Biogeochemistry of tungsten alloys in soils

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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 lead 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 (WO₄²⁻) 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.

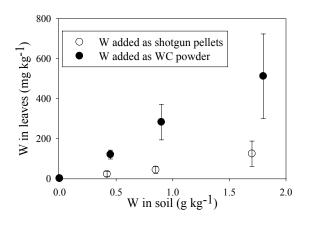


Figure 1: Effects of increasing tungsten carbide (WC) and Wmetal shot additions on W concentrations in alfalfa.

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

Spectroscopic studies of uranyl sorption in PO₄ / α-Al₂O₃ systems

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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 coadsorb with dissolved U to form ternary surface complexes. To address the study of U sorption in PO_4/α -Al₂O₃ 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 ($[P]_{aq} \leq 100 \mu M$), 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 $[P]_{a0}$ (10 – 400 µM). The isoelectric point of alumina (8.5) is shifted towards lower pH values with an increase of [P]_{aq}. At low pH (3.5), the ζ value decreases sharply with increasing P surface coverage up to 25 µmol/g ([P]aq≤100 µM), 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 PO_4/α -Al₂O₃ systems, at low pH. Fluorescence emission characteristics of U in solutions/a-Al₂O₃ 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.