

Biogeochemistry of tungsten in the plant soil environment

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1. Introduction

Tungsten (W) is a Group VI transition metal (along with chromium and molybdenum) that has strategic importance in industry, technology, and military applications because of its hardness, density, alloying properties, thermal and electrical conductivity, and high melting point. Despite being of such high strategic value, a recent life-cycle assessment of W has shown that the end-of-life losses are considerable since products are either discarded or unrecoverable after use (U.S. Geological Survey, 2008). Tungsten adds an unequalled hardness to alloys and is therefore frequently used for cutting and drilling tools. In the military, tungsten replaces depleted uranium in high-kinetic-energy penetrators and armour plating. More recently, tungsten has become a popular metal replacing lead in small-calibre and shotgun ammunition and fishing sinkers because it is considered to be significantly less toxic than lead in the environment. There has been a long-standing notion that tungsten is environmentally benign and at present, there are no drinking water standards or discharge limits for air, surface water, groundwater, or soils in Europe or the U.S.

However, recently tungsten was implicated in childhood leukemia clusters in three western U.S. communities although further investigations found no causal relationship between W and leukemia at one of the sites (Rubin 2007). Samples of drinking water, vegetation, blood and urine from these locations had elevated W concentrations and the Centres for Disease Control and Prevention successfully petitioned the National Toxicology Program of the National Institute of Environmental Health Sciences, National Institutes of Health, to prioritize research regarding the health effects of tungsten exposure. Tungsten now occupies the top of “to do” lists of various regulatory, health, and environmental agencies.

As of today, neither anthropogenic nor geogenic soil-W have been subject to extensive toxicological and/or fate and transport studies. Therefore the aim of my research visit at the UC Riverside California was to join Professor Chris Amrhein and Dr Alex Dellantonio in an ongoing project on the biogeochemistry of tungsten in soil and contribute with the cooperative

development of new ideas and experiments to get a better understanding of the fate and behaviour of tungsten in soil.

In uncontaminated soils, background concentrations of W seldom exceed 1 mg kg^{-1} , however, a survey conducted in the European Union has shown that some soils contain up to 83 mg kg^{-1} . Similar concentrations have been detected by our group in mine spoils in the Sierra Nevada (CA). Use of W containing ammunitions has lead to elevated concentrations ($\sim 5200 \text{ mg kg}^{-1}$) in surface soils at military firing ranges. In addition, W-Fe-Ni alloys and W-polymer composites are becoming the preferred alternative to lead, iron, and bismuth in waterfowl shotgun ammunition. The fate of such W shotgun pellets under environmental conditions in soils is still not completely understood. Pioneer laboratory experiments on the dissolution kinetics of powdered tungsten-metal alloys used in ammunitions have suggested that substantial amounts of W are potentially solubilized. Preliminary experiments carried out in the UCR laboratory on two types of W-containing bullets have shown that redox conditions are a potential key factor controlling dissolution of W from W-containing bullets. While under anaerobic conditions most of the W is insoluble, aerobic conditions favor the dissolution of considerable amounts of W, which leads to locally increased W concentrations in soils with up to 2500 mg kg^{-1} of potentially bioavailable W.

Additionally, little is known about the uptake behaviour of W by plants. Occurring in soils mostly as anion (WO_4^{2-}), W is thought to be a potential competitor for molybdate (MoO_4^{2-}) and phosphate (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , depending on soil pH) uptake, two elements which are both essential for plant growth. Particularly molybdenum (Mo) has drawn considerable attention to the research community in respect to the biogeochemistry of W.

Having an almost identical atomic and ionic radii, W and Mo exhibit a striking similarity in their geochemical behaviour and properties. However, despite their similarity, molybdenum is considered an essential micronutrient for plants and animals but being potentially toxic at higher concentrations as it leads to secondary Cu deficiency, which has shown to be particularly problematic for ruminants. Furthermore the essential role of molybdenum (Mo) in a variety of fundamental biological processes has been known for over 60 years. Moreover, Mo-containing enzymes are ubiquitous in nature and have been found in the vast majority of different forms of life (Kletzin, 1996). In contrast to Mo, neither an

essential metabolic function nor a distinct toxic reaction of W in eukaryotes has been reported. However, a handful of highly specialized and oxygen-sensitive tungsten enzymes in microorganisms has been discovered in the past decades and it was assumed that these enzymes might occur in a much wider range in other prokaryotes than previously thought (Ljungdahl, 1979).

Considering the high chemical identity of tungsten and molybdenum, it has been speculated that W might be able to replace Mo in its various enzymes. However, results of microbial studies in the 70s showed that tungstate can replace molybdate in molybdenum-based enzymes, but renders them inactive (Johnson, 1974; Johnson and Rajagopalan, 1976 from Bednar 08).

So far, little is known about the plant-internal pathway of W following uptake as well as the possible competitive/inhibiting effect of W in molybdenum uptake as it is highly likely that W is taken up via the molybdenum uptake. Early plant uptake studies suggest that W accumulation by plants does not lead to detrimental effects (Kovalevskiy, 1966; Petrunina, 1974; Furr, 1980) and so far W related phytotoxicity has not been reported yet. Moreover, the total W content of plants seems to depend largely on the origin of soil they are grown in.

In order to better understand plant uptake behaviour, a comprehensive understanding of tungsten speciation and geochemistry is needed since these parameters determine sorption to soil, and therefore mobility, bioavailability, and toxicity.

Therefore the experimental object of my research visit at UC Riverside was to further investigate sorption dynamics of W and Mo in different soils at different oxidation states as well as the effect of competing anions at different oxidation states. Furthermore a plant uptake study with alfalfa (*Medicago sativa*) was carried out to examine the uptake behaviour and possible negative effects when different sources of W were supplied (W shotgun pellets and W carbide powder).

2. Materials and Methods

2.1 Comparison of different sample stabilization methods

Due to the known tendency of W to form polymer precipitates when present in high concentrations and at low pH, the commonly used acidification of samples for stabilization purposes prior to analysis was compared to either no stabilization treatment or sample alkalization. Briefly soil from Fallbrook, CA was spiked with 5 mg kg⁻¹ Mo and 10, 50, and 200 mg kg⁻¹ W respectively and a soil saturation extract (SSE) in 3 replicates per W concentration with an equilibration time of 24h was carried out. Each sample was split into 3 and either 0.1 ml of HNO₃ (69%), H₂O (dest.) or 1M NaOH were added and samples were analysed by ICP-OES.

2.2 Effect of increasing incubation time under O₂ exclusion on water-extractable element concentration

Soil (Riverside, CA) was spiked with different concentrations of W and Mo (Table 1) and left for incubation for 5 months at 30°C. To provide sufficient C for microbial growth each soil treatment was mixed with 2.2 g kg⁻¹ of dried and grinded alfalfa biomass. An incubation time row was set up with triplicates of each treatment being incubated for 0, 1, 2, 3, 6, 9, 12, 15, 18, and 21 days under O₂ free conditions. Briefly, soil (20g) was weighed into 50 ml polypropylene tubes and 0.04g S as Na₂SO₄ was added (5 ml, degased). The remaining O₂ in the air filled space in the tubes was dispersed by blowing N₂ into the bottles for 10 seconds before the tubes were carefully closed. To avoid accumulation of CO₂ in the samples a thin tube was inserted through a hole in the lid with the end of the tube being submersed in a water filled beaker allowing CO₂ to leave and

W (mg kg ⁻¹)	Mo (mg kg ⁻¹)
50	0
0	50
100	100
500	500
500	0
0	500

Table 1 Concentrations of W and Mo added to the soil

preventing O₂ to enter the sample. To further minimize O₂ diffusion, samples were additionally placed in N₂ filled box. At the end of each incubation period, samples were extracted with degased distilled water (15 ml, SSR 1:1) for 2 hours, centrifuged for 10 min at 3000 g and filtered through a 0.45 µm nylon syringe filter (Whatman GD/X). After measuring electric conductivity and pH in the filtrates, samples were stabilized by adding 0.1 ml of 1M NaOH and analysed for metal content by ICP-OES.

2.3 *Desorption dynamics of W from a mine soil at 3 different oxidation states*

Availability and replenishment rates of W in a soil from a Californian W mine at 3 different oxidation states were investigated by conducting a sequential desorption isotherm as well as desorption kinetic studies. All desorption studies were conducted with NaCl (EC = 364 µS cm⁻¹ = EC soil (SSE)) as background electrolyte. To examine the minimum equilibration time required for W desorption under different O₂ regimes, soil (10g, dry weight) was incubated under O₂ free conditions after the addition of 2 ml degased NaCl (EC = 364 µS cm⁻¹) for 0, 5, and 10 days respectively. At the end of the incubation time, 8 ml of degased NaCl (EC = 364 µS cm⁻¹) were added to the samples to achieve a final soil to solution ratio of 1:1 and a set of triplicates for each incubation regime was shaken for either 0.5, 1, 2, 4, 6, 8, 24, 48 hours with an end-over-end shaker at 10 rounds per minute. Samples were centrifuged, filtered and analyzed as described above.

For the sequential desorption study, triplicates of soil samples were incubated under O₂ free conditions as described above. The results of the desorption kinetic study suggested that after a shaking time of 8 hours equilibrium conditions were reached, therefore 16 sequential steps of repeated extraction were carried out to investigate the desorption behaviour of W under different redox conditions in this soil. The same extraction solution and procedure as in the kinetic study were used. To minimize O₂ influence on the incubated soils, with N₂ degased extraction solution was used and the O₂ in the air filled space in the shaking bottles was dispersed by blowing N₂ into the bottles for 10 seconds after each change of extraction solution.

2.4. Sorption dynamics of W with competing anions on goethite

Competitive sorption interactions and the mobilization of W from goethite by other anions was investigated by extracting freshly adsorbed and aged W with different concentrations of PO₄ and citrate at 2 different pH levels.

A 10 ml aliquot of a goethite suspension (1.25g L⁻¹) was pipetted under continuous agitation into 25 ml polypropylene tubes together with 10 ml of NaWO₄ (1.79 mg L⁻¹), resulting in a total W concentration of 5.44 μmol W per sample. To investigate the effect of aging and pH on W sorption dynamics, three sets of samples were prepared. The pH of set 1 and set 2 was adjusted with 1M HCl to 5.8, with set 1 being left for equilibration for 14 days and set 2 for 24 hours. Set 3 was also equilibrated for 24 hours but with the pH kept one unit below the pH of set 1 & 2 (4.8). The effect of competing anions on W sorption was studied by adding either 0.544, 5.44, or 544 μmol of PO₄ and citrate in the form of 5 ml of 0.109 mM, 1.09 mM, and 10.9 mM NaH₂PO₄-Na₂HPO₄ or Na₃-cit-Na₂H-cit with the pH adjusted to either 4.8 or 5.8. Samples were shaking for 2 hours at 50 revolutions min⁻¹, centrifuged at 2000 g for 10 minutes and an aliquot of the supernatant was analyzed by ICP-OES.

2.5. Plant uptake experiment

Plant uptake of W derived from weathering two different types of W-alloys (shot gun pellets and tungsten carbide (WC) powder) was studied in a pot experiment. Briefly, soil (Grangeville, CA) was spiked with varying amounts of W-based shotgun pellets (supershot, ~85% W) and with varying amounts of WC powder, respectively. Treatments consisted of 500g soil per pot with additions of either 0, 5, 10, and 20 shotgun pellets per pot (corresponding to 0, 935, 1870, and 3740 mg kg⁻¹ total W, respectively) or WC powder additions at rates of 0, 0.5 g, 1.0 g, and 2.0 g (corresponding to 0 mg kg⁻¹, 935 mg kg⁻¹, 1870 mg kg⁻¹, and 3740 mg kg⁻¹ total W, respectively). Thereafter, 5 alfalfa (*Medicago sativa*) seedlings per pot were planted and plants were grown for a total of 80 days in growth chambers (T =25°C, humidity 70%, photoperiod 10h) and watered daily with ~50 mL DI water. After the growth period of 80 days, plants were harvested and shoots were dried, weighed and grinded. To determine the total metal content in the plant tissue, acid digestions were carried out with the grinded plant material and samples were analysed by ICP-OES.

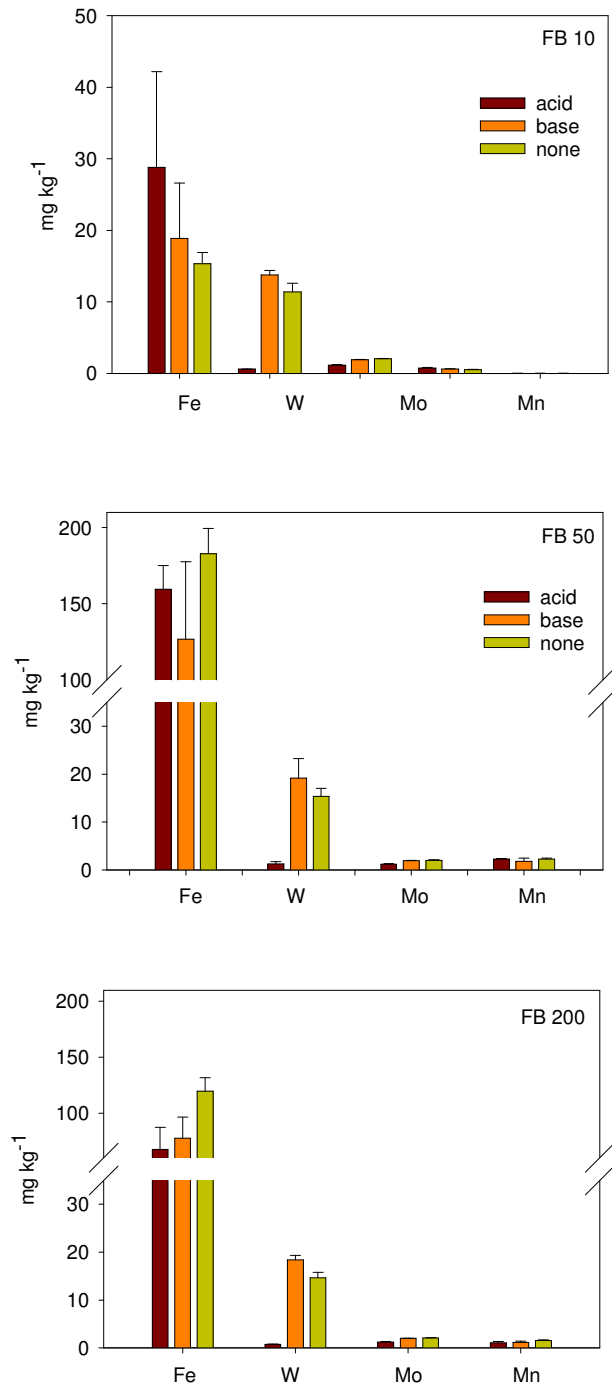
3. Results and Discussion

3.1 Comparison of different sample stabilization methods

The comparison of different sampling conservation methods (Figure 1) clearly showed that acidification significantly decreased the recovery of measured W in soil extracts while the addition of small amounts of 1M NaOH resulted in slightly higher or similar measured W concentrations compared to the none treatment. Tungsten, as well as Mo, has the tendency to polymerize at low pH and when present at high concentrations. Depending on the size of the polymers, they might act as precipitates and are therefore removed from the measurable liquid phase. Despite similar chemical behaviour of W and Mo, W seems to be considerably more sensitive to acidification which might either be due to the intrinsic higher W concentration in this particular case study or due to a higher tendency of W to form precipitate polymers. Additionally, the high density of tungsten ($19.25 \text{ g}\cdot\text{cm}^{-3}$) compared to molybdenum ($10.28 \text{ g}\cdot\text{cm}^{-3}$) might further enhance precipitate behaviour of the formed polymers.

Further investigation is needed to elucidate the pH and concentration dependent polymerization of W and Mo in pure solutions as well as in soil extracts. Acidification is commonly used for sample stabilization in trace element analysis and has proved to work well for most elements. However our results suggest that when W and/or Mo are the elements of interest, the addition of acid can significantly decrease measurable W in soil extract solutions. Therefore we suggest that if sample conservation is needed, base should be added instead to prevent W and Mo polymerization and precipitation, particularly at high concentrations

Figure 1 Comparison of different sample stabilization methods



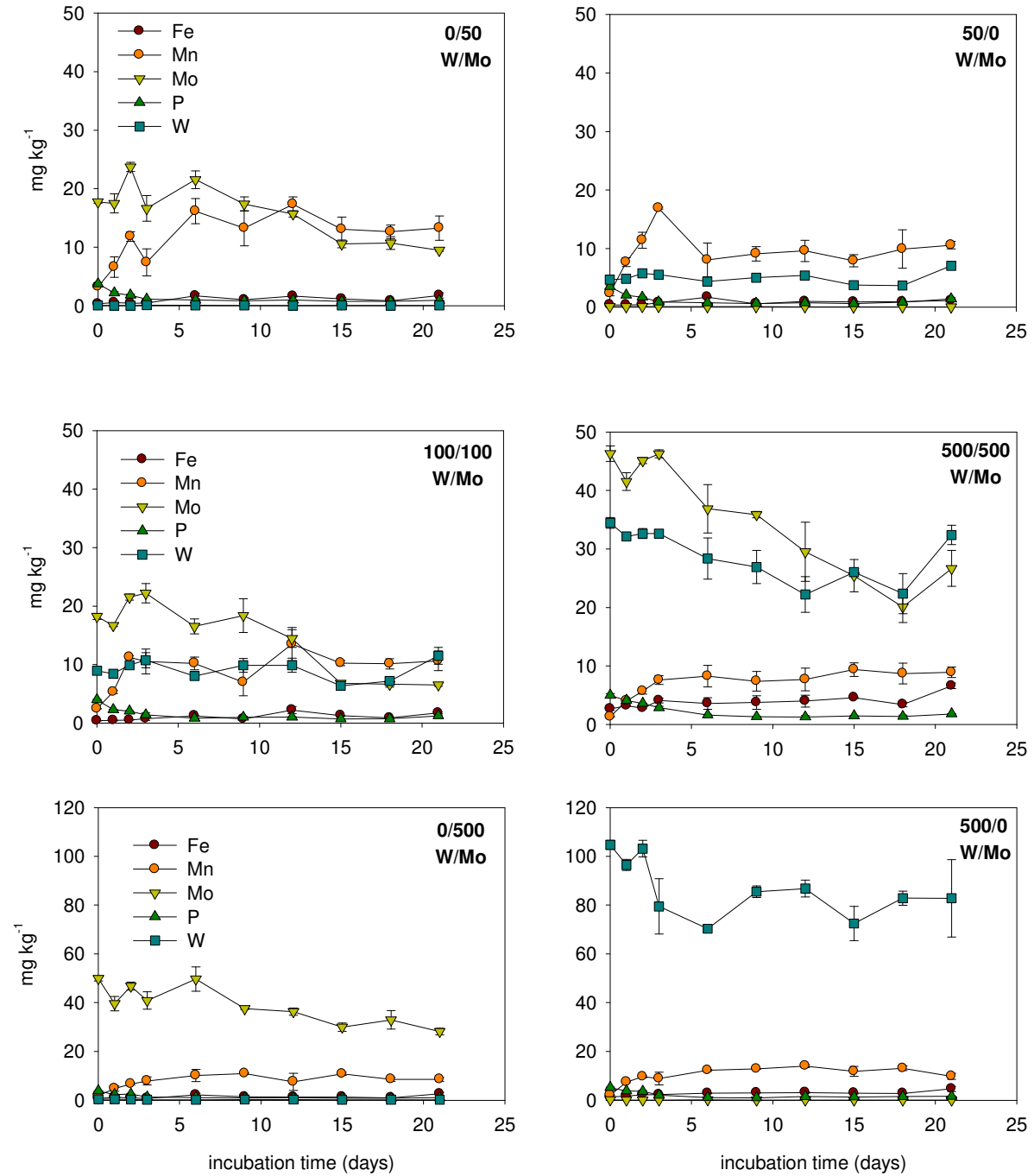
3.2. Effect of increasing incubation time under O₂ exclusion on water-extractable element concentration

Tungsten, as well as Mo, occurs in soils as divalent anion (WO_4^{2-} , MoO_4^{2-}) with their oxidation state being sensitive to changes in redox potential. Redox processes in soil are driven by the soil microbial community that start using other elements than oxygen for electron transfer under anaerobic conditions. Changes in oxidation number of an element in soil are usually accompanied with changes in sorption behaviour. Previous experiments have shown that W and Mo availability decreases under increasing anaerobic conditions. Due to the striking similarity of W and Mo (same ionic radius, same valence), we investigated the availability of W and Mo alone and as competing anions at different concentrations in soil with decreasing redox potential over a period of 21 days.

As expected, W and Mo concentrations decreased with increasing incubation time; however different mobility patterns and competing effects of the 2 anions could be observed (Figure 2).

Molybdenum availability was generally higher than W availability in all treatments, except the 500/0 W/Mo treatment. In this treatment tungsten showed a surprisingly high availability of 21% of the total W added that decreased to 17% (of total W added) after 21 incubation days whereas in all other W treatments approximately 10% of the added W was extractable under aerobic conditions. The extractability of W under increasing anaerobic conditions decreased by approximately 30%. Molybdenum on the other hand was generally more available than W and a decrease in redox potential reduced the available Mo fraction by almost 50% in all treatments. When both Mo and W were added to the experimental soil in the same concentration, W again seemed to be generally stronger bound to the soil matrix and its extractability was influenced to a lesser extent throughout the incubation period.

Figure 2 Effect of increasing incubation time under O₂ exclusion on water-extractable element concentration



The mechanism involved in the immobilization of W and Mo still remain to be identified. It has been assumed that the reduced W^{IV} might form insoluble $W^{IV}S_2$, $W^{IV}O_2$ or thiotungstates ($W^{IV}S_4^{2-}$). The formation of stable W- Fe^{II} compounds has also been discussed, but direct evidence for this is still missing. Further experiments including synchrotron radiation techniques are on their way to elucidate the fate of tungsten and molybdenum in soils with decreasing redox potential.

2.3 *Desorption dynamics of W from a mine soil at 3 different oxidation states*

Investigations of the desorption kinetics of W and Mo in the experimental mine soil showed that the desorption reaction was at equilibrium after 6 hours (Figure 3). Consequently this time was used as time interval for the sequential desorption isotherm. In contrast to the previous experiment, the kinetic study showed increasing W and Mo availability with decreasing redox potential. However, no clear trend could be observed in the kinetic study as 5 days of anoxic incubation appeared to render more Mo and W available than 10 days of incubation. This might be explained by the interaction with other redox sensitive ions whose transformation of oxidation state and consequently change in adsorption behaviour follows different time dynamics. This assumption is supported by the results of the sequential desorption experiment (Figure 4). Again we find a higher availability of W and Mo, as well as Mn, Ni, Zn with decreasing redox potential. But Figure 4 also shows that the expected decrease in availability is probably counteracted by significant dissolution of iron oxides that occurs when Fe^{III} is reduced to Fe^{II} and is reflected by a sharp increase in Fe availability. The loss of potential sorption sites will certainly render W and Mo more available. Additionally, the increase in pH by approximately half a pH unit with increasing number of extraction steps favours iron oxide dissolution and further decreases W and Mo adsorption.

The results of this desorption study show that W and Mo follow the same trend in sorption behaviour but with W being generally less mobile. Availability of W and Mo in soil is strongly influenced by redox conditions as well as the redox dynamics and behaviour of other elements, particularly Fe and S.

Figure 3 Desorption kinetic parameters of a mine soil incubated under O₂ exclusion for 0, 5 and 10 days

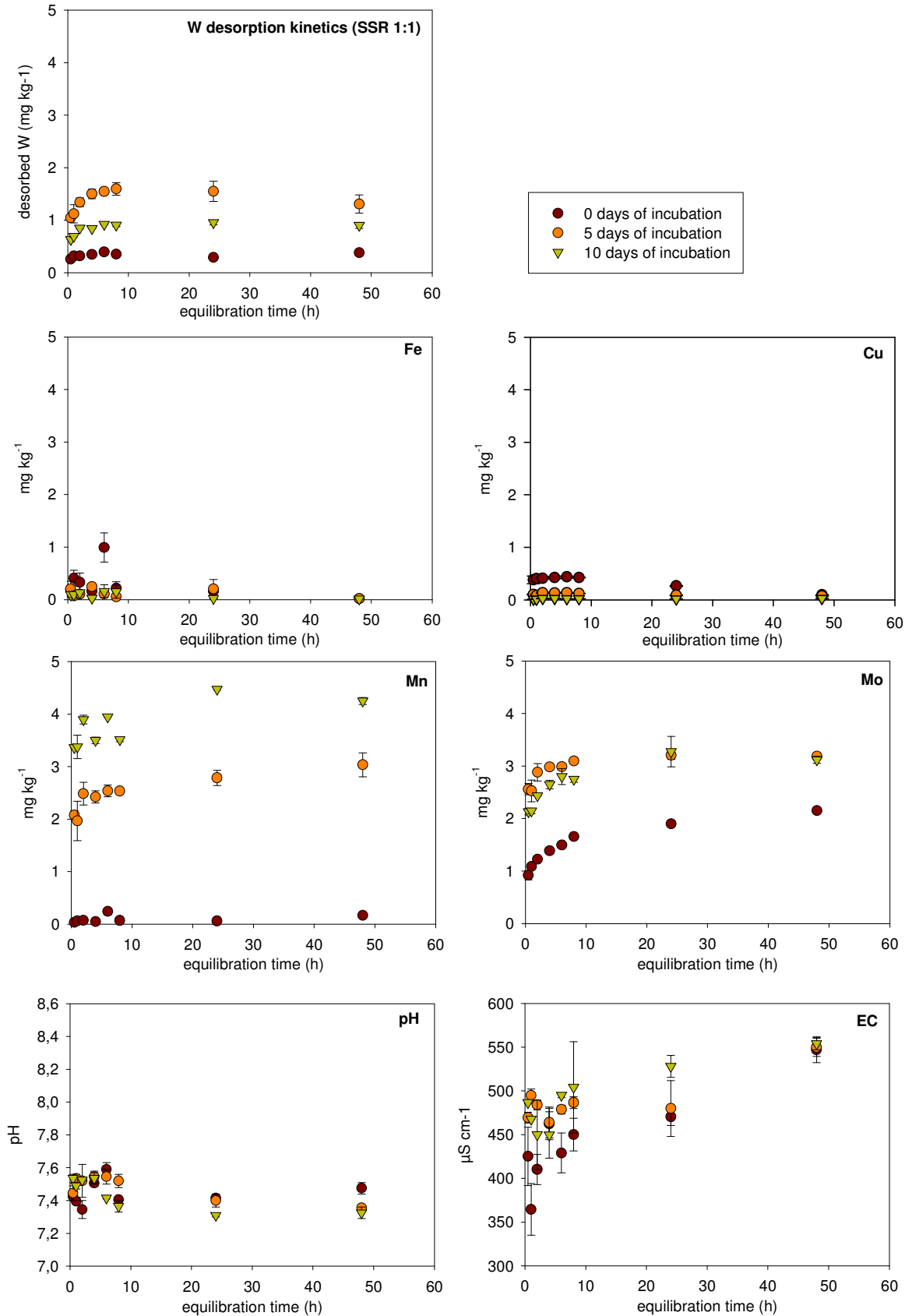
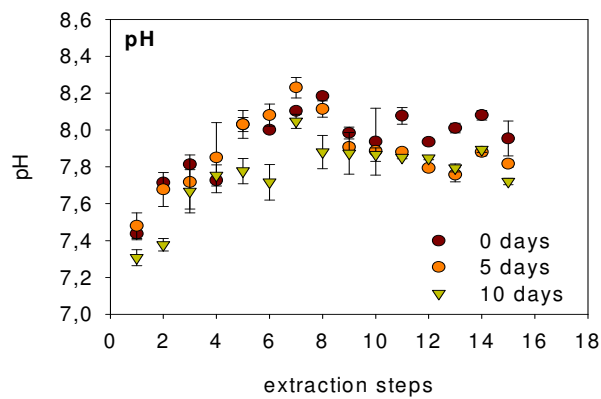
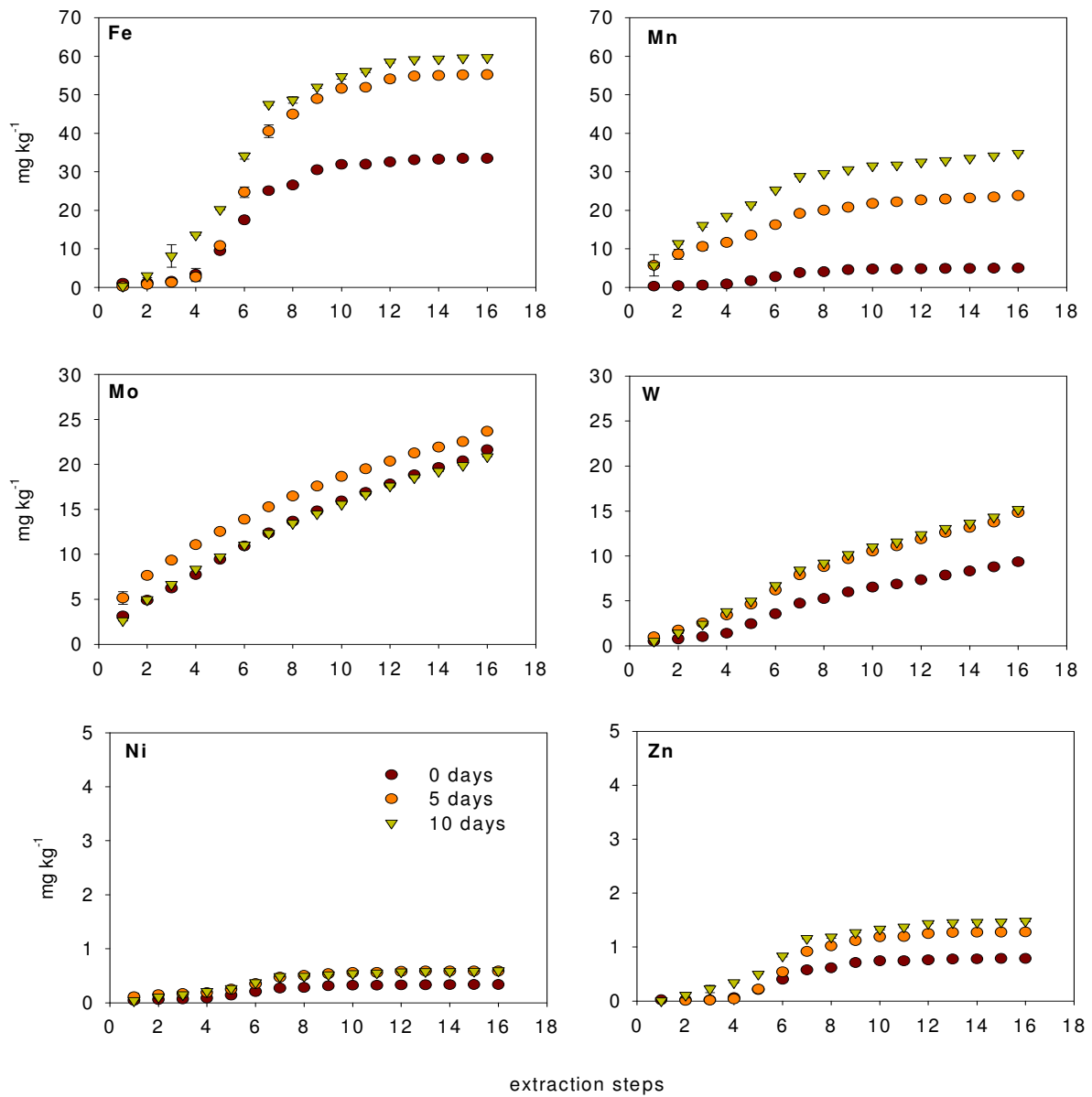


Figure 4 Sequential desorption isotherm



3.4. Sorption dynamics of W with competing anions on goethite

The competitive effect of other organic and inorganic anions on tungsten adsorbed on goethite was investigated by extracting freshly adsorbed and aged W with different concentrations of phosphate and citrate at 2 different pH levels (4.8 and 5.8).

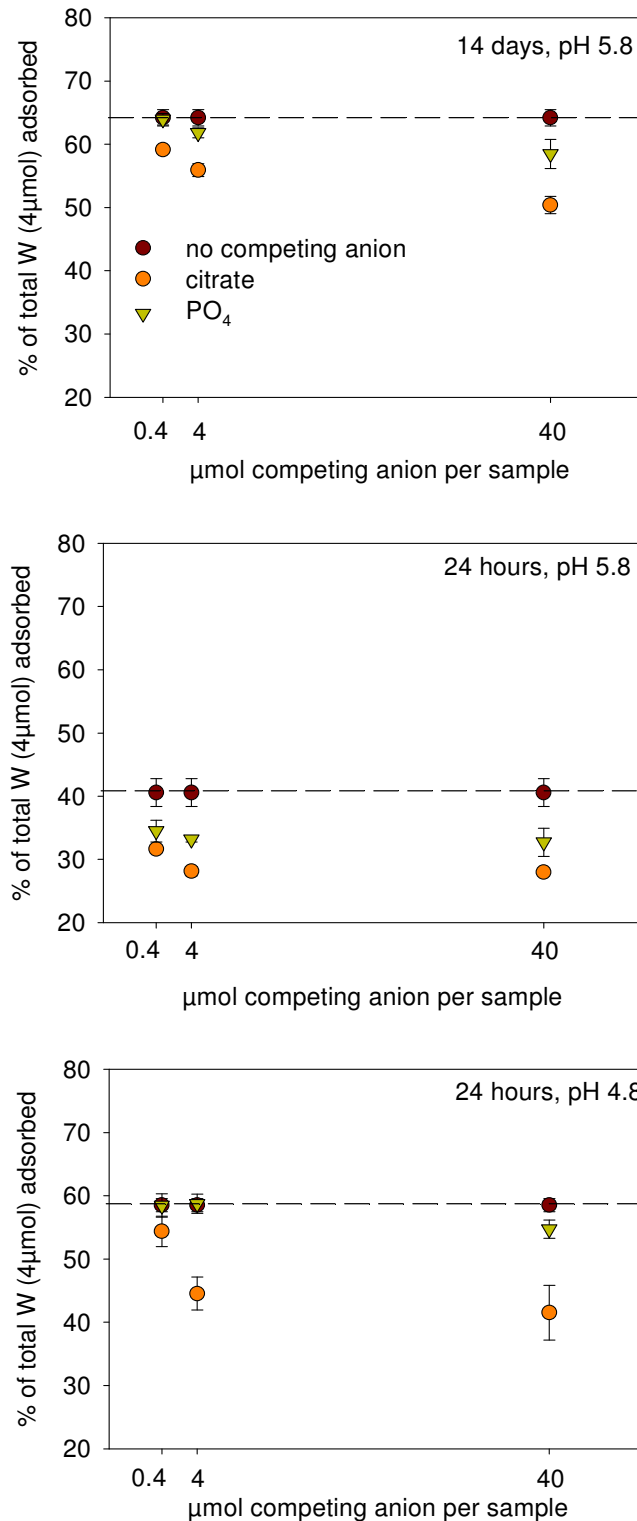
Results showed that tungsten adsorption on goethite was significantly influenced by reaction time and pH (figure 5). An ageing period of 14 days resulted in an increase of adsorbed W by 36% at pH 5.8 compared to freshly adsorbed W (24h). This commonly observed ageing effect is caused by increasing diffusion into inner crystal layers of the ions over time rendering the ions less exchangeable. At pH 4.8 with an equilibration time of 24h, almost the same amount of W ($59\pm 1\%$) was adsorbed as in the aged treatment at pH 5.8 ($61\pm 1\%$).

Being a variable charge mineral, the positive surface charge of goethite increases with decreasing pH providing a higher electrochemical attraction for anions at low pH. However, this is partly counteracted by the increasing protonation of the anion in the solution, which depends on the speciation properties of each anion. At pH 4.8, the dominating citrate species is Hcit^{2-} , with increasing amounts of cit^{3-} at pH 5.8 while H_2PO_4^- is the predominant phosphate species for both experimental pH ranges. Ion exchange processes from mineral surfaces are predominantly governed by ion valence, with increasing exchange tendency with increasing ion valence. Therefore it is not surprising that we find citrate to be significantly more efficient in exchanging W from goethite. Across all pH and ageing treatments, the same amount of competing anion resulted in a decrease of adsorbed W by $22\pm 5\%$ for citrate and $7\pm 6\%$ for phosphate respectively. A 10 fold higher concentration of competing anion further reduced the amount of W adsorbed by $27\pm 3\%$ and $12\pm 4\%$ for citrate and phosphate respectively, while when a 10 fold lower concentration was added only citrate was able to mobilize $12\pm 5\%$ of adsorbed W across all treatments.

Interestingly, both competing anions showed a fairly constant W mobilization capacity in the treatment with freshly sorbed W at pH 5.8 across all 3 concentration ranges ($28\pm 3\%$ and $17\pm 1\%$ W desorbed by citrate and phosphate respectively). This indicates that at a higher pH a certain proportion of the freshly adsorbed W is only loosely bound to the mineral surfaces and is easily exchanged by even small amounts of competing anions. The more

pronounced effect of competing anion concentration in the aged and low pH treatment reflects the stronger binding forces either over time or at a more positive surface charge.

Figure 5 Sorption dynamics of W with competing anions on goethite

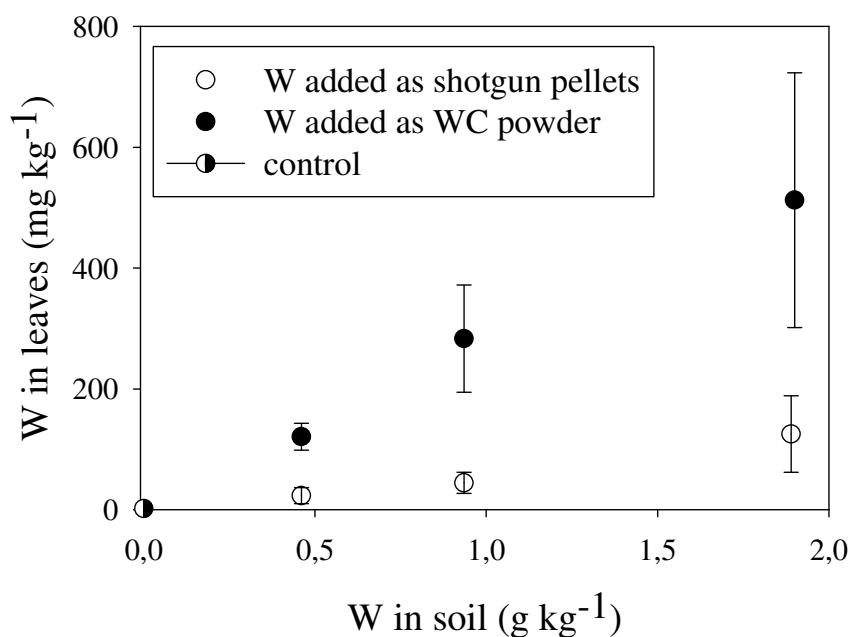


Overall our results showed that sorption and competitive desorption of anions onto goethite are significantly affected by pH and time with stronger binding occurring with increasing time and at lower pH. Furthermore, the pH dependent valence of the competing anion governs its competitiveness for sorption sites.

3.5. Tungsten and molybdenum uptake by alfalfa

Tungsten derived from WC and metallic W-shot proved readily plant available, with WC treatments yielding consistently higher foliar W concentrations than the W-shot treatments (Figure 6). This may be due to the fine powdered nature and the consequently much larger surface area of the added WC.

Figure 6 W content in alfalfa leaves dependent on concentration and nature of the added W- alloy



The addition of five pellets per pot, which correspond to $0.94 \text{ g total W kg}^{-1}$, resulted in leaf W concentrations of 23.3 mg kg^{-1} . When the same amount of W was added as WC powder, 121.0 mg kg^{-1} of W were found in the leaves. Further increase of W additions resulted in an almost linear increase of foliar W concentrations: leaves from alfalfa growing in the 10 pellets treatment (1.88 g W kg^{-1}) and the 20 pellets treatment (3.75 g W kg^{-1}) contained $44.3 \text{ mg W kg}^{-1}$ and $125.3 \text{ mg W kg}^{-1}$, respectively. When aliquot amounts of W were added as WC, leaf W concentrations were significantly higher with an average of $283.3 \text{ mg W kg}^{-1}$ and $512.6 \text{ mg W kg}^{-1}$, respectively. Even at such high W concentrations, alfalfa aboveground biomass did not significantly differ from the controls and no adverse effects on plant health and vigour could be observed. So far, there is limited knowledge about mean W concentrations in plant biomass as well as plant toxic W concentrations and therefore toxicity levels of W in soils are virtually unknown. Only a hand full of reports exists concerning W concentrations in various plant biomass samples. Koutsospyros et al. (2006) found W concentrations ranging from 0.1 mg kg^{-1} in oak bark to 50 mg kg^{-1} in beech leaves. In the same review, the authors gave a concentration range of $5 - 100 \text{ mg kg}^{-1}$ for trees and shrubs. However, to our knowledge there are no comprehensive studies investigating concentration dependent W uptake and toxicity levels for a broad range of plants and soils as there have been for other Group VI elements such as Cr and Mo.

Elevated concentrations of Mo, which closely resembles W in terms of ionic radius and redox chemistry, have been associated with hypocuprosis, a secondary Cu deficiency responsible for severe nutritional disturbances in ruminants. High levels of thiomolybdates, which are formed by the ruminal reduction of molybdate in the presence of sulphide, bind Cu in an insoluble form and thus render it non-bioavailable.

In general, Cu:Mo ratios less than 2.0 are generally regarded as hazardous. In our study molybdenum concentrations in alfalfa leaves were generally low and decreased with increasing W concentrations when W was supplied as W carbide powder (WC) while the presence of different amounts of weathered shotgun pellets resulted in similar to slightly increased Mo concentrations in the harvested alfalfa leaves (Table 2). Table 2 also shows that while leaf tissue Cu:Mo ratios were higher than 2.0 throughout the WC treatment, Cu:W ratios were less than 0.29 in all the treatments with a minimum of 0.01 in the highest WC treatment. As of to date, such Cu:W ratios have not been addressed as a potential hazard.

However, thermodynamic considerations lead to the assumption that in the rumen tungstate (WO_4^{2-}) is progressively reduced to tetrathiotungstate (WS_4^{2-}), with the reaction proceeding at lower formation rates than the corresponding Mo-reduction. Based on these assumptions, the same authors used radiolabeled thiotungstates as a proxy for thiomolybdates in a series of animal studies and found that thiotungstate interacted in the Cu-metabolism of sheep in a way analogous to thiomolybdates. In view of the large concentrations found in the biomass from the WC pot experiments and the close similarity between Cu-thiomolybdate and Cu-thiotungstate interactions, such Cu:W ratios appear as potentially hazardous to ruminants.

Table 2

W added	Mo in leaves	Mo in leaves	Cu:Mo	Cu:W
	WC	BB	WC	
mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹		
	mean ± sem	mean ± sem		
0	1.07 ± 0.40	1.07 ± 0.40	5.03	2.69
0.94	1.10 ± 0.47	0.85 ± 0.38	6.76	0.06
1.88	0.43 ± 0.19	1.53 ± 1.00	17.02	0.03
3.76	0.44 ± 0.06	1.85 ± 1.33	17.34	0.01

Considering the toxic potential of high Mo uptake for ruminants, increasing efforts should be made to investigate the effect of tungsten on other organisms once entering the food chain.

Conclusion

Our results show that W and Mo mobility in soil is strongly influenced by redox conditions and pH. Also the redox dynamics of other redox sensitive ions, particularly iron and sulphur, seem to play an important role for W and Mo availability under increasing anaerobic conditions. Further experiments are on its way to elucidate the exact mechanisms involved in W and Mo release and retention respectively in soil.

Our plant uptake study showed that different sources of W resulted in different phytoavailability of W and consequently different amounts of W were taken up by our model plant alfalfa. Even rather high additions of W to the experimental soil didn't seem to affect plant health and vigour but W leave tissue content increased almost linear with increasing W concentration in soil.

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Until further notice, I kindly ask not to publish this research report on the Marshallplan homepage or anywhere else before the end of 2011, as we intend to publish the results in scientific journals.

Thanks for your understanding.

Eva Oburger

Wien, 30.03.2009