

Biogeochemistry of tungsten alloys in soils

A. DELLANTONIO, M.H. DAVIS AND C. AMRHEIN*

Department of Environmental Sciences, University of California, Riverside, California 92521

(*correspondence: christopher.amrhein@ucr.edu)

Tungsten (W) is widely used as tungsten carbide (WC) in industrial applications due to its hardness and high density. Tungsten has also become a popular metal replacing lead in small-caliber and shotgun ammunition and fishing sinkers because it is considered to be significantly less toxic than lead in the environment. However, recent findings have led to a growing concern about the environmental risks associated with tungsten (W) [1]. However, there is limited knowledge about soil properties controlling the dissolution of W-metal and W-alloys, and the effect of tungstate (WO_4^{2-}) on plants.

Discussion of Results

We found evidence that W-metal shot incubated under aerobic conditions rapidly oxidized producing high concentrations of bioavailable tungstate (WO_4^{2-}). The largest concentrations of WO_4^{2-} were present in aerobic soils with low Fe-oxide minerals. Our experiments show that W derived from the oxidation of W-metal shotgun pellets is readily taken up by alfalfa (*Medicago sativa*) and translocated into the foliar biomass. Effects of W on Mo uptake were studied in a hydroponic experiment. We were able to show that W interacts with the Mo and N metabolism of higher plants.

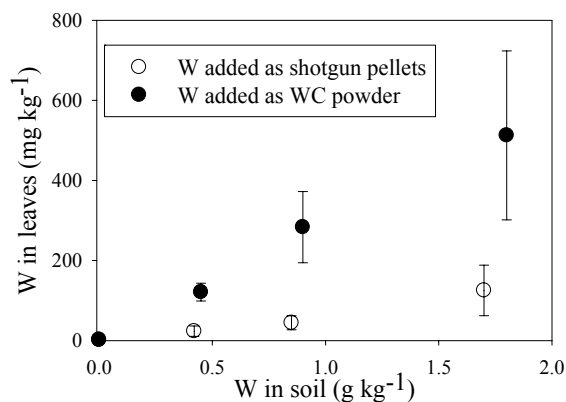


Figure 1: Effects of increasing tungsten carbide (WC) and W-metal shot additions on W concentrations in alfalfa.

[1] Petkewich (2009) *Chem. & Eng. News* **87** (3), 63-65.

Spectroscopic studies of uranyl sorption in $\text{PO}_4 / \alpha\text{-Al}_2\text{O}_3$ systems

M. DEL NERO^{1*}, C. GALINDO¹, E. HALTER²
AND B. MADE²

¹IPHC, CNRS/ULP, 67037 Strasbourg, France

(*correspondence: mireille.delnero@ires.in2p3.fr)

²Centre Géosciences, ENSMP, Fontainebleau, France

Modelling of the environmental behaviour of U requires knowledge of uranyl sorption species forming at surfaces of minerals or colloids. Of particular interest for the geo-cycling of U is the binding of phosphate ions (P) on oxides, which is expected to influence surface reactivity of soils. P can co-adsorb with dissolved U to form ternary surface complexes. To address the study of U sorption in $\text{PO}_4 / \alpha\text{-Al}_2\text{O}_3$ systems, we investigated the adsorption and in-situ speciation of phosphate on alumina colloids, using adsorption envelopes, zeta potential (ζ) measurements and ATR-FTIR spectroscopy. Adsorption of P, over a wide range of pH and aqueous P concentration ($[\text{P}]_{\text{aq}} \leq 100 \mu\text{M}$), induces a significant shift and enlargement of the IR vibration bands characteristics of phosphate, which evidences a strong interaction between P and aluminol surface groups. The P sorption envelopes in alumina suspensions show that adsorption decreases with an increase of pH (3-8). At pH 3.5, P adsorption conforms to the Freundlich sorption isotherm in a wide range of $[\text{P}]_{\text{aq}}$ (10 – 400 μM). The isoelectric point of alumina (8.5) is shifted towards lower pH values with an increase of $[\text{P}]_{\text{aq}}$. At low pH (3.5), the ζ value decreases sharply with increasing P surface coverage up to 25 $\mu\text{mol/g}$ ($[\text{P}]_{\text{aq}} \leq 100 \mu\text{M}$), and remains constant at higher P loading. Experimental features at low pH provide evidence for formation of inner-sphere, P surface complexes at low P coverage on alumina, and subsequent formation of (surface) precipitates of Al-phosphate (and/or sorption of aqueous Al-phosphate) with increasing P loading. We also investigated by TRLFS the speciation of uranyl in $\text{PO}_4 / \alpha\text{-Al}_2\text{O}_3$ systems, at low pH. Fluorescence emission characteristics of U in solutions/ $\alpha\text{-Al}_2\text{O}_3$ suspensions suggest that phosphate-promoted sorption of U is due to formation of ternary inner-sphere surface complexes, and to (surface) precipitation of Al-U-phosphates at high P concentrations.