Biogeochemistry of Tungsten in California Soils

Christopher Amrhein*, Myles Davis, and David R. Parker

Project Objectives

This project encompasses soil biogeochemical processes of tungsten (W) at multiple scales ranging from the atomic/micro-scale to a regional scale. We were also able to study processes involving W at spatial and temporal scales ranging from the atomic/micro-scale of surface reactions and oxidation states; plant-soil interactions from W-contaminated soils; and a regional distribution of W from naturally occurring and mining activities. Because tungsten is commonly replacing lead in shotgun pellets and has the potential to be dispersed across many different soil environments and it also occurs due to past management of W-mine waste, this research will be useful for land management and policy decisions due to increasing amounts of W entering our ecosystems in California.

A) Atomic/micro-scale: study the speciation and solubility of W-pellets weathering in soil and water. X-ray absorption spectroscopy was applied to examine surface adsorbed or precipitated forms of weathered W-pellets and W in natural systems.

B) Soil-plant interactions: The factors affecting plant uptake of W, with potential interactions with Mo, were examined in W-contaminated soil experiments. The use of μ-XAS was utilized to image roots, root nodules, and leaves to spatially locate W within plant tissue.

C) Regional scale: We were able to build upon this project by collecting soils in the Owens Valley thought to have naturally occurring tungsten and/or tungsten from mining activities. This was an investigation of the spatial and chemical distribution of tungsten in soils. Willow tree leaf W-concentrations were also measured in the study area.

Approach and Procedures

A) Atomic/micro-scale: Two types of shotgun pellets were used in this study. One of the shotgun pellets contained 97% W, combined with 2% Ni and 1% Fe (density 17.5 g cm$^{-3}$) and is identified as “High-W”. The “Low-W” pellets contained 50% W combined with 15% Ni and 35% Fe (density 12 g cm$^{-3}$). Both types of pellets were size #8, 2.3 mm in diameter. Both High-W and Low-W pellets were placed in moist, aerobic Holland and Grangeville soils for 100 days. After incubation, the soils were dried at room temperature and impregnated under vacuum with epoxy resin. The impregnated soil blocks were cut and polished through an imbedded pellet, and analyzed using XANES and micro X-ray absorption spectroscopy (μ-XAS) to characterize metal speciation, distribution, oxidation state, and adsorption complexes of W in soil. Precipitates from both W-pellet types, incubated in DI water were also collected and analyzed using XANES and μ-XAS techniques.

B) Soil-plant interactions: Alfalfa (*Medicago sativa*) uptake of W derived from oxidizing shotgun pellets was studied in a pot experiment carried out under controlled light and temperature conditions in growth chambers. The Grangeville soil (500 g) was spiked with increasing amounts of W-shotgun pellets with treatments consisting of 0, 5, 10, and 20 W-
Biogeochemistry of Tungsten in California Soils - Amrhein

shotgun pellets per pot (corresponding to 0, 0.9, 1.9, and 3.7 g kg\(^{-1}\) total W, respectively). Alfalfa uptake of W from spiked soil was also evaluated using Grangeville and Holland soils spiked with 0, 50, 200, 500, 1000, and 2000 mg W kg\(^{-1}\) soil. Leaf concentrations of W, Mo, and Cu were measured by ICP-OES. The use of \(\mu\)-XAS was utilized to image roots, root nodules, stems, and leaves to spatially locate W within plant tissue and \(\mu\)-XAFS was used to determine metal speciation, structure, and location within plant tissue.

C) Regional scale: Soil samples were taken at over 80 locations in the Owens Valley where W-mineral deposits and previous mining activity exists. Sampling was focused on the distribution of tungsten down two watersheds in the Tungsten Hills. A sequential extraction scheme was used to determine mobility and complexes in soils and sediments. Bioaccumulation of tungsten in willow and cottonwood trees was evaluated.

Results

A) **Atomic/micro-scale distribution of W from W-pellets:**

W-pellet composition and soil characteristics are important for W-pellet oxidation in soil and water. High-W pellets incubated for 100 days in Grangeville and Holland soils were examined for distribution of weathering products around the W-pellet, oxidation state, and elemental associations as an in situ experiment. The pellets were preserved with an epoxy resign and ground down to expose the W-pellet and surrounding soil. The \(\mu\)-XAS analysis was used to differentiate between oxidation states (\(\text{\textsuperscript{5+}}\) and \(\text{\textsuperscript{4+}}\)) in the pellet and in the soil. Total Fe distribution in the soil and in the W-pellet (binder phase) was mapped. The \(\text{\textsuperscript{5+}}/\text{Fe}\) correlation map shows where both \(\text{\textsuperscript{5+}}\) and Fe are found together, most likely as W-adsorbed to Fe-oxide minerals. The High-W pellet incubated in the Grangeville soil, clearly shows tungsten was oxidized and transported away from the W-pellet as \(\text{\textsuperscript{5+}}\) or \(\text{\textsuperscript{4+}}\) (Figure 1a). The top image (Figure 1a) is a photograph of the embedded High-W pellet in the Grangeville soil. The mapped area is the black rectangle and the white box is a 1-mm scale bar. The \(\text{\textsuperscript{5+}}\) image shows tungsten metal only exists as the W-pellet and did not slough off or breakaway from the pellet. The lighter colored areas inside the pellet are the seams or binder phase of Fe and Ni. The \(\text{\textsuperscript{4+}}\) image shows that the oxidized W extends from the edge of the pellet out into the soil. The oxidized tungsten decreases in concentration away from the W-pellet edge and is clustered in hot spots (areas of yellow, orange, and red). The Fe image in Figure 1a is the total Fe mapped in the W-pellet (binder) and out into the soil. The Grangeville soil is low in Fe-oxides, though the areas in red and orange are most likely Fe-oxide coatings of soil particles, some soil Fe-oxides (ferrihydrite and goethite), and a few mafic minerals. The \(\text{\textsuperscript{5+}}/\text{Fe}\) correlation map (Figure 1a, bottom) shows the areas where \(\text{\textsuperscript{5+}}\) and Fe both coexist, most likely as \(\text{\textsuperscript{5+}}\)-adsorbed to Fe-oxides in the soil. The High-W pellet incubated in the Holland soil shows tungsten was oxidized but transported only slightly into the soil (Figure 1b). The top image (Figure 1b) is a photograph of the embedded High-W pellet in the Holland soil. The mapped area is the black rectangle and the white box is a 1-mm scale bar. The \(\text{\textsuperscript{5+}}\) image shows tungsten metal only exists as the W-pellet and the binder phase of Fe and Ni are the dark areas inside the W-pellet. The \(\text{\textsuperscript{5+}}\) image shows the oxidized W only extends about 1 mm from the edge of the pellet out into the soil. The highest concentrations of \(\text{\textsuperscript{5+}}\) are at the W-pellet/soil interface. Iron was mapped throughout the soil and in the W-pellet (binder) (Figure 1b). The Holland soil is high in Fe-oxides and areas of red, orange, and yellow are high Fe concentrations. The blue area in the middle is most likely a pore space or non-mafic mineral. The \(\text{\textsuperscript{5+}}/\text{Fe}\) correlation (Figure 1b,
Figure 1. X-ray absorption microprobe image of a High-W pellet from a) Grangeville incubation and b) Holland incubation for 100 days under moist, aerobic conditions. The top images are photographs of the pellet embedded in the soil. The white bar in the figure is a 1-mm scale bar. The black box shows the area that was micro-probed. The four lower images show the distribution of total W, \( W_0 \), total Fe, and \( W_0 \) associated with Fe. Arrows indicate the edge of the pellet.

(bottom) is high in the soil area in contact with the pellet to about 1 mm into the soil. This suggests the transport of \( W_0 \) is low in the Holland soil because the \( W_0 \) is strongly adsorbed by the Fe-oxides in the soil.

The XANES spectra of three selected hot-spots from the High-W pellet incubated in the Grangeville soil were used to determine W-solid phase composition. The goal of PCA is to distinguish principal components from secondary ones, with a principle component accounting for greater than 10% of the variance. Based on the results of the PCA and component exclusion, linear combination fitting (LCF) analysis was applied to determine the fraction of each W-species present in the soil/W-pellet surface. LCF analysis is an additive of the absorption from each species in the sample and is presently the most common approach for semi-quantitative XANES analysis (Kelly et al., 2008).

The PCA analysis shows the likelihood of two to three W-solids making up the XANES spectra for each of the three hot-spots. Reconstructions of the data sets using LCF for the High-W pellet incubated in the Grangeville soil are shown with the sample spectra of each location and superimposed reference standard compounds, scaled according to their fractions in the LCF (Figure 2). The fractions contribute to the fitted curve. At the High-W pellet/soil interface (Figure 2c), LCF shows the XANES spectrum of Poly-W (83%) with small contributions of W-metal (13%) and Fe-oxide adsorbed \( \text{Fe(OH)}(s) \) (3%). Oxidized W at the surface of the W-pellet has formed W-polymers. The hot-spot approximately 30-50 \( \mu \)m from the pellet surface in the soil (Figure 2b), has Poly-W (45%) and almost equal parts (s) (28%) and \( \text{Fe(OH)}(s) \) (24%) characteristics. The hot-spot approximately 100-200 \( \mu \)m from the pellet surface in the soil (Figure 2a), is mostly all Fe-oxide adsorbed \( \text{Fe(OH)}(s) \) (93%), with little Poly-W
Figure 2. Experimental and linear combination fits for the W -edge near-edge spectra of High-W pellet incubated in Grangeville soil: (a) "hot-spot" in the soil matrix, away from the W-pellet, (b) "hot-spot" close to surface, (c) at the pellet surface. Each spot is the sample spectra, together with spectra of the best standard fits, and scaled according to their fractional contributions to the fitted spectra. The white bar in the top-right of figure is a 500-μm scale bar.

characteristics (7%). All W-XANES reference compounds were considered (W-reference XANES spectra not shown).

The W-pellets incubated in DI water for 1.5 years, formed two different types of precipitates and had interesting solution chemistry. The W solution concentrations from the High-W pellet incubation were much greater than predicted (585.3 mg L\(^{-1}\)) and almost twice as high as the Low-W pellet incubation (296.8 mg L\(^{-1}\)). The solid precipitate from the oxidation of W-pellets; a yellowish-white precipitate (from the high-W pellets) and an orange-light brown precipitate...
(from the Low-W pellets) were analyzed using μ-XAS analysis, XANES spectra, PCA, and LCF (Figures 3a and 3b). The results for the High-W precipitate are best represented by \((s), \text{\(\sim\)} \text{(aq)}, \) and \(\text{\(\sim\)}\text{Fe(OH)}(s)\). The Low-W precipitate is best fit with only \(\text{\(\sim\)}\text{Fe(OH)}(s)\). The LCF analysis was conducted over an energy range of 10200 to 10240 eV. Sample spectra of High-W precipitate (Figure 3a) and Low-W precipitate (Figure 3b) with superimposed reference standard compounds, scaled according to their fractions in the LCF. The fractions contribute to the fitted curve. The absorption spectrum from \((s)\) primarily contributes to the High-W spectrum (55%), with contributions from the \(\text{\(\sim\)} \text{(aq)}\) (32%) and to a lesser extent from \(\text{\(\sim\)}\text{Fe(OH)}(s)\) (18%) (Figure 3a). The \(\text{\(\sim\)} \text{(aq)}\) portion of the fit was included because of the contribution to the narrow shape of the “white-line” peak. The shape of the “white-line” peak (sharpness, width, double-humps, etc.) is a function of the symmetry and coordinating environment of the absorbing atom.

**Figure 3.** Experimental and linear combination fits for the W -edge near-edge spectra of (a) High-W precipitate and (b) Low-W precipitate samples together with spectra of the best standard fits, scaled according to their fractional contributions to the fitted spectra. (c) X-ray absorption microprobe image of a low-W pellet with oxidized precipitate rind. The top images show the distribution of total Fe in the low-W pellet and the precipitate. The next images down show total W, \(\text{\(\sim\)}\), and \(\text{\(\sim\)}\) associated with Fe. Arrows indicate edge of pellet.
The $\mu$-XAS was a method we used to evaluate the precipitate at the surface of the oxidizing W-pellet. Here we were able to take the oxidized Low-W pellet and preserve it in epoxy resin. This allows for the preservation of oxidation state and the use of $\mu$-XAS to get an in situ spatial analysis of the oxidation process. The incubated Low-W pellet with oxidized precipitate can be seen in Figure 3c. The small arrows point to the edge of the W-pellet. The top image shows the distribution of total Fe in the Low-W pellet and the precipitate. The precipitate has Fe all throughout and extends away from the surface. Tungsten is mapped and seen as grains or round areas on the pellet (Figure 3c (W)). The W-grains are a result of the sintering process of W-metal alloys. Fe and Ni metals have lower melting points than W and melt first to form a matrix around the W-grains. Tungsten precipitate extends out away from the pellet. The $\mu$-XAS analysis can differentiate between oxidation states ($-$ and $\text{^+}$). The mapped oxidized W ($\text{^+}$) is only on the W-pellet surface and in the precipitate. The $\text{^+}/\text{Fe}$ is a correlation elemental map, which shows where both $\text{^+}$ and Fe are found together or most likely as W-adsorbed to ferrihydrite ($\text{-Fe(OH)(s)}$). Almost all of the mapped $\text{^+}$ is associated with Fe (Figure 3c (WO2$\text{-}/\text{Fe}$)).

**B) Soil-Plant Interactions:**

Alfalfa grown in soil with W-pellets (Table 1) and soil spiked with (Table 2) had increased levels of W in the leaves corresponding with increased soil-W. Tungsten was more plant available in the Grangeville soil, which has low amounts of Fe-oxide minerals and neutral to slightly alkaline pH. Conversely the Holland soil has a pH of 5.4 and much higher Fe-oxide content. The leaf-W concentration from alfalfa growing in the highest spiked Holland soil was about 375 mg kg$^{-1}$ dry leaf weight compared to 883 mg kg$^{-1}$ dry leaf weight of the alfalfa growing in the highest spiked Grangeville soil. Plant health was affected at the 1000 and 2000 ppm spiked Grangeville soil but not in the Holland soil. The availability of W in the Grangeville soil seemed to cause a decrease in leaf weight, number of leaves, and plant height. The W was specifically adsorbed to the clay minerals of the Holland soil, which made W less plant available.

Elevated plant concentrations of Mo, which closely resembles W in terms of ionic radius and redox chemistry, have been associated with secondary Cu deficiency in ruminants. In the rumen, molybdate reacts with sulfide forming thiomolybdate ($\text{-}$), which binds Cu in an insoluble and thus non-bioavailable form (Mason, 1981). As a general rule, feeds with Cu:Mo ratios less than 2.0 are regarded as hazardous to ruminants. Analogously to $\text{-}$, thiotungstate ($\text{^+}$) may be formed by the step-wise substitution of O atoms for S atoms in the rumin (McQuaid et al., 1994a, 1994b). Because W concentrations in animal fodder are typically low, hypocuprosis induced by adverse Cu:W ratios has never been addressed as a potential problem. McQuaid et al. (1994a, 1994b) used radio-labeled $\text{-}$ as a proxy for $\text{-}$ in a series of animal studies and found that $\text{-}$ interacted in the Cu-metabolism of sheep in a way analogous to $\text{-}$. While leaf tissue Cu:Mo ratios were higher than 2.0 throughout all treatments (Tables 1 and 2), Cu:W ratios were consistently lower than 0.3. In the case of Mo, such low ratios would be disconcerting. Because of the potential hazards of elevated W concentrations found in the biomass and the close similarity between Cu-thiomolybdate and Cu-thiotungstate interactions, such Cu:W ratios should be considered for further research.
Table 1: Concentrations of W and Mo in alfalfa leaves ± standard error. Grangeville soil has <1 mg W kg$^{-1}$, 0.6±0.1 mg Mo kg$^{-1}$, and 24.4±0.6 mg Cu kg$^{-1}$. Holland soil has <1 mg W kg$^{-1}$, 1.0±0.4 mg Mo kg$^{-1}$, and 17.6±0.5 mg Cu kg$^{-1}$.

<table>
<thead>
<tr>
<th>Soil</th>
<th>W In leaves</th>
<th>Mo In leaves</th>
<th>Cu In leaves</th>
<th>Cu:Mo Ratio</th>
<th>Cu:W Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grangeville</td>
<td>1.2±0.8</td>
<td>3.3±0.5</td>
<td>11.5±0.2</td>
<td>3.5</td>
<td>9.6</td>
</tr>
<tr>
<td>50</td>
<td>40.6±10.1</td>
<td>1.0±0.7</td>
<td>12.1±0.3</td>
<td>12.0</td>
<td>0.3</td>
</tr>
<tr>
<td>200</td>
<td>57.6±7.2</td>
<td>1.2±0.3</td>
<td>6.8±0.9</td>
<td>5.8</td>
<td>0.1</td>
</tr>
<tr>
<td>500</td>
<td>134.8±19.0</td>
<td>2.1±1.2</td>
<td>10.5±0.3</td>
<td>4.9</td>
<td>0.08</td>
</tr>
<tr>
<td>1000</td>
<td>291.8±7.8</td>
<td>4.4±0.4</td>
<td>8.8±0.6</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>2000</td>
<td>883.1±81.4</td>
<td>2.6±0.9</td>
<td>10.5±0.1</td>
<td>4.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Holland</td>
<td>&lt; 1</td>
<td>1.2±0.5</td>
<td>6.6±0.7</td>
<td>5.3</td>
<td>33.1</td>
</tr>
<tr>
<td>50</td>
<td>30.9±12.5</td>
<td>5.4±1.3</td>
<td>7.0±0.2</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>200</td>
<td>63.4±20.3</td>
<td>4.4±2.1</td>
<td>14.8±0.6</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>500</td>
<td>95.5±17.6</td>
<td>2.7±1.5</td>
<td>6.9±0.2</td>
<td>2.6</td>
<td>0.07</td>
</tr>
<tr>
<td>1000</td>
<td>248.0±75.9</td>
<td>1.7±0.8</td>
<td>9.0±0.2</td>
<td>5.3</td>
<td>0.04</td>
</tr>
<tr>
<td>2000</td>
<td>375.5±47.9</td>
<td>2.8±1.5</td>
<td>10.9±0.6</td>
<td>3.9</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 2. Concentrations of W, Mo, and Cu in alfalfa leaves (± standard error) grown in soil with High-W pellets.

<table>
<thead>
<tr>
<th>W-alloy added</th>
<th>Yield in leaves</th>
<th>W In leaves</th>
<th>Mo In leaves</th>
<th>Cu In leaves</th>
<th>Cu:Mo Ratio</th>
<th>Cu:W Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
</tr>
<tr>
<td>0.0</td>
<td>6.9</td>
<td>&lt; 1</td>
<td>1.1±0.4</td>
<td>5.4±0.4</td>
<td>5.0</td>
<td>27</td>
</tr>
<tr>
<td>0.9</td>
<td>6.8</td>
<td>23±13</td>
<td>0.9±0.4</td>
<td>6.7±0.8</td>
<td>7.9</td>
<td>0.3</td>
</tr>
<tr>
<td>1.9</td>
<td>7.4</td>
<td>44±17</td>
<td>1.5±1.0</td>
<td>7.9±2.6</td>
<td>5.2</td>
<td>0.03</td>
</tr>
<tr>
<td>3.7</td>
<td>6.6</td>
<td>125±63</td>
<td>1.9±1.3</td>
<td>5.6±2.1</td>
<td>3.0</td>
<td>0.04</td>
</tr>
</tbody>
</table>

We used μ-XAS and XANES techniques to determine: 1) if W replaces Mo in the nitrate reductase enzyme (causing it not to function correctly) and 2) if inside the root nodules is reduced like Mo ($^{\text{+}} \rightarrow ^{\text{2+}}$) or is not reduced and causes the enzyme not to function correctly. The data were inconclusive as to whether W actually replaces Mo in the nitrate reductase enzyme and causes it not to function correctly. We did find evidence of $^{\text{+}}$ and no reduced W within the root nodule (Figure 4), supporting our original hypothesis that W does not become reduced like Mo ($^{\text{+}} \rightarrow ^{\text{2+}}$), rendering the enzyme non-functional.
Biogeochemistry of Tungsten in California Soils - Amrhein

Figure 4. Alfalfa leaf with W distributed throughout with no specific areas of W concentration. W appears to be distributed throughout the root and areas of high W-concentrations appear specifically located within the root nodule, possibly replaces Mo in N-fixing nitrogenase enzymes in root nodules.

C) Regional scale distribution of W:

Soils were collected from the Owens Valley with an emphasis on the main areas: Owens dry lakebed, Pine Creek, and the Tungsten Hills. Owens dry lakebed samples were collected mostly along the east and northeast portions. Most of the samples contained < 5 mg W kg\(^{-1}\) soil, except for one outlier, which had 54 mg W kg\(^{-1}\) soil. Mine spoils along Pine Creek had W concentrations ranging from 48 to 78 mg W kg\(^{-1}\) soil. The Tungsten Hills became the main area to collect samples along Deep Canyon Creek and an unnamed tributary to the north. Historically, this area was mined for scheelite, a calcium tungstate, from 1916 to 1919, and then again in 1946. The soils in the watershed above the abandon mines were low in W (< 5 mg W kg\(^{-1}\); Table 3). W-concentrations were highest at the mines (540 – 5800 mg W kg\(^{-1}\)) and ranged from 48 to 386 mg W kg\(^{-1}\) in the mine spoil piles (Table 3). Below the abandon mines, down the watershed, we sampled in the active wash and on stable landforms. In the active wash, tungsten concentrations ranged from 19 to 392 mg W kg\(^{-1}\) indicating that W is being actively transported downstream during rain events from the mines and spoil piles. On the more stable alluvial and stream terraces, the W concentrations ranged from 75 to 1090 mg W kg\(^{-1}\) (Table 3). Willow trees growing in and around the active channel (below mine tailing piles), had leaf W concentrations up to 48 mg W kg\(^{-1}\).

Table 3. Location and soil-W concentration of acid digested samples.

<table>
<thead>
<tr>
<th>Location</th>
<th>Above Mines</th>
<th>At Mines</th>
<th>Spoils</th>
<th>Below Mines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Active Channel</td>
</tr>
<tr>
<td>Soil (total)</td>
<td>&lt;</td>
<td>540 –</td>
<td>48 –</td>
<td>19 –</td>
</tr>
</tbody>
</table>

a – 15 samples; b – 6 samples; c – 10 samples; d – 18 samples; e – 10 samples
We devised a sequential extraction procedure to target different pools of W in the soils and sediment. Based on a phosphorus extraction procedure, we targeted W-associations of soluble and loosely bound, Al-oxides, Fe-oxides (NaOH and CBD extractable), ( extraction), and the residual (acid digest extractable) fractions. This scheme was applied to downstream landforms of the active stream channel (active deposits), stream terraces (somewhat stable, receives some inputs), and alluvial terraces (most stable, little inputs). In all three landforms, the majority of the W was in the residual fraction (Figure 5). XANES analysis showed most of the W was in the form. The sequential extraction scheme targeting did not work very well because the was mostly disseminated throughout the rock matrix and ended up in the residual fraction (Figure 5). The tungsten moving down the watershed from the mines and spoil piles is most likely moving by physical means (erosion). However, there was an increase in the W associated with Fe-oxide pools based on landform. The most stable landform (alluvial terrace) had about 14 mg W kg\(^{-1}\) in the Fe-oxide associated fraction. The least stable or most active landform (active channel) had less than 3 mg W kg\(^{-1}\) and the intermediate landform (stream channel) had about 7 mg W kg\(^{-1}\) (Figure 5). The more stable the landscape, the more Fe-oxides formed. These Fe-oxides then adsorb W from the chemical weathering of the W-bearing rocks and minerals.

**Figure 5.** Sequential extraction of W on three different landforms. The stream terrace had the greatest W-concentrations (1090 mg W kg\(^{-1}\)) and the older, more stable alluvial terrace had the highest amounts of W associated with the iron oxide reducible form.

**Discussion**
Previously we studied the dissolution of two W-shotgun pellets formulations. The “High-W” shotgun pellets contained 97% W, combined with 2% Ni and 1% Fe and the “Low-W” pellets contained 50% W combined with 15% Ni and 35% Fe. Both pellets were incubated in different soils, and in oxidizing and reducing conditions. The High-W pellets incubated under aerobic conditions were readily oxidized, resulting in high concentrations of bioavailable W. The largest concentrations of bioavailable W (1,700 – 3,000 mg W kg\(^{-1}\) after a 3-month incubation time) were extracted from aerobic soils with low Fe-oxide minerals. Very little bioavailable W was extracted from anaerobic incubations (11 – 29 mg W kg\(^{-1}\)) or soils high in Fe-oxides (9 – 27 mg W kg\(^{-1}\)). The Low-W pellets were less susceptible to oxidative attack and produced < 20 mg W kg\(^{-1}\) in all soils and redox conditions.

The High-W pellets have the capability to oxidize and solubilize greater than predicted amounts of W due to the formation of soluble W-polymers. Depending on the pH of the solution, the condensation of W-polymers into (s) was observed. The high concentrations of solubilized W from the corrosion of the high-W pellet could be of environmental concern.

The Low-W pellets also have the capability to oxidize and solubilize greater than predicted amounts of W as well, however, it appears that the larger amount of Fe in these pellets precipitates Fe-oxide (probably poorly crystalline goethite or ferrihydrite), and quickly adsorbs soluble \(\text{Fe(OH)}(s)\) to the surface. The \(\text{Fe(OH)}(s)\) adsorption complex was the majority of the Low-W precipitate. The formation of \(\text{Fe(OH)}(s)\) complex directly from the weathering of the Low-W pellets, makes this 50% W, 15% Ni, and 35% Fe formulation desirable in retaining solubilized W locally around the W-pellet and minimizes the fate and transport of \(\text{W}^\text{3+}\) in the environment.

In soil, tungsten is oxidized and transported away from the W-pellet as \(\text{W}^\text{6+}\). At approximately 30-50 µm from the pellet surface, W-polymers, (s) and \(\text{Fe(OH)}(s)\) have formed. Approximately 100-200 µm from the pellet surface in the soil, almost all of the oxidized W is Fe-oxide adsorbed \(\text{W}^\text{6+}\). In a low Fe-oxide containing soil, the oxidized W decreases in concentration away from the W-pellet edge and is adsorbed to Fe-oxide coatings of soil particles, some soil Fe-oxide minerals (ferrihydrite and goethite). In soils with high Fe-oxide mineral content, the oxidized W is transported only slightly into the soil because the \(\text{W}^\text{6+}\) is strongly adsorbed by the Fe-oxides in the soil.

The bioavailability of W to alfalfa in W-contaminated soils was examined. Alfalfa grown in low Fe-oxide soil with W-pellets or W-spiked, showed that \(\text{W}^\text{6+}\) is highly available to alfalfa, accumulates in specific areas of the root nodule, and is readily translocated into the foliar biomass. Alfalfa grown on soils with high Fe-oxide content also take-up W into the leaves but the concentrations were lower. At 1000 ppm W in the soil, some decline in plant health was noticed. The high concentrations of plant-available W we have observed in soils containing W-shot suggests field-scale impacts are likely.

Copper to tungsten ratios in the alfalfa biomass did raise some concerns about the quality of feed for ruminant animals. Potential hazards for secondary Cu deficiency from low Cu:Mo ratios were far exceeded by Cu:W ratios even at low W-contamination levels. Because of the close similarity between Cu-thiomolybdate and Cu-thiotungstate interactions, Cu:W ratios in alfalfa feed should be considered for further research.

We were able to show W in alfalfa root nodules but the data were inconclusive as to whether W actually replaces Mo in the nitrate reductase enzyme and causes it not to function correctly. We did find evidence of \(\text{W}^\text{6+}\) within the root nodule, which would support our original hypothesis that W does not become reduced like Mo (\(\text{Mo}^\text{6+} \rightarrow \text{Mo}^\text{3+}\)), rendering the enzyme non-functional.
On a regional scale, we investigated the spatial distribution of W in the Owens Valley. W-rich mine tailings left over from past mining activities are the source from which W is moving down Deep Canyon watershed in the Tungsten Hills area. Concentrations were highest at the abandon mines and in the spoil piles. Elevated levels of W in soils and sediments were measured down the watershed. Tungsten also bioaccumulates in willow tree biomass.

Using a sequential extraction scheme, we determined the majority of the soil and sediment W was in a residual form (dispersed in rock matrix) and appears to have translocated by physical means. On more stable landscape positions, Fe-oxide associated W increases. We hypothesize that the stable landscape position allows for chemical weathering to take place, forming Fe-oxides. These Fe-oxides then adsorb and immobilize soluble W.

Tungsten is considered to be environmentally benign and currently no drinking water standards or discharge limits exist for air, surface water, groundwater, or soils in the U.S., however, the U.S. EPA does list W as an “emerging contaminant” (US EPA, 2010). This information is critical to evaluate the fate of tungsten in various soil environments and to make effective management decisions regarding areas receiving W-metal shot from recreational hunting and movement of W from abandon mines and mine tailings.

References


Biogeochemistry of Tungsten in California Soils - Amrhein

List of Publications/Presentations Resulting from Project


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