# Oxidation of W-Metal Shot in Soils and Plant Response to Tungstate

Myles H. Davis, Alex Dellantonio, Chris Amrhein, and David R. Parker

Funding provided by the University of California Kearney Foundation of Soil Science

UC RIVERSIDE UNIVERSITY OF CALIFORNIA
*Department of Environmental Sciences*
*Graduate Program in Soil and Water Sciences*

## Introduction

Tungsten (W) is becoming a popular metal replacing lead in small-caliber and shotgun ammunition because it is considered to be significantly less toxic than lead in the environment. However, questions have been raised about the environmental risks associated with tungsten and its interactions with molybdenum in soil and plants. W-pellets entering the soil environment are subjected to weathering conditions, locally increasing tungsten concentrations.

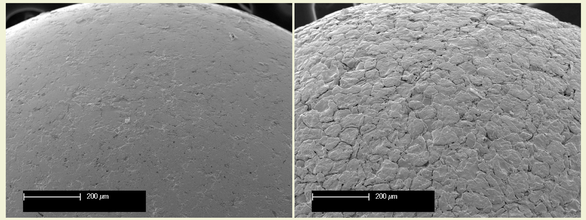
The goal of these experiments was to examine W-pellet oxidation in the soil environment, fate and transport of W in soil, and effects of tungstate ($WO_4^{2-}$) on plant uptake and development.

## Experimental Set-up

- All W-metal pellets are $\sim$ 90 % W (W-Ni-Fe alloy)
- XANES spectrum was collected at SSRL, beam line 11-2
- $\mu$-XAS elemental maps were collected at SSRL, beam line 2-3
- Pellet incubations were set-up with five W-alloy shotgun pellets in five grams of Grangeville soil for 133 days
- All soils used were Grangeville sandy loam (pH = 6.6; $Fe_{CBD}$ = 21cmol$_c$ Fe kg$^{-1}$)

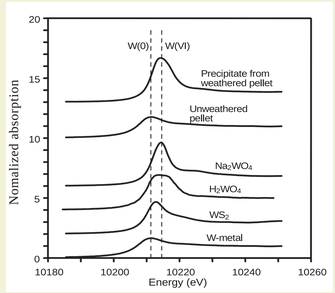
## SEM of W-Pellet Surfaces and XANES Confirmation of W-Metal Oxidation

**Un-Weathered W-Pellet** **Oxidized W-Pellet Surfaces**



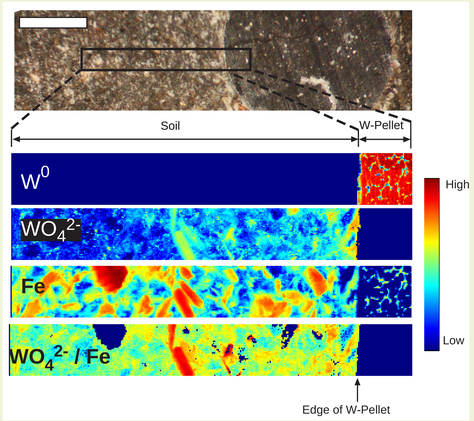

**Clean Surface**

**Incubated in Soil for 4 Months**




**XANES spectra shows the oxidation of from W-metal ($W^0$) to $WO_4^{2-}$ ($W^{6+}$).**

## $\mu$-XAS of W-BB Oxidation in Soil

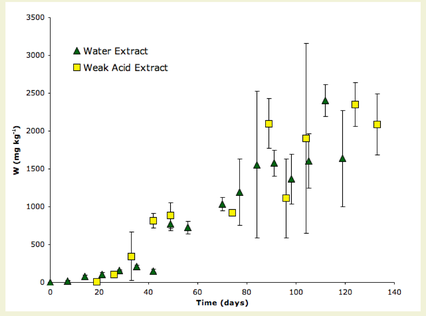



- W-metal pellet oxidizes to $WO_4^{2-}$

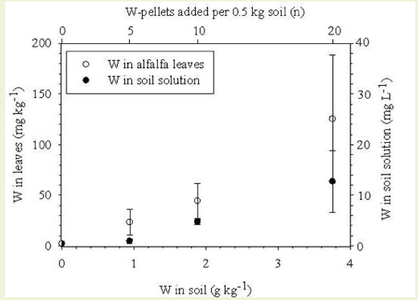
$$2\,W(s) + 3\,O_2 + 4\,OH^- \rightarrow 2\,WO_4^{2-} + 2\,H_2O$$

- $WO_4^{2-}$ diffuses away from W-pellet
- Fe in the soil appears to be coating soil particles (aside from a few mafic minerals)
- $WO_4^{2-}$ and Fe locations are highly correlated

## W-Metal Pellets Rapidly Oxidize to Produce water soluble and plant available $WO_4^{2-}$ in the local soil environment

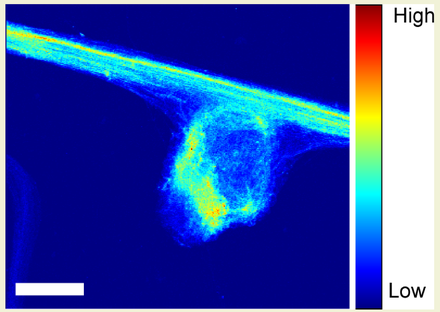



**W-Metal pellets incubated in low Fe-oxide soil (approx. 4 months), rapidly oxidize to produce more than 2000 mg kg$^{-1}$ of water soluble and plant available $WO_4^{2-}$ in the local soil environment.**

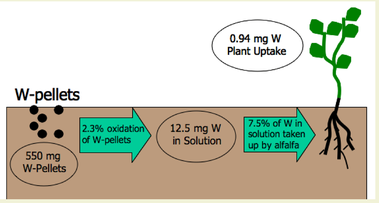



**Increasing W-pellets in soil, increases W in soil solution, consequently, alfalfa leaf W-concentrations increase.**

## Spatial Distribution of W within an Alfalfa Root and Root Nodule by $\mu$-XAS




## Conclusions




- W-Pellets rapidly oxidize to $WO_4^{2-}$ producing $>$ 2000 mg kg$^{-1}$ of plant available $WO_4^{2-}$
- $WO_4^{2-}$ diffuses away from the oxidizing W-pellet and adsorbs to Fe-oxides in soil
- Alfalfa can directly uptake oxidized W from W-pellets
- $WO_4^{2-}$ appears to be concentrated in specific locations in the root nodules and transported in the roots
- W possibly replaces Mo in N-fixing nitrogenase enzyme in root nodules of alfalfa