Biogeochemistry of Tungsten in California Soils

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Project Objectives

This project evaluated the biogeochemical processes of tungsten (W) in soils at scales ranging from regional to millimeter scale.

A) Regional scale: Soil and alfalfa (Medicago sativa) specimens were sampled from the San Joaquin Valley, in order to assess the spatial distribution of geogenic W and Mo in agricultural soils. Additionally, soil, water and vegetation samples were taken at abandoned mine tailings in two areas in California. Various methods were tested to determine bioavailable W and Mo in these soils.

B) Meso-scale studies: Adsorption experiments on soils and mine spoils were conducted to quantify the chemical processes affecting fate and transport of tungstate and molybdate. The factors affecting plant uptake of W, with potential interactions with Mo, were examined in hydroponic experiments.

C) Micro-scale studies: The main parameters controlling weathering and dissolution of W-metal alloy shotgun pellets were studied in soil incubation studies reflecting environmentally relevant soil conditions. Samples from these experiments were analyzed on the Stanford synchrotron using X-ray absorption spectroscopy.

Approach and procedures

Soil and plant samples were taken at 30 locations where high concentrations of W and Mo had been previously reported in benchmark soils of California and from abandoned W mines in California (Bradford et al., 1996; Phillip and Meyer, 1993). Total and bioavailable W concentrations were determined by evaluating extractants (strong acid, ammonium bicarbonate, weak acid, and water). Tungsten adsorption isotherms and adsorption envelopes were generated for a variety of soils, ionic strengths, and pH values. The fate and transport of W in soils were investigated in a series of soil incubation studies, which were carried out using the experimental procedures previously published by Amrhein et al. (1993). The weathering of W-pellets was studied in various soils (both aerobically and anaerobically) and extracted with a weak acid that was identified as a good indicator of plant bioavailability. W-pellets were also placed in moist aerobic Holland and Grangeville soils for 100 days. After incubation, the soil was dried at room temperature and impregnated under vacuum with epoxy resin. The impregnated soil blocks were cut and polished through an imbedded pellet for micro X-ray absorption imaging. Synchrotron radiation is ideally suited to characterize metal speciation, distribution, and oxidation state of W in soils. Micro X-ray absorption spectroscopy imaging (Stanford synchrotron beam line 2-3) was used to map the distribution of W-metal, WO₄²⁻, Fe, and Ni around the imbedded pellet and in the soil. Anaerobic tungsten-spiked Holland and Grangeville soils were simultaneously prepared for X-ray absorption near edge structure (XANES) analysis to characterize metal speciation and oxidation state of precipitates and solid phases.

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A series of germination experiments were conducted to determine the effects of W on germination rate and early seed development. In these experiments, seedlings were germinated in Petri dishes spiked with tungstate solutions ranging from 0 to 1000 mg W L$^{-1}$. The plant uptake potential of W was investigated in a hydroponic study under varying concentrations of W (0 – 10 µM) as well as varying sources of N (no N added, NaNO$_3$, NH$_4$Cl, NH$_4$NO$_3$). Alfalfa (Medicago sativa) was selected as the model plant due the importance of Mo in its physiology and widespread planting.

**Results**

**A) Spatial distribution of W:** The soil collected from the San Joaquin Valley, (identified as the same soil series as those collected by Bradford et al. 2006 with high W concentrations), showed slightly elevated tungsten concentrations (1.02 – 3.01 mg kg$^{-1}$) compared to the average background levels (0.77 mg kg$^{-1}$) of the 50 benchmark California soils. The alfalfa and grasses collected at these sites had low W-leaf concentrations (0.17 – 1.17 mg kg$^{-1}$) suggesting that W was not of concern on most soils in California. However, soils collected on W-mine spoils from the Bishop area were high in total tungsten (50 mg kg$^{-1}$) and plants growing in these spoils had elevated W concentrations in the leaves (4.5 mg kg$^{-1}$).

**B) Fate and transport of W:** Adsorption was clearly favored in soils with high concentrations of Fe-oxide minerals (adsorption max = 35.5 mmol kg$^{-1}$) compared to soils low in Fe-oxides (adsorption max = 1.85 mmol kg$^{-1}$). Soil pH values were adjusted to evaluate the pH effect of W-adsorption. Lowering of the pH greatly increased the W-sorption capacity of all soils tested, especially soils with high concentrations of Fe-oxide minerals.
Tungsten adsorption as a function of pH on a variety of soils with a wide range of chemical and physical characteristics showed adsorption was greatest (100%) near pH 3-4 and decreased with increasing pH up to 6.5. Above pH 6.5, adsorption was very low. Soils with Fe-oxides and greater clay percentages adsorbed more tungsten than sandy soils with low Fe-oxide concentrations.
Soil redox conditions significantly affected W mobility in soils. Soluble W concentrations steadily decreased from solution as soils became increasing anaerobic. It remains to be determined if the loss of $\text{WO}_4^{2-}$ from solution under low redox was due to reduction of the tungstate [W(VI)] to W(IV) and precipitation of $\text{WO}_2$ or due to the formation of Mn$^{2+}$- and Fe$^{2+}$-tungstate solids.

**C) Dissolution of W-shotgun pellets:** W-metal shotgun pellets incubated under aerobic conditions were readily oxidized, resulting in high concentrations of bioavailable W. The largest concentrations of bioavailable W (1700 – 3000 mg kg$^{-1}$ after a 4 month incubation time) were extracted from aerobic soils with low Fe-oxide minerals (Figure 2). Very little bioavailable W was extracted from anaerobic incubations (11 – 29 mg kg$^{-1}$) or soils high in Fe-oxides (9 – 27 mg kg$^{-1}$).

![Figure 2: Water soluble WO$_4^{2-}$ from 4-month incubations of W-pellets in a) Grangeville soil (low Fe-oxide, pH 6.5) and b) Holland soil (high Fe-oxides, pH 5.4) under aerobic or anaerobic redox conditions.](image)
SEM investigation of surface characteristics for W-pellets recovered from the incubations revealed that incubated W-pellet surfaces were significantly more weathered in the aerobic, acidic soil than either anaerobic incubation or slightly alkaline soil (Figures 3a, b, c). The aerobic samples showed significant pitting and weathering. The W-pellet from the Grangeville soil appears to have the majority of the corrosion along the Fe- and Ni-seams (Figure 3b). The pitting appears to result from the preferential loss of Fe and Ni from the binder phase leaving the larger W-grains (Ogundipe et al., 2006). The W-pellet from the Holland soil has much deeper pitting and is more extensive than the W-pellet from the Grangeville soil (Figure 3c). Again the corrosion appears to occur in the Fe- and Ni-seams but the W-grains are much smaller which would presumably mean oxidation and dissolution of the W-metal grains.

The two anaerobically incubated W-pellets, one from the Grangeville and the other from the Holland soil, show little pitting or corrosion (Figures 3d and 3e). The W-pellet recovered from the Grangeville soil appears as new and unaltered as the new non-incubated sample (compare 3a with 3d). The W-pellet recovered from the Holland soil shows light surface pitting but appears to have a patina or corrosion product coating parts of the surface (Figure 3e). The Fe/Ni-seams, visible in the new sample, appear to have been smoothed over or covered possibly in an iron-oxide coating or a ferberite (FeWO$_4$) coating. EDX was unable to distinguish between the surface coating and the bulk pellet.

**Fig. 3a:** “Fresh” non-incubated W-pellet surface

**Fig. 3b:** SEM images of W-pellet aerobically incubated in Grangeville soil
Fig. 3c: SEM images of W-pellet aerobically incubated in Holland soil

Fig. 3d: SEM images of W-Pellet incubated in Grangeville soil with anaerobic conditions

Fig. 3e: SEM images of W-Pellet incubated in Holland soil with anaerobic conditions
XAS microprobe analyses of W-pellets incubated in soil were examined for distribution of weathering products around W-pellet, oxidation state, and elemental associations as an *in situ* experiment. Pellets were incubated in soil for 100 days, preserved with an epoxy resin, and ground down to expose the W-pellet and surrounding soil. A micro X-ray absorption image of the pellet in soil showed oxidation and diffusion of $\text{WO}_4^{2-}$ away from the W-pellet (Figure 4). The $W^0$ image shows tungsten metal only exists as the W-pellet. The lighter colored areas inside the pellet are the seams or binder phase of Fe and Ni. From the edge of the pellet out into the soil, the oxidized tungsten decreases in concentration and is clustered in “hot spots”. These “hot spots” are areas of high Fe concentrations, most likely soil Fe-oxides (ferrihydrite and goethite) where tungstate is strongly adsorbed.

![Image of W-pellet incubated in soil](image)

**Figure 4:** X-ray absorption microprobe image of a W-pellet incubated in soil for 100 days under moist, aerobic conditions. The top image is a photograph of the pellet imbedded in the soil. The white bar in the figure is a scale bar = 1 mm. The three lower images show the distribution of total W, Fe, and $\text{WO}_4^{2-}$ associated with Fe. Areas of high Fe without associated $\text{WO}_4^{2-}$ indicate unweathered mafic minerals.
XANES analysis of a precipitate collected directly from the W-pellet (a yellowish-white precipitate that turned reddish-brown upon drying) confirmed it contained tungstate (Figure 5). The solution from the 1.5-year incubation had a pH of 6.3 and contained 585 mg L\(^{-1}\) soluble W. Thus, the oxidation of tungsten metal alloys in water can generate high concentrations of soluble WO\(_4^{2-}\) and potentially form secondary precipitates.

**Figure 5:** XANES spectra of unweathered W-pellet and the precipitate from the weathered W-pellet compared to W standards, sodium tungstate dihydrate, tungstic acid, WS\(_2\), and W-metal.

**D) Plant uptake of W:** Tungsten concentrations of up to 100 mg L\(^{-1}\) did not significantly affect germination rate and root length development. However, at concentrations of 1000 mg L\(^{-1}\) early radical and shoot development was reduced, though germination rates did not differ from the lower W treatments. When N was added as NO\(_3^-\), foliar W concentrations were consistently higher than in the NH\(_4^+\) treatment. Addition of 10 µM W (1.84 mg L\(^{-1}\)) to the nutrient solution resulted in mean W leaf tissue concentrations of 470 and 300 mg kg\(^{-1}\), respectively (Figure 6). Contrary to the fertilized treatments where foliar Mo concentrations were unaffected by W (data not shown), a potential antagonistic behavior between Mo and W uptake was observed in the unfertilized treatments (Figure 7). The addition of 0.5 µM W to the nutrient solution resulted in the depression of foliar Mo.
Figure 6: Effect of W concentrations in the nutrient solution (W\textsubscript{n.s.}) and N-source (NO\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+}) on W uptake by alfalfa.

Figure 7: Effect of W concentrations in the nutrient solution (W\textsubscript{n.s.}) on foliar Mo concentrations without N added.

Micro XAS imaging of alfalfa root/bacteria nodules showed W accumulation (Figure 8).
This suggests that $\text{WO}_4^{2-}$ may compete with $\text{MoO}_4^{2-}$ in the nitrogenase enzyme used by nitrogen fixing bacteria in the alfalfa root nodules. We observed that the uptake of nitrogen and $\text{MoO}_4^{2-}$ were influenced by the $\text{WO}_4^{2-}$ concentration in the hydroponic solutions and it would be interesting to determine if the tungstate was reduced to $\text{W(V)}$ in the nodule, analogous to the reaction with Mo in the nitrogenase enzyme.

![Microprobe image of an alfalfa root and root nodule showing W accumulation.](image)

**Figure 8:** Microprobe image of an alfalfa root and root nodule showing W accumulation. The white scale bar is 1 mm long.

**Discussion**

Tungsten concentrations in sampled soils of the San Joaquin Valley slightly exceeded the average background W concentrations from the 50 Californian benchmark soils, but the remarkably high concentrations (10 mg kg$^{-1}$) reported by Bradford et al. (1996) could not be confirmed. However, elevated W concentrations were found in mine spoils (50 mg kg$^{-1}$). The adsorption of W in soils was highly correlated to Fe-oxide minerals and acidic conditions. W-pellets oxidized readily under aerobic conditions, resulting in large concentrations of bioavailable W.

Clearly the redox conditions and the soil characteristics are important to W-pellet weathering. Aerobic incubation of W-pellets causes the loss of the binder phase, Fe and Ni, while increasing the surface area for W to be oxidized. W-pellet weathering is dependent upon oxygen to oxidize $\text{W}^0$ to $\text{WO}_4^{2-}$ and a low soil pH solubilizes the Fe and Ni binder metals from the W-pellet.

Although it might act as a potential competitor for essential oxyanionic elements, such as Mo and P, little is known about mechanisms controlling plant uptake of W. Results from our hydroponic study clearly indicate that W is highly available to alfalfa and readily translocated into the foliar biomass. Our experiments have also shown for the first time that W bears the potential to significantly reduce Mo uptake by alfalfa. Similar to observations previously made for Mo (Adriano, 2001), W uptake was highest in nitrate fertilized treatments indicating that W interacts with Mo in the N metabolism of higher plants. Our findings have brought up a whole new set of implications regarding W effects on nutrition of higher plants. Thus, the key question to be answered in follow-up experiments is: How does W interact with Mo in N metabolism?
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Since the 1950’s it has been well known that elevated Mo concentrations potentially cause serious nutritional disturbances in ruminants. However, such high W concentrations have never been addressed as a potential risk. Due to the striking geochemical similarity between Mo and W we suspect that elevated W concentrations might induce hypocuprosis in ruminants similar to the effect of elevated Mo.

References


List of Publications/Presentations Resulting from Project


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