassner and Schubert, 1999).

74
75 Adsorption on iron (Fe) (oxyhydr)oxides appears to be crucial in W(VI) retention in natural systems
76 (Bostick et al., Submitted.; Johannesson et al., 2013). Tungstate adsorption on such phases is believed to
77 be strong and rapid at circumneutral pHs (Dermatas et al., 2004; Gustafsson, 2003; Johannesson et al.,
78 2013; Xu et al., 2006). Tungstate adsorption is so strong that it is capable of displacing phosphate from
79 adsorption sites at acidic pHs (Gustafsson, 2003). However, this is in opposition to observations of high
80 aqueous W concentrations in some environmental systems (Bednar et al., 2008; Clausen and Korte, 2009;
81 Dermatas et al., 2004; Johannesson et al., 2013; Strigul et al., 2005). The equilibrium constants derived
82 from Gustafsson (2003), in which tungstate adsorption on ferrihydrite was studied, considerably under-
83 predict aqueous W concentrations in real soils and sediments (Bostick et al., Submitted.; Seiler et al.,
84 2005). One possible explanation is that equilibrium solution speciation was assumed in the experimental
85 systems of Gustafsson (2003), despite the fact that many metastable polytungstate ions could form.
86 Environmental systems may also contain W POMs, which are even more stable. An unambiguous
87 understanding of the links between W(VI) solution composition and its adsorption properties, especially
88 the basic adsorption behavior of W(VI) polyoxoanions, therefore, is required.

89
90 The main objective of this study was to examine the impacts of W(VI) polymerization on the rate and
91 extent of W(VI) adsorption on ferrihydrite. By varying total W concentration, pH or pre-equilibration
92 temperature, a variety of systems with different combinations of tungstates and (metastable)
93 polytungstates were investigated. By adding phosphates and silicates to the systems or allowing different
94 reaction time for systems started with phosphotungstate (a model POM), the impacts from
95 formation/depolymerization of POMs were also studied. In addition, the structure of solid-phase W(VI)
96 on ferrihydrite was investigated using synchrotron based X-ray absorption spectroscopy (XAS). In all, the
97 results reveal the weak adsorption and lack of kinetic stability of W(VI) polyoxoanions compared to
98 tungstate monomers, both of which have a profound effect on W solubility in waters, and potentially W
99 mobilization and bioavailability.

100 101 **2. MATERIALS AND METHODS**

102 **2.1. Ferrihydrite Synthesis**

103 Ferrihydrite used in this study was synthesized following Schwertmann and Cornell (2000): ferric nitrate
104 solution was stirred vigorously and potassium hydroxide solution was added to bring the pH to 7 – 8; the
105 resulting solid-solution slurry was centrifuged and dialyzed until free of electrolytes, and the solid was

freeze dried and stored as powder. (All chemicals used for ferrihydrite synthesis and the rest of this study were of reagent grade or higher purity; Milli-Q water used had a resistivity of 18.2 M Ω cm.) Solid identity was confirmed as 2-line ferrihydrite by X-ray diffraction (XRD) of random powder mounts (Supplementary Material **Figure S1**). The surface area of ferrihydrite was 273 ± 2 m² g⁻¹, as determined by a 3-point Brunauer–Emmett–Teller (BET) isotherm using nitrogen gas as adsorbate, although the actual surface area of ferrihydrite is likely underestimated by the BET method (Dzombak and Morel, 1990; Gustafsson, 2003).

2.2. Adsorption Thermodynamics: Isotherms and Effect of pH

The extent of tungstate polymerization in aqueous solutions can change with pH and W concentration. The W(VI) solution speciation, i.e. initial speciation and its evolution over time, may influence adsorption. Thermodynamic adsorption experiments as a function of W concentration at constant pH (adsorption isotherms) and as a function of pH at constant W concentration (adsorption envelopes), therefore, were conducted to assess how various W(VI) species adsorb onto ferrihydrite (**Table 1**). The experiments varied in the initial species of W(VI), as either tungstate or phosphotungstate. The effect of the presence of phosphate or silicate on W adsorption was also examined.

2.2.1. Adsorption Isotherms.

To perform adsorption isotherm experiments, buffered tungstate solutions with initial W concentrations of 0 to 100 mg L⁻¹ were prepared in capped 50 mL polypropylene centrifuge tubes. Tungstate was added from a freshly prepared stock solution of sodium tungstate (Na₂WO₄). Most of the solutions were buffered with 10 mM 3-(N-morpholino)propanesulfonic acid (MOPS), and adjusted to pH 7 with 0.1 M sodium hydroxide (NaOH) or hydrochloric acid (HCl) and measured using a calibrated pH electrode. Parallel isotherm experiments were performed with the presence of phosphate (added as potassium phosphate) or silicate (added as sodium silicate). Both phosphate and silicate were added in slight excess to yield equivalent soluble concentrations, either 10 or 20 mg L⁻¹ phosphorus (P) or silicon (Si), after adsorbing to ferrihydrite. Additional isotherms were also obtained at pH 4 and 8.5, buffered with 10 mM acetic acid/sodium acetate and tris(hydroxymethyl)methylamine (Tris), respectively. Prior to ferrihydrite addition, the pH-adjusted solutions were pre-equilibrated (heated) at 40°C for 24 hours to facilitate the formation of polymeric species (Bar-Nahum et al., 2007; Lassner and Schubert, 1999; Pope and Muller, 1991; Spiccia and Casey, 2007; Zhu et al., 2003), which might otherwise be limited during the investigated time period. The resulting solutions thus contained a mixture of W(VI) species, including monomeric tungstate and a spectrum of ill-defined W(VI) polyoxoanions. After pre-equilibration, they were readjusted to the target pHs, and subsampled for initial bulk elemental concentrations. Ferrihydrite

was then added to the solutions, with a solid density of 0.5 g L^{-1} . The suspensions were equilibrated for 48 hours at room temperature (22°C) to ensure near steady-state adsorption (although based on our kinetics data, not true equilibrium due to the slow transformations in W solution speciation), and then filtered to $0.2 \text{ }\mu\text{m}$. The W(VI)-bearing ferrihydrite on filter membranes was immediately stored at -20°C until it was analyzed by XAS. The solutions were preserved with a 0.2% ammonium hydroxide/0.1% ethylenediamine tetraacetic acid (EDTA) matrix, which was necessary to maintain aqueous W (W is insoluble in acidic matrix if no complexation occurs; thus the method normally used to preserve samples in dilute HCl or HNO_3 is ineffective) (Bostick et al., Submitted.). The solutions were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo IRIS Intrepid II XSP with radial optics) for aqueous W, P and Si concentrations. Each sample was run three times and averaged. Quantification was based on comparison to a five-point standard curve. Tungsten is spectrally rich, with several lines suitable for analysis; the 207.9 nm emission line was used for quantification, which had a detection limit of $6 \text{ }\mu\text{g L}^{-1}$. Accuracy of ICP-OES analysis was verified against known quality controls. No ferrihydrite controls were used to confirm no loss of W onto the container walls or filters.

2.2.2. Adsorption Envelopes.

The adsorption envelopes were conducted on a series of unbuffered W(VI) solutions, in which the initial W concentration was 10 mg L^{-1} . The adsorption envelopes were created by varying pH between 3 and 10 with different amounts of 0.1 M NaOH or HCl. Tungstate adsorption envelopes were measured using pre-equilibrated tungstate solutions (tungstate added as Na_2WO_4 , pH adjusted, and the resulting solution pre-equilibrated for 24 hours at 40°C) and 48 hour reaction time with 0.5 g L^{-1} ferrihydrite, similar to isotherm experiments. Parallel adsorption envelopes were performed with solutions also containing silicate (10 mg L^{-1} Si, added as sodium silicate, and pre-equilibrated), to assess the potential effect of competitive adsorption and/or POMs formation. Adsorption envelopes for phosphotungstate $\text{PW}_{12}\text{O}_{40}^{3-}$ (PWO) were measured by adding 10 mg L^{-1} from a stock PWO solution which was freshly prepared by dissolving phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, a Keggin-type heteropolyacid) in Milli-Q water. Phosphotungstate solutions were reacted with ferrihydrite for either 48 hours, during which the depolymerization of phosphotungstate may partially occur and produce various (poly)tungstates, or 2 hours, which is sufficient for adsorption to proceed but short enough to minimize depolymerization. The final “steady-state” pH of each sample was measured, and the suspensions were then filtered to $0.2 \text{ }\mu\text{m}$. The solutions and solids were preserved and analyzed as described above. Replicate experiments were also performed and established that the results were reproducible within $100 \pm 7\%$.

2.3. Adsorption Kinetics

To ascertain how W(VI) adsorption proceeds over time with the evolution of W(VI) solution speciation, a series of kinetics experiments were conducted with buffered suspension containing 0.5 g L⁻¹ ferrihydrite, 10 mg L⁻¹ total W (added as Na₂WO₄) and 10 mg L⁻¹ dissolved Si (Table 1). Kinetics experiments were conducted in capped 500 mL high-density polyethylene bottles. They varied in pH or pre-equilibration temperature, to form polyoxoanion to different extents. Experiments performed at pH 6, 7 and 8 were created by buffering with 10 mM 2-(N-morpholino)ethanesulfonic acid (MES), MOPS and Tris, respectively. Prior to the addition of ferrihydrite, three experiments buffered at pH 6, 7 and 8 were pre-equilibrated (heated) for 24 hours at 40°C, and another two experiments buffered at pH 7 were pre-equilibrated for 24 hours also at 22 and 60°C. Solution pH should impact not only the extent of polytungstate formation but their stability, with polytungstates being more (meta)stable at acidic conditions: pH 6 > pH 7 > pH 8 (Lassner and Schubert, 1999). The pre-equilibration at higher temperatures should favor additional polymeric tungstates (Lassner and Schubert, 1999); therefore, the amount of polymeric complexes present at the onset of kinetics experiments follows the order: 60°C > 40°C > 22°C. Kinetics experiments began (time zero) once ferrihydrite was added to the pre-equilibrated solutions. Subsamples were collected at various time intervals over the following 8 weeks, filtered and preserved. The aqueous W concentrations in subsamples were analyzed using ICP-OES as described above.

2.4. X-ray Absorption Spectroscopy: Solid-phase Analysis

Tungsten extended X-ray absorption fine structure (EXAFS) spectra were collected on a representative suite of W(VI)-containing ferrihydrite from the above adsorption experiments. This technique can detect even trace amounts of solid W phases and provide a quantitative measurement of their presence (Bostick et al., Submitted.). The analysis was conducted at the Stanford Synchrotron Radiation Laboratory (SSRL) on Beamline 4-1. The beamline was configured with a Si(220) monochromator and a 90 degree phi angle. A 13-element germanium (Ge) detector in combination with 6 µm copper (Cu) filter was used to collect spectra in fluorescence mode. Scans were calibrated to the W L₃ edge of W metal (10207 eV) using a metal foil placed between the second and third ionization chambers. Each of the samples was sealed in Kapton tape and mounted between the first and second ionization chambers. Tungsten EXAFS spectra were collected on samples from -235 to +600 eV at the edge. At least three EXAFS scans were obtained for each sample and then averaged. There was no noticeable change in structure between parallel scans.

The spectra were processed using the SixPACK software (Webb, 2005). Tungsten EXAFS spectra were converted to chi functions with k³ weighting. Least squares linear combination fitting of k³-weighted spectra was conducted to determine the relative abundance of each of the references. In this case, there

were two references – ammonium tungstate ((NH₄)₂WO₄), representing monomeric tungstates, and H₃PW₁₂O₄₀, representing polytungstates and POMs. (Target transform of the k³-weighted spectra supported the use of these two references, Supplementary Material **Table S1**.) These two references should be regarded as representative model compounds rather than discrete species (Bostick et al., Submitted.). Fitting with H₃PW₁₂O₄₀ does not imply that phosphotungstic acid is present (although it may be), rather it is representative of a spectrum of polymeric complexes more generally. Although in acidic conditions WO₃·H₂O_(s) (amorphous tungstic acid, also written as H₂WO₄) may form (Lassner and Schubert, 1999), including WO₃·H₂O_(s) in the fitting was not necessary. The EXAFS spectra were also Fourier transformed (FT) to produce the radial structure functions (RSF), which were used to verify the identity of tungstate and/or polymeric tungstate. Shell fitting using theoretical phase and amplitude functions was also done. For these fits, the coordination number, interatomic distance, and Debye-Waller factors of W-O and W-W or W-Fe shells were measured. Due to the limited data range, the Debye-Waller factors and interatomic distances of W-O in tungstate and polytungstate were constrained based on model compound values. This is discussed in more detail in the Supplementary Material.

3. RESULTS AND DISCUSSION

3.1. Thermodynamics: Adsorption of Tungsten(VI) Polyoxoanions.

3.1.1. Isotherms: Adsorption of Tungsten(VI) on Ferrihydrite.

Adsorption isotherms in this study were performed on suspensions containing numerous metastable W(VI) aqueous species and thereby should not strictly be regarded as equilibrium controlled. As such, our data provide a means of evaluating general adsorption patterns of the metastable species over the studied timescale. Gustafsson (2003) measured adsorption of fresh sodium tungstate solutions. Because these solutions were not fully equilibrated, those solutions presumably contained primarily tungstate, WO₄²⁻. Their data thus accurately describes the adsorption of monomeric tungstate on ferrihydrite, but may differ considerably from the adsorption of metastable polyoxoanions that should be present in our experiments.

The tungstate adsorption isotherm at pH 7 (**Figure 1**) showed substantial adsorption at low total W(VI) concentrations and a clear asymptote in sorbed W concentrations. This characteristically high retention on ferrihydrite is consistent with reported tungstate adsorption isotherms (Gustafsson, 2003; Xu et al., 2006). Our data, however, differ somewhat from other studies at low pHs. Tungstate adsorption, like many other anions, is thought to be pH dependent, with increased adsorption occurring at acidic pH and little at pH > 9 (Gustafsson, 2003). In contrast, we observed much lower retention at pH 4 than at neutral pH (**Figure 1**). We attribute this contradiction to differences in experimental procedures that influence the abundance of aqueous W(VI) polyoxoanions, which adsorb on mineral surfaces differently than do monomeric

tungstates. As described above, tungstates condense to polymeric complexes at acidic pHs (Baes and Mesmer, 1986; Koutsospyros et al., 2006; Lassner and Schubert, 1999). Because of the pre-equilibration (heating) step and long reaction time, W(VI) polymeric complexes were relatively abundant in our experiments. However, when there is no pre-equilibration, WO_4^{2-} may persist in (weakly) acidic solutions despite its thermodynamic instability under the experimental conditions. If so, the short (24 hour) reaction with fresh tungstate stock solutions employed in Gustafsson (2003) should contain mostly WO_4^{2-} . Based on the comparison of our experiments with those of Gustafsson (2003), polymeric tungstates appear to adsorb less than monomeric species at equivalent pH.

3.1.2. Isotherms: Effect of Other Components on Tungsten(VI) Adsorption.

A number of common environmental species could compete with W(VI) for surface sites and also alter its solution speciation, and thereby influence W(VI) adsorption. To assess such effects, we examined the effect of phosphate and silicate on the extent of W(VI) adsorption. Even at low concentrations (10 mg L^{-1}), these anions significantly inhibited the extent of W retention on ferrihydrite at pH 7 (Figure 2A). These anions could adsorb to ferrihydrite under the experimental conditions, but surface complexation models suggest that these concentrations only decrease available surface sites by a few percent (Gustafsson, 2003; Xu et al., 2006). Therefore, the addition of phosphate and silicate must have affected the system in other ways.

One way to explain the decreased adsorption is that tungstates can complex with phosphate and silicate and produce POMs in solutions. These POMs probably include the relatively common and stable Keggin clusters, $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$, present as a central tetrahedron of XO_4 ($\text{X} = \text{P}$ or Si) surrounded by twelve octahedra of WO_6 (Castillo et al., 1996; Chen et al., 2004; Keggin, 1934; Pope and Muller, 1991), although the equilibrium constants for their formation are not well-established:

The formation of POMs depends both on W concentration and pH (similar to the formation of polytungstates), and generally results in more stable anions than the corresponding “conventional” polytungstates (Cruywagen, 2000; Lassner and Schubert, 1999). The Keggin-type species are commonly formed in slightly acidic solutions where the combination of H^+ and WO_4^{2-} activities are maximized (WO_4^{2-} activity would decrease under more acidic conditions due to the formation of polytungstates and $\text{WO}_3 \cdot \text{H}_2\text{O}_{(\text{s})}$). It is difficult to determine the quantity of POMs produced in these experiments, but based on common reaction stoichiometries (Reactions 1 and 2), the amounts of phosphate and silicate used were more than enough to convert the tungstates to one or more kinds of POMs. Assuming these POM species

have low adsorption affinities for ferrihydrite, their presence would effectively decrease the extent of adsorption by decreasing the amount of particle-active WO_4^{2-} (see below).

The aqueous phosphate concentration is minimally impacted by W(VI) because only a small fraction of phosphate is complexed in POMs. POM formation can indirectly enhance phosphate adsorption though, because formation of POMs prevents tungstate from competing for adsorption sites. The difference between observed and modeled P concentrations, therefore, would increase as the W concentration increases because the amount of W(VI) polymeric species increases, exactly as observed in our experiments (Figure 2B).

3.1.3. Adsorption Envelopes.

Solution pH should exert a controlling effect on W(VI) adsorption by affecting surface site protonation, and tungstate complexation and hydrolysis. Indeed, W(VI) adsorption envelopes show a complex relationship between pH and adsorption (Figure 3A). The most extensive adsorption occurred at around pH 6.5. Adsorption was minimal at high pH, increased as pH decreased toward neutral pH, and decreased again between neutral pH and pH 4. Below pH 4, W retention on ferrihydrite significantly increased, probably due to W-containing precipitates such as $\text{WO}_3 \cdot \text{H}_2\text{O}_{(s)}$ (Gustafsson, 2003). The presence of silicate decreased the extent of adsorption, but did not change the shape of the W(VI) adsorption envelope compared to that of tungstate alone.

Comparisons between experimental (observed) and theoretical (modeled) adsorption were used to evaluate potential W(VI) adsorption mechanisms (Figure 3A). The thermodynamically stable W(VI) solution phases and equilibrium tungstate adsorption on ferrihydrite as a function of pH were modeled in Visual MINTEQ, which uses formation constants from Gustafsson (2003). Observed W retention is consistent with model predictions at high pHs, but inconsistent between pH 7 and 4. The agreement between modeled and observed adsorption above pH 7 suggests that the modeled reactions based on WO_4^{2-} adsorption faithfully reproduce experimental results where WO_4^{2-} is the major solution species. The suppressed W retention between pH 7 and 4, however, indicates that processes or species present in the experiments cannot be well described by the existing model, and that precipitation, which would increase sorption, is not occurring. This pH range is where WO_4^{2-} condenses to polytungstates and also to POMs if silicates are present (Baes and Mesmer, 1986; Lassner and Schubert, 1999; Pope and Muller, 1991). The transition between monomeric tungstate- and polymeric tungstate-dominance correlates with the pH at which observed and modeled adsorption diverges (Figure 3B). We thus attribute the model inconsistency to the weak adsorption characteristics of polytungstates and POMs compared to monomeric

tungstate. Bednar et al. (2009) also found that the presence of phosphate dramatically increased W solubility in acidic solutions. Although it is difficult to assess the concentrations of specific W(VI) polyoxoanions, due to the lack of thermodynamic data, their formation evidently plays a role in W(VI) solid-solution partitioning.

The adsorption affinity of POMs can be probed directly by conducting adsorption envelope experiments using PWO. PWO adsorption was suppressed relative to tungstate (Figure 4). The adsorption envelopes of PWO also varied considerably with reaction time, with solid-solution systems equilibrated for 48 hours resulting in more retention on ferrihydrite than those equilibrated for 2 hours. Part of this discrepancy could result from slow adsorption process, but tungstate adsorption on ferrihydrite is believed to be rapid (Dermatas et al., 2004; Gustafsson, 2003; Xu et al., 2006). The difference in retention with time, therefore, likely reflects slow changes in W(VI) solution speciation which accordingly led to changes in adsorption behavior. The parent 12-W PWO is only stable at low pH (and high concentration), and decomposes to smaller POMs (and produces H^+) over time and eventually to monomeric tungstate and phosphate in basic solutions (Holclajtner-Antunovic et al., 2008; Zhu et al., 2003). PWO added in unbuffered solutions decreased pH over time (data are not shown), with changes between initial and final pH in 48 hour solutions more than changes in 2 hour solutions, which can be explained by the production of H^+ during depolymerization. Because the depolymerization takes time, reactions that proceed for 2 hours should still contain primarily PWO. The diminished adsorption of PWO in the 2 hour systems is thus consistent with PWO's low adsorption affinity for ferrihydrite. This implies that the gradual depolymerization of PWO should lead to a continued increase in W adsorption, as was observed in the 48 hour systems. Bednar et al. (2008) also showed that the mobility of polymeric tungstates decreased over time, as W became more firmly bound to soil surface in neutral soils where the polymeric species decompose.

3.1.4. Structure of Solid-phase Tungsten(VI).

The EXAFS spectrum of tetrahedral monomeric tungstate is dominated by a highly ordered W-O shell at 1.78 Å (Bostick et al., Submitted.). The W atoms in polymeric tungstates are in a disordered octahedral environment with two separable W-O shells. Because of their disordered nature, the two W-O shells have much lower intensity than the single W-O shell in tungstates. For polymeric tungstates, besides the two W-O shells, there are additional shells between 3 and 4.5 Å that are attributed to W-W and W-Fe shells (Bostick et al., Submitted.; Martin et al., 1998). Although it is difficult to differentiate between various W(VI) polyoxoanions due to their structural similarity, it is quite simple for W EXAFS to differentiate between W(VI) polyoxoanions and tungstates (Bostick et al., Submitted.).

Using EXAFS linear combination fitting, the fraction of monomeric and polymeric tungstates retained in each solid sample was determined. Solid-phase W(VI) samples were from three types of experiments (Table 2): PWO adsorption envelopes, tungstate adsorption envelopes, and tungstate adsorption isotherms containing phosphate. At pH > 9 and when the W concentration was low, the dominant ($\geq 85\%$) W species on ferrihydrite surfaces were adsorbed monomeric tungstates. This is consistent with the predominance of WO_4^{2-} in solution under those conditions. In most systems where polymerization was prevalent (as discussed above), EXAFS spectroscopy suggests that solid-phase monomeric tungstates were still in the majority ($\geq 51\%$). This implies that tungstates adsorb on ferrihydrite preferentially, in agreement with the macroscopic results of our adsorption experiments. Polytungstates and/or POMs were also present and, in some samples, accounted for $\geq 40\%$ of the W(VI) (Table 2). Shell fitting of three such samples, from the three experiment types respectively, was used to further characterize the surface species that are present (Figure 5). This fitting revealed W-Fe and W-W shells (See Supplementary Material Table S2 and Figure S2.) The samples were intentionally selected from slightly acidic to neutral systems to minimize the spectral contribution of $\text{WO}_3 \cdot \text{H}_2\text{O}_{(s)}$, thereby the W-W backscattering corresponds to the W-W shells in polymeric tungstates. The W-Fe shell at 3.54 Å is consistent with bidentate binuclear complexation of tungstate similar to that observed in wolframite (FeWO_4). Care should be exercised in interpreting shell fitting results, however, due to the possible presence of multiple species, each with a complicated structure.

It is interesting to observe adsorbed polytungstates, despite their apparently weak affinity for mineral surfaces. One explanation reconciling their presence involves an associative mechanism (e.g., Mikola et al., 1999; Vissenberg et al., 2000). Through this mechanism, adsorbed tungstates can be activated towards further reaction and gradually incorporate additional tungstates:

The coordination environment of W atoms in adsorbed tungstates is thereby altered directly on mineral surfaces and becomes similar to that in polymeric complexes. The surface may also catalyze polymerization in this manner. Once polymerized (Reaction 3), stable polytungstates should be easily released during leaching procedures. Extensive leaching loss (desorption) indeed has been observed in such systems (Bostick et al., Submitted.; Clausen and Korte, 2009; Dermatas et al., 2004).

3.1.5. Adsorption Thermodynamics.

Tungstate adsorption was highly affected by reaction conditions that affect its solution speciation, including pH and solution composition. Because solutions contained many unidentified tungstate species,

it is difficult to describe chemical equilibria for adsorption. However, our data indicate that polymeric W(VI) species have lower adsorption affinities for mineral surfaces than tungstate, WO_4^{2-} . Furthermore, the presence of silicates and phosphates influences adsorption, likely by stabilizing W POMs in solution. Given that metastable W(VI) solution polyoxoanions can persist for weeks (Baes and Mesmer, 1986; Koutsospyros et al., 2006; Lassner and Schubert, 1999), and silicates and, to a lesser extent, phosphates are ubiquitous in natural environment, the formation of polytungstate and POM might be more prevalent than previously recognized and their effect on W solubility might be widespread, especially in W-contaminated systems where solution W concentrations are elevated and conducive to polymerization.

The tungstate polymerization could do more than enhance solubility. Conversion from monomeric tungstates to polymeric species may influence W toxicity via the same mechanism that Al eco-toxicity is elevated by the formation of Keggin type Al_{13} polycation (Etou et al., 2009). Indeed, Strigul et al. (2009, 2010) suggest that polytungstates are more toxic than monomeric tungstate. Increased solubility is also typically connected with amplified bioavailability and exposure (Traina and Laperche, 1999). Nevertheless, the sizes of some W(VI) polyoxoanions are large, such as the 12-W Keggin clusters, 18-W Wells–Dawson clusters and 30-W Preyssler clusters (Tarlani et al., 2005; Tarlani et al., 2006). Because the biological incorporation of these polymeric anions may be not as effective as that of small WO_4^{2-} , W bioavailability may be decreased by their formation.

3.2. Kinetics: Slow Tungsten(VI) Adsorption.

3.2.1. Kinetics Framework and Conceptual Model.

In most of the adsorption experiments above, the (poly)tungstate species present when adsorption started (directly added and forced to form because of elevated temperature) were not thermodynamically stable and should gradually convert to other species. The rates of conversion between various W(VI) solution species can differ widely, with many metastable polyoxoanions persisting for days to months (Lassner and Schubert, 1999). Because different W(VI) species have different affinities for mineral surfaces, W(VI) adsorption should respond at similar rates to the changes in its solution speciation.

The adsorption of tungstates to Fe (oxyhydr)oxides is rapid (Dermatas et al., 2004; Gustafsson, 2003; Xu et al., 2006). However, apparent equilibria for W(VI) adsorption on ferrihydrite in our kinetics experiments was not achieved or took weeks (Figure 6). These reactions are not well described by conventional kinetics expressions such as first- or second-order reactions, nor can they be described by diffusional or other physical processes. We attribute the sustained adsorption to the slow depolymerization of solution-persistent polymeric tungstates to their component ions (exemplified by

two-stage **Reaction 4**) (Kepert and Kyle, 1978; Koutsospyros et al., 2006; Lassner and Schubert, 1999; Pizzio et al., 1997; Smith and Patrick, 2002; Smith and Patrick, 2004; Zhu et al., 2003), followed by the rapid WO_4^{2-} adsorption on ferrihydrite (**Reaction 5**) (Gustafsson, 2003).

The highly condensed Keggin anion, silicotungstate, $\text{SiW}_{12}\text{O}_{40}^{4-}$ is adopted as the starting polymeric parent in **Reaction 4**. In the first stage of **Reaction 4**, $\text{SiW}_{12}\text{O}_{40}^{4-}$ partially decomposes, with removal of W=O units, to a POM with less W atoms, $\text{SiW}_9\text{O}_{34}^{10-}$, which is known to be the last POM species that persists in solution before complete depolymerization; in the second stage, $\text{SiW}_9\text{O}_{34}^{10-}$ completely decomposes to tungstate and silicate (Kepert and Kyle, 1978; Pizzio et al., 1997; Smith and Patrick, 2002; Smith and Patrick, 2004; Zhu et al., 2003). Given the stability of $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{SiW}_9\text{O}_{34}^{10-}$, they might exist more dominantly over other POMs and “conventional” polytungstates in the systems and contribute more measurably to the overall reactions (Baes and Mesmer, 1986; Bar-Nahum et al., 2007; Kepert and Kyle, 1978; Lassner and Schubert, 1999; Pizzio et al., 1997; Smith and Patrick, 2002; Smith and Patrick, 2004; Zhu et al., 2003). Therefore, the two-stage expression in **Reaction 4** is posited as the conceptual model. Nevertheless, many other polymeric anions might also form, depolymerize, and affect W(VI) partitioning.

3.2.2. Adsorption Kinetics: Qualitative Description.

Solution pH can influence the thermodynamic stability of W(VI) solution complexes, and the kinetics of polymerization/depolymerization and adsorption reactions. Thus pH should control both the extent and the rate of W(VI) adsorption. **Figure 6A** illustrates the uptake of W(VI) by ferrihydrite at pH = 6, 7 and 8, and shows that decreasing pH increased the rate of adsorption. Each system in **Figure 6A** was pre-equilibrated at 40°C to encourage the partial formation of POMs and polytungstates, with abundance and stability varying with pH. The experiments conducted at pH 6 and 7 had roughly equal levels of adsorption, and both were in excess of the level of adsorption at pH 8, which is consistent with results from adsorption envelopes. Although the equilibrium adsorption was nearly equal at pH 6 and 7, the adsorption reaction proceeded faster at pH 6. The overall rate at pH 8 was much slower, and it still did not reach equilibrium or even steady-state after almost 8 weeks.

The effect of pre-equilibration temperature further illustrates the role of slow depolymerization on the rate of W(VI) adsorption. Tungstates and silicates could combine as POMs in the solutions, especially in the

heated solutions, including silicotungstate, which is commonly synthesized by refluxing circumneutral tungstate solutions containing silicates at elevated temperatures (Lassner and Schubert, 1999). The experiments conducted with solutions pre-equilibrated at higher temperatures should have more abundant (metastable) polyoxoanions and thereby less adsorption, at the beginning. These experiments should have increased adsorption over time as the W(VI) polyoxoanions decompose, and eventually have equal amounts of adsorption following equilibration. Figure 6B describes three pH 7 systems that were compositionally identical but differ with respect to the pre-equilibration temperature. Initially, the system pre-equilibrated at room temperature experienced more rapid and complete adsorption than those pre-equilibrated at 40 and 60°C. After several weeks, which corresponds to the time required for depolymerization from polymeric tungstates to monomeric tungstates (Lassner and Schubert, 1999), adsorption in the 40 and 60°C systems converged.

3.2.3. Adsorption Kinetics: Quantitative Description.

Our experiments delineate the relationship between the evolution of W(VI) solution speciation and adsorption over time. Fitting kinetics data allows examination and extraction of quantitative information for the conceptual model (i.e., W(VI) depolymerization followed by WO_4^{2-} adsorption). As expected, the removal of W from solution cannot be fit with a single reaction model. Instead, the removal is well described by three separate ranges (Figure 7, which takes the system pre-equilibrated at 40°C and conducted at pH 6 for example), with a relatively fast reaction at the onset attributed to adsorption of tungstates and two subsequent slow reactions characteristic of the rate limiting depolymerization of polymeric species (idealized by the depolymerization sequence in Reaction 4). These three reactions can then be studied independently, using simple kinetic models.

Pseudo first-order expressions are often used to describe the kinetics of sorption on solid surfaces (Ho and McKay, 1998; Lagergren, 1898), and this type of expression is adopted for WO_4^{2-} adsorption on ferrihydrite:

$$\frac{dq_t}{dt} = k'_{\text{WO}_4^{2-}} \times (q_e - q_t) \quad (6)$$

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k'_{\text{WO}_4^{2-}} \times t \quad (7)$$

in which k' is the pseudo-first-order rate constant (in min^{-1}), q_t is the amount of sorbed W on ferrihydrite at time t , and q_e is the amount at equilibrium. The rate expressions for the depolymerization processes could be also described by pseudo first-order kinetics expressions with respect to the polymerized species:

$$\frac{d[\text{SiW}_{12}\text{O}_{40}^{4-}]_{aq}}{dt} = -k'_1 \times [\text{SiW}_{12}\text{O}_{40}^{4-}]_{aq} = -k''_1 \times [\text{H}^+]^m \times [\text{SiW}_{12}\text{O}_{40}^{4-}]_{aq} \quad (8)$$

$$\frac{d[SiW_9O_{34}^{10-}]_{aq}}{dt} = -k'_2 \times [SiW_9O_{34}^{10-}]_{aq} = -k''_2 \times [H^+]^n \times [SiW_9O_{34}^{10-}]_{aq} \quad (9)$$

Pseudo first-order rate constants were obtained for each of the three reactions (Table 3). The reaction in Range I occurred primarily over the first hour, in agreement with the rates of WO_4^{2-} adsorption (Dermatas et al., 2004; Gustafsson, 2003; Xu et al., 2006). The reactions that occurred later are much slower, with the length of the apparent reaction time ranging from a day to a few weeks.

Hydrogen⁺ activity, pH, should impact the reaction kinetics in all three ranges, because it can impact both adsorption and depolymerization. The reaction order with respect to H^+ activity (for example, the exponents, m and n, in Equation 8 and 9) can possibly be evaluated by comparing the pseudo first-order rate constants at a variety of pHs:

$$\frac{k'_{system1}}{k'_{system2}} = \left(\frac{[H^+]_{system1}}{[H^+]_{system2}} \right)^p \quad (10)$$

The rate constants at pH 6 indeed are larger than those at pH 7 and 8 (Figure 6A and Table 3). In range I, the pseudo first-order rate constant approximately doubles with a decrease of one unit in pH (a 10-fold change in H^+ activity), which suggests a fractional reaction order p for H^+ activity of about 0.3. The dependence of the rate constant on $[H^+]$ changes when proceeding to a different range. The variation in p in range II and III may reflect different mechanisms of depolymerization in different pH systems.

Regarding how pre-equilibration temperature impacts kinetics (Figure 6B and Table 3), our data suggest that higher pre-equilibration temperature decreased the overall rate of W retention on ferrihydrite, but its effect on the rate constants was marginal. The effect on reaction rates but not rate constants was expected: the fraction of each W(VI) species should change with different pre-equilibration temperature (elevated temperature encourages the formation of polytungstates and POMs), affecting the rate of reaction, but the reaction mechanism, which influences the rate constants, should not change. In this regard, the effect on kinetics should be the length of time over which depolymerization occurs. Range II was much shorter at 60°C than at 40°C and room temperature. This implies that the species formed at room temperature were kinetically stable, whereas the polymeric tungstates forced to form at higher temperatures might relatively quickly decompose to other metastable forms. Given that natural processes on Earth surface often occur at “low” temperature, the W(VI) polymeric species, if present, may both adsorb less strongly and persist in waters for a longer time, relative to the monomeric species.

4. CONCLUSIONS

This study demonstrates that W(VI) solution speciation is of critical importance for regulating W(VI) adsorption. Tungsten(VI) adsorption may be extensive (and aqueous concentration may be low), when

particle-reactive tungstate is stable. Polytungstates and POMs, on the other hand, adsorb to a lesser degree than tungstates onto ferrihydrite and presumably other solids. Tungsten(VI) solid-solution partitioning is also kinetically-controlled. Because the depolymerization of metastable polytungstates and POMs is slow, they can persist in solution for weeks, further contributing to W's high solubility. Although this study does not conclusively identify transformations between monomeric and polymeric tungstates, it represents the first study to systematically suggest that such processes may have a significant effect on W adsorption.

This study helps reconcile the incongruity between strong tungstate adsorption and unexpectedly high solution W concentrations in some natural systems (Bednar et al., 2009; Bostick et al., Submitted.; Clausen and Korte, 2009; Gustafsson, 2003). Although natural waters often contain low W concentrations which are probably not conducive to polymerization, a number of polytungstates could exist under the circumneutral W-contaminated conditions. Environmental systems also often contain various oxyanions that may promote the formation of POMs, many of which may not only be kinetically inert but also thermodynamically stable.

Many factors should be taken into account when dealing with W, such as pH, W concentration, reaction time and the performance of different analytical techniques. There is little information regarding the equilibrium and kinetic stability of various W(VI) polymeric species, and even less is known about how they associate with mineral surfaces. This study focused on a single adsorbent and solutions with relatively uncomplicated compositions, and even in this case found W(VI) adsorption to be anything but simple. Natural systems have variable solution and mineral compositions and organic compounds including chelators, complicating the fate of W much further. Continued efforts are required to better understand W solid-solution partitioning, and its environmental fate and exposure.

ACKNOWLEDGEMENTS

This study was funded by National Science Foundation-Environmental Chemistry (NSF-CHE-1010368), and the Department of Defense BAA program. Some of the analyses were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL), a national user facility operated by Stanford University for the U.S. Department of Energy. We would like to thank J. Landis of Dartmouth College for assistance with laboratory work and ICP analysis, and J. Rogers of SSRL for technical support during XAS data collection.

542 **SUPPLEMENTARY MATERIAL**

543 Table S1 lists result of EXAFS target transform; Figure S1 shows XRD of the ferrihydrite synthesized;
544 Table S2, Table S3 and Figure S2 provide the results from EXAFS shell-by-shell fitting.

545

REFERENCES

- Babula, P. et al., 2008. Uncommon heavy metals, metalloids and their plant toxicity: a review. *Environmental Chemistry Letters*, 6(4): 189-213.
- Baes, C.F., Mesmer, R.E., 1986. The hydrolysis of cations, 2nd ed. Krieger Publishing Company, Malabar, FL.
- Bar-Nahum, I., Ettekgui, J., Konstantinovski, L., Kogan, V., Neumann, R., 2007. A new method for the synthesis of organopolyoxometalate hybrid compounds. *Inorganic Chemistry*, 46(14): 5798-5804.
- Bednar, A.J. et al., 2009. Investigations of tungsten mobility in soil using column tests. *Chemosphere*, 75(8): 1049-1056.
- Bednar, A.J., Jones, W.T., Boyd, R.E., Ringelberg, D.B., Larson, S.L., 2008. Geochemical parameters influencing tungsten mobility in soils. *Journal of Environmental Quality*, 37(1): 229-233.
- Bednar, A.J. et al., 2007. The determination of tungsten, molybdenum, and phosphorus oxyanions by high performance liquid chromatography inductively coupled plasma mass spectrometry. *Talanta*, 72(5): 1828-1832.
- Bostick, B.C., Sun, J., Landis, J.D., Clausen, J.L., Submitted. Quantitative Tungsten Speciation and Solubility in Munitions-Impacted Soils. *Geochimica Et Cosmochimica Acta*.
- Castillo, M.A., Vazquez, P.G., Blanco, M.N., Caceres, C.V., 1996. Adsorption studies and species characterization in catalysts obtained from aqueous solutions or phosphomolybdic acid and gamma-alumina. *Journal of the Chemical Society-Faraday Transactions*, 92(17): 3239-3246.
- Chen, Y.G., Gong, J., Qu, L.Y., 2004. Tungsten-183 nuclear magnetic resonance spectroscopy in the study of polyoxometalates. *Coordination Chemistry Reviews*, 248(1-2): 245-260.
- Clausen, J.L., Korte, N., 2009. Environmental fate of tungsten from military use. *Science of the Total Environment*, 407(8): 2887-2893.
- Cruywagen, J.J., 2000. Protonation, oligomerization, and condensation reactions of vanadate(V), molybdate(VI), and tungstate(VI), *Advances In Inorganic Chemistry*, Vol 49. *Advances In Inorganic Chemistry*. Academic Press Inc, San Diego, pp. 127-182.
- Dermatas, D. et al., 2004. Solubility, sorption, and soil respiration effects of tungsten and tungsten alloys. *Environmental Forensics*, 5(1): 5-13.
- Dzombak, D.A., Morel, F.M., 1990. Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons.
- Etou, A. et al., 2009. Formation conditions and stability of a toxic tridecameric Al polymer under a soil environment. *Journal Of Colloid And Interface Science*, 337(2): 606-609.
- Furrer, G., Phillips, B.L., Ulrich, K.U., Pothig, R., Casey, W.H., 2002. The origin of aluminum flocs in polluted streams. *Science*, 297(5590): 2245-2247.

580 Gustafsson, J.P., 2003. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chemical Geology*,
581 200(1-2): 105-115.

582 Himeno, S., Takamoto, M., Ueda, T., 2005. Formation of alpha- and beta-Keggin-type [PW12O40](3-)
583 complexes in aqueous media. *Bulletin of the Chemical Society of Japan*, 78(8): 1463-1468.

584 Ho, Y., McKay, G., 1998. A comparison of chemisorption kinetic models applied to pollutant removal on
585 various sorbents. *Process Safety and Environmental Protection*, 76(4): 332-340.

586 Holclajtner-Antunovic, I. et al., 2008. Spectroscopic study of stability and molecular species of 12-
587 tungstophosphoric acid in aqueous solution. *Canadian Journal of Chemistry-Revue Canadienne*
588 *De Chimie*, 86(10): 996-1004.

589 Inouye, L.S., Jones, R.P., Bednar, A.J., 2006. Tungsten effects on survival, growth, and reproduction in
590 the earthworm, *Eisenia fetida*. *Environmental Toxicology and Chemistry*, 25(3): 763-768.

591 Johannesson, K.H., Dave, H.B., Mohajerin, T.J., Datta, S., 2013. Controls on tungsten concentrations in
592 groundwater flow systems: The role of adsorption, aquifer sediment Fe(III) oxide/oxyhydroxide
593 content, and thiotungstate formation. *Chemical Geology*, 351: 76-94.

594 Johnson, D.R., Ang, C., Bednar, A.J., Inouye, L.S., 2010. Tungsten Effects on Phosphate-Dependent
595 Biochemical Pathways are Species and Liver Cell Line Dependent. *Toxicological Sciences*,
596 116(2): 523-532.

597 Karakostas, L., Bourikas, K., Lycourghiotis, A., 1996. Tungsten-oxo-species deposited on alumina .1.
598 Investigation of the nature of the tungstates deposited on the interface of the gamma-
599 alumina/electrolyte solutions at various pH's. *Journal of Catalysis*, 162(2): 295-305.

600 Keggin, J.F., 1934. The structure and formula of 12-phosphotungstic acid. *Proceedings of the Royal*
601 *Society of London Series a-Mathematical and Physical Sciences*, 144(A851): 0075-0100.

602 Kelly, A.D. et al., 2012. In vivo tungsten exposure alters B cell development and increases DNA damage
603 in murine bone marrow. *toxicological sciences: kfs324*.

604 Kepert, D.L., Kyle, J.H., 1978. Stepwise Base Decomposition of 12-Tungstosilicate(4-). *Journal of the*
605 *Chemical Society-Dalton Transactions*(2): 137-141.

606 Koutsospyros, A., Braida, W., Christodoulatos, C., Dermatas, D., Strigul, N., 2006. A review of tungsten:
607 From environmental obscurity to scrutiny. *Journal of Hazardous Materials*, 136(1): 1-19.

608 Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska*
609 *Vetenskapsakademiens. Handlingar*. 24 (4), 1-39. *Microchemical Journal Environ. Sci. Technol. J.*
610 *Colloid Interface Sci J. Colloid Interface Sci Environ. Sci. Technol. Rev. Soc. Quím. Perú,*
611 *American Water Works Association Chem. Eng. J.*

612 Lassner, E., Schubert, W.-D., 1999. Tungsten: Properties, chemistry, technology of the element, alloys,
613 and chemical compounds. *Plenum Press, New York*.

614 Lemus, R., Venezia, C.F., 2015. An update to the toxicological profile for water-soluble and sparingly
 615 soluble tungsten substances. *Critical reviews in toxicology*, 45(5): 388-411.

616 Manning, B.A., Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and
 617 molybdate on oxide minerals. *Soil Science Society of America Journal*, 60(1): 121-131.

618 Martin, C., Malet, P., Solana, G., Rives, V., 1998. Structural analysis of silica-supported tungstates.
 619 *Journal Of Physical Chemistry B*, 102(15): 2759-2768.

620 Mikola, M., Klika, K.D., Hakala, A., Arpalahti, J., 1999. Substitution reactions of platinum(II)-
 621 nucleobase complexes by associative mechanism involving pseudorotation of the five-coordinate
 622 intermediate. *Inorganic Chemistry*, 38(3): 571-578.

623 Petkewich, R., 2009. Unease over Tungsten. *Chemical & Engineering News*, 87(3): 63-65.

624 Pizzio, L.R., Caceres, C.V., Blanco, M.N., 1997. Adsorption of tungstophosphoric or tungstosilicic acids
 625 from ethanol-water solutions on carbon. *Journal Of Colloid And Interface Science*, 190(2): 318-
 626 326.

627 Pokrovsky, O.S., Schott, J., Dupre, B., 2006. Trace element fractionation and transport in boreal rivers
 628 and soil porewaters of permafrost-dominated basaltic terrain in Central Siberia. *Geochimica Et*
 629 *Cosmochimica Acta*, 70(13): 3239-3260.

630 Pope, M.T., Muller, A., 1991. POLYOXOMETALATE CHEMISTRY - AN OLD FIELD WITH NEW
 631 DIMENSIONS IN SEVERAL DISCIPLINES. *Angewandte Chemie-International Edition in*
 632 *English*, 30(1): 34-48.

633 Schwertmann, U., Cornell, R.M., 2000. *Iron Oxides in the Laboratory. Preparation and Characterization.*
 634 2nd ed. Wiley, Weinheim.

635 Seiler, R.L., Stollenwerk, K.G., Garbarino, J.R., 2005. Factors controlling tungsten concentrations in
 636 ground water, Carson Desert, Nevada. *Applied Geochemistry*, 20(2): 423-441.

637 Sen Tuna, G., Braida, W., Ogundipe, A., Strickland, D., 2012. Assessing tungsten transport in the vadose
 638 zone: From dissolution studies to soil columns. *Chemosphere*, 86(10): 1001-1007.

639 Smith, B.J., Patrick, V.A., 2002. Quantitative determination of sodium dodecatungstosilicate speciation
 640 by W-183 nuclear magnetic resonance spectroscopy. *Australian Journal of Chemistry*, 55(4): 281-
 641 286.

642 Smith, B.J., Patrick, V.A., 2004. Quantitative determination of aqueous dodecatungstophosphoric acid
 643 speciation by NMR spectroscopy. *Australian Journal of Chemistry*, 57(3): 261-268.

644 Spiccia, L., Casey, W.H., 2007. Synthesis of experimental models for molecular inorganic geochemistry -
 645 A review with examples. *Geochimica Et Cosmochimica Acta*, 71(23): 5590-5604.

646 Strigul, N., 2010. Does speciation matter for tungsten ecotoxicology? *Ecotoxicology and environmental*
 647 *safety*, 73(6): 1099-1113.

- Strigul, N. et al., 2009. Influence of speciation on tungsten toxicity. *Desalination*, 248(1): 869-879.
- Strigul, N. et al., 2005. Effects of tungsten on environmental systems. *Chemosphere*, 61(2): 248-258.
- Strigul, N., Koutsospyros, A., Christodoulatos, C., 2010. Tungsten speciation and toxicity: acute toxicity of mono-and poly-tungstates to fish. *Ecotoxicology and environmental safety*, 73(2): 164-171.
- Tarlani, A., Abedini, M., Khabaz, M., Amini, M.M., 2005. Adsorption of Wells-Dawson tungsten heteropolyacid on sol-gel alumina: Structural features and thermal stability. *Journal Of Colloid And Interface Science*, 292(2): 486-492.
- Tarlani, A., Abedini, M., Nemati, A., Khabaz, M., Amini, M.M., 2006. Immobilization of Keggin and Preyssler tungsten heteropolyacids on various functionalized silica. *Journal Of Colloid And Interface Science*, 303(1): 32-38.
- Traina, S.J., Laperche, V., 1999. Contaminant bioavailability in soils, sediments, and aquatic environments. *Proceedings of the National Academy of Sciences of the United States of America*, 96(7): 3365-3371.
- Tyrrell, J. et al., 2013. High urinary tungsten concentration is associated with stroke in the National Health and Nutrition Examination Survey 1999–2010.
- Vissenberg, M.J. et al., 2000. Tungstate versus molybdate adsorption on oxidic surfaces: A chemical approach. *Journal Of Physical Chemistry B*, 104(35): 8456-8461.
- Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Physica Scripta*, T115: 1011-1014.
- Xu, N., Christodoulatos, C., Braidia, W., 2006. Modeling the competitive effect of phosphate, sulfate, silicate, and tungstate anions on the adsorption of molybdate onto goethite. *Chemosphere*, 64(8): 1325-1333.
- Zhu, Z.R., Tain, R., Rhodes, C., 2003. A study of the decomposition behaviour of 12-tungstophosphate heteropolyacid in solution. *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, 81(10): 1044-1050.

FIGURE LEGEND

Figure 1: Adsorption isotherms for W(VI) solutions (0 – 100 mg L⁻¹ W, added as sodium tungstate) in equilibrium with ferrihydrite (0.5 g L⁻¹) at different pHs. All solutions were pre-equilibrated at 40°C, prior to the addition of ferrihydrite.

Figure 2: (A) Tungstate adsorption isotherms in equilibrium with ferrihydrite. The addition of phosphates and silicates significantly decreased adsorption. (B) In regards to the isotherm containing phosphates, the comparison of experimental phosphate concentrations ([PO₄³⁻]_{exp}) with those that are modeled using Visual MINTEQ ([PO₄³⁻]_{model}). The numbers labeled by the side of the data points are the concentrations, in μmol L⁻¹, of W added in the samples.

Figure 3: (A): Measured and modeled adsorption envelopes for tungstate solutions in equilibrium with ferrihydrite. Tungsten(VI) was added as sodium tungstate and all solutions were pre-equilibrated at 40°C. (B): Visual MINTEQ modeled pC-pH diagram for tungstate solution containing 10 mg L⁻¹ W without solid mineral phases (i.e., no adsorption).

Figure 4: Adsorption envelopes for tungstate and phosphotungstate (PWO) solutions in equilibrium with ferrihydrite (all began with 10 mg L⁻¹ W). The symbols/lines labeled as tungstate or PWO indicate the initial W(VI) species added, and thus would not actually represent pure tungstate or PWO adsorption given the pre-equilibration process, varying pH and/or time for adsorption. Compared to tungstate adsorption, PWO adsorption was highly suppressed. For reaction time used in PWO experiments, 2 hours resulted in considerably less W(VI) retention on ferrihydrite than did 48 hours.

Figure 5: The radial structure functions (RSFs) obtained from W EXAFS spectra of the references and three representative samples. The samples show W-Fe/W backscattering indicative of polytungstates/POMs.

Figure 6: Results from adsorption kinetics experiments. Each experiment contained 0.5 g L⁻¹ ferrihydrite, 10 mg L⁻¹ W and 10 mg L⁻¹ dissolved Si. Experiments all contained a mixture of tungstates, polytungstates and POMs, but contained different fractions of them between each other and at different time periods. (A) Effect of pH on the extent and rate of W(VI) adsorption over time. Solutions were all pre-equilibrated at 40°C. Both the extent and rate of W(VI) adsorption decreased as pH increased. (B) Effect of varying pre-

equilibration temperature on the extent and rate of W(VI) adsorption. Experiments were all conducted at pH 7. The rate of W(VI) adsorption increased as pre-equilibration temperature increased.

Figure 7: Linearized first-order kinetics plot for tungstate adsorption in the presence of 10 mg L⁻¹ total W and 10 mg L⁻¹ total dissolved Si, with pH buffered at 6 and pre-equilibration at 40°C (corresponding to the black solid circles in Figure 6A). The data are well described by first-order reaction kinetics in three separate time domains, with the fast reaction at the onset attributed to WO₄²⁻ adsorption followed by two slow rate limiting depolymerization processes.

Figure 1: Adsorption isotherms for W(VI) solutions (0 – 100 mg L⁻¹ W, added as sodium tungstate) in equilibrium with ferrihydrite (0.5 g L⁻¹) at different pHs. All solutions were pre-equilibrated at 40°C, prior to the addition of ferrihydrite.

Figure 3: (A): Measured and modeled adsorption envelopes for tungstate solutions in equilibrium with ferrihydrite. Tungsten(VI) was added as sodium tungstate and all solutions were pre-equilibrated at 40°C. (B): Visual MINTEQ modeled pC-pH diagram for tungstate solution containing 10 mg L⁻¹ W without solid mineral phases (i.e., no adsorption).

Figure 4: Adsorption envelopes for tungstate and phosphotungstate (PWO) solutions in equilibrium with ferrihydrite (all began with 10 mg L⁻¹ W). The symbols/lines labeled as tungstate or PWO indicate the initial W(VI) species added, and thus would not actually represent pure tungstate or PWO adsorption given the pre-equilibration process, varying pH and/or time for adsorption. Compared to tungstate adsorption, PWO adsorption was highly suppressed. For reaction time used in PWO experiments, 2 hours resulted in considerably less W(VI) retention on ferrihydrite than did 48 hours.

70 **Figure 5:** The radial structure functions (RSFs) obtained from W EXAFS spectra of the references and
 71 three representative samples. The samples show W-Fe/W backscattering indicative of sorbed
 72 polytungstates/POMs.

73
 74

Figure 6: Results from adsorption kinetics experiments. Each experiment contained 0.5 g L⁻¹ ferrihydrite, 10 mg L⁻¹ W and 10 mg L⁻¹ dissolved Si. Experiments all contained a mixture of tungstates, polytungstates and POMs, but contained different fractions of them between each other and at different time periods. (A) Effect of pH on the extent and rate of W(VI) adsorption over time. Solutions were all pre-equilibrated at 40°C. Both the extent and rate of W(VI) adsorption decreased as pH increased. (B) Effect of varying pre-equilibration temperature on the extent and rate of W(VI) adsorption. Experiments were all conducted at pH 7. The rate of W(VI) adsorption increased as pre-equilibration temperature increased.

Figure 7: Linearized first-order kinetics plot for tungstate adsorption in the presence of 10 mg L⁻¹ total W and 10 mg L⁻¹ total dissolved Si, with pH buffered at 6 and pre-equilibration at 40°C (corresponding to the black solid circles in Figure 6A). The data are well described by first-order reaction kinetics in three separate time domains, with the fast reaction at the onset attributed to WO₄²⁻ adsorption followed by two slow rate limiting depolymerization processes.

TABLE LEGEND

Table 1. Summary of experiment setup.

Table 2: Speciation of solid-phase W(VI) (sorbed on ferrihydrite (Fh)) in samples from various adsorption experiments, as determined by W EXAFS linear combination fitting. Errors are from linear combination fitting as reported by SixPACK.

Table 3: Pseudo first-order rate constants for kinetics experiments performed as a function of pH and pre-equilibration temperature. Range I, II and III correspond to the adsorption of WO_4^{2-} on ferrihydrite, the partial depolymerization of $\text{SiW}_{12}\text{O}_{40}^{4-}$, and the complete depolymerization of $\text{SiW}_9\text{O}_{34}^{10-}$, respectively.

15 **Table 1.** Summary of experiment setup.

16

Adsorption experiment set		pH	Pre-equilibration temperature	W added as	Initial W	Presence of other oxyanions	Ferrihydrite	Time for adsorption
Thermodynamics	Isotherm	4	40°C	Tungstate	0–100 mg L ⁻¹	--	0.5 g L ⁻¹	48 hours
		7	40°C	Tungstate	0–100 mg L ⁻¹	--	0.5 g L ⁻¹	48 hours
		8.5	40°C	Tungstate	0–100 mg L ⁻¹	--	0.5 g L ⁻¹	48 hours
		7	40°C	Tungstate	0–100 mg L ⁻¹	10 mg L ⁻¹ dissolved P as phosphate	0.5 g L ⁻¹	48 hours
		7	40°C	Tungstate	0–100 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	48 hours
		7	40°C	Tungstate	0–100 mg L ⁻¹	20 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	48 hours
	Envelope	3 – 11	40°C	Tungstate	10 mg L ⁻¹	--	0.5 g L ⁻¹	48 hours
		3 – 10	40°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	48 hours
		3 – 10	--	PWO	10 mg L ⁻¹	--	0.5 g L ⁻¹	48 hours
		3 – 10	--	PWO	10 mg L ⁻¹	--	0.5 g L ⁻¹	2 hours
Kinetics	6	40°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	7–8 weeks	
	7	40°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	7–8 weeks	
	8	40°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	7–8 weeks	
	7	22°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	7–8 weeks	
	7	60°C	Tungstate	10 mg L ⁻¹	10 mg L ⁻¹ dissolved Si as silicate	0.5 g L ⁻¹	7–8 weeks	

17

18

Table 2: Speciation of solid-phase W(VI) (sorbed on ferrihydrite (Fh)) in samples from various adsorption experiments, as determined by W EXAFS linear combination fitting. Errors are from linear combination fitting as reported by SixPACK.

<i>Experiment set</i>	<i>Reaction time</i>	<i>pH</i>	<i>W added^a</i> (mg L ⁻¹)	<i>W sorbed</i> ($\mu\text{mol g}^{-1}$ Fh)	<i>Polymeric tungstate</i>	<i>Monomeric tungstate</i>
<u><i>PWO adsorption envelope</i></u>	2 h	4.3	10	10.1	40 $\pm$ 3 %	60 $\pm$ 3 %
	2 h	5.2	10	28.6	37 $\pm$ 4 %	63 $\pm$ 4 %
	2 h	6.9	10	22.5	45 $\pm$ 4 %	55 $\pm$ 4 %
	2 h	9.3	10	14.8	11 $\pm$ 4 %	89 $\pm$ 4 %
	48 h	4.4	10	39.1	36 $\pm$ 3 %	64 $\pm$ 3 %
	48 h	6.9	10	69.4	42 $\pm$ 3 %	58 $\pm$ 3 %
<u><i>tungstate adsorption envelope</i></u>	48 h	3.6	10	35.3	49 $\pm$ 3 %	51 $\pm$ 3 %
	48 h	6.0	10	76.7	50 $\pm$ 3 %	50 $\pm$ 3 %
	48 h	7.5	10	59.1	41 $\pm$ 3 %	59 $\pm$ 3 %
	48 h	10.0	10	3.3	0 $\pm$ 15 % ^b	100 $\pm$ 15 % ^b
<u><i>tungstate+phosphate isotherm</i></u>	48 h	7	3	12.5	15 $\pm$ 5 %	85 $\pm$ 4 %
	48 h	7	10	35.2	31 $\pm$ 4 %	69 $\pm$ 4 %
	48 h	7	40	95.9	34 $\pm$ 3 %	66 $\pm$ 3 %
	48 h	7	100	201.3	44 $\pm$ 3 %	56 $\pm$ 3 %

(a): The total amount of W added into the systems.

(b): Error is large due to its low adsorbed W concentration, which makes EXAFS spectrum noisy.

Table 3: Pseudo first-order rate constants for kinetics experiments performed as a function of pH and pre-equilibration temperature. Range I, II and III correspond to the adsorption of WO_4^{2-} on ferrihydrite, the partial depolymerization of $\text{SiW}_{12}\text{O}_{40}^{4-}$, and the complete depolymerization of $\text{SiW}_9\text{O}_{34}^{10-}$, respectively.

T_{pre}^a	pH	Range I: WO_4^{2-} adsorption			Range II: $SiW_{12}O_{40}^{4-}$ depolymerization			Range III: $SiW_9O_{34}^{10-}$ depolymerization		
		range (min)	$k'_{WO_4^{2-}}$ (min^{-1})	r^{2b}	range (min)	k_1' (min^{-1})	r^{2b}	range (min)	k_2' (min^{-1})	r^{2b}
<u>Varying pH</u>										
40°C	6	0 - 35	6.4×10^{-3}	0.90	35 - 1380	4.8×10^{-4}	0.99	1380 - 17780 ^c	2.6×10^{-4}	1.00
40°C	7	0 - 35	3.3×10^{-3}	0.84	35 - 2100	3.8×10^{-4}	0.98	2100 - 46710 ^c	8.5×10^{-5}	0.98
40°C	8	0 - 150	1.2×10^{-3}	0.95	150 - 4310	1.5×10^{-4}	0.95	4310 - 59600 ^c	4.4×10^{-5}	1.00
<u>Varying T_{pre}^a</u>										
22°C	7	0 - 35	5.6×10^{-3}	0.69	35 - 4275	3.7×10^{-4}	0.99	4275 - 43840 ^c	1.4×10^{-4}	0.97
40°C	7	0 - 35	3.3×10^{-3}	0.84	35 - 2100	3.8×10^{-4}	0.98	2100 - 46710 ^c	8.5×10^{-5}	0.98
60°C	7	0 - 35	2.4×10^{-3}	0.96	35 - 1370	3.7×10^{-4}	0.99	1370 - 59640 ^c	6.8×10^{-5}	0.99

(a): Pre-equilibration temperature, the temperature at which W(VI) solutions were aged for 24 hours prior to the addition of ferrihydrite.

(b): r squared for the fits.

(c): The sorbed W(VI) concentration in the next subsample right after this range was assumed to be equilibrium concentration (q_e), although in some cases not true equilibrium concentration.

1 GRAPHICAL ABSTRACT: