

# Tungsten: A Preliminary Environmental Risk Assessment

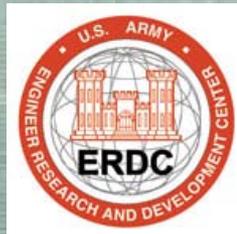
David R. Johnson

Environmental Laboratory

U.S. Army Engineer Research & Development Center

Vicksburg, MS

June 17, 2010



US Army Corps of Engineers  
**BUILDING STRONG**



# Report Documentation Page

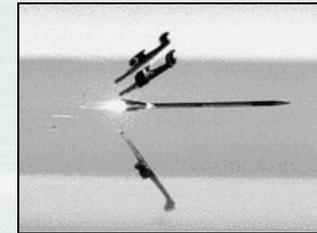
Form Approved  
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>MAY 2011</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2011 to 00-00-2011</b>	
4. TITLE AND SUBTITLE <b>Tungsten: A Preliminary Environmental Risk Assessment</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Road, Vicksburg, MS, 39180-6199</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>Presented at the NDIA Environment, Energy Security &amp; Sustainability (E2S2) Symposium &amp; Exhibition held 9-12 May 2011 in New Orleans, LA.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>30</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

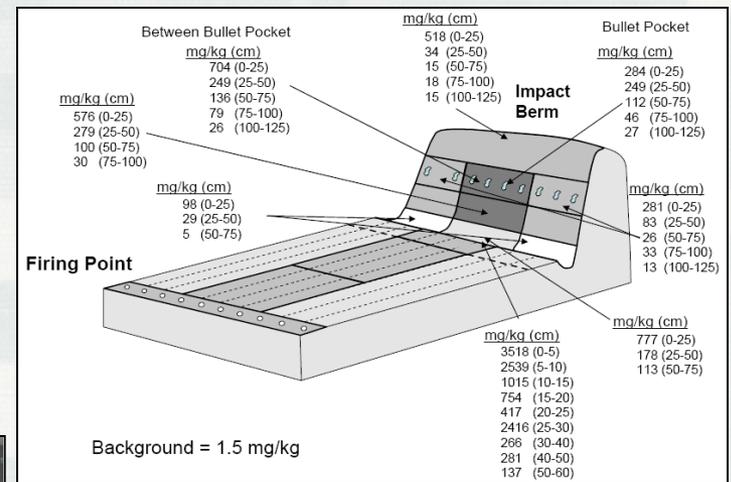
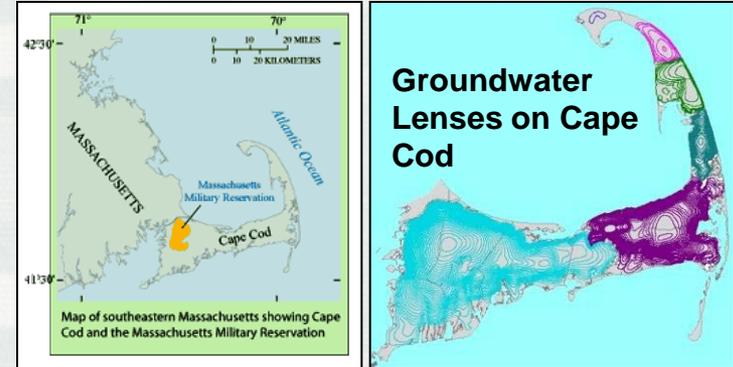
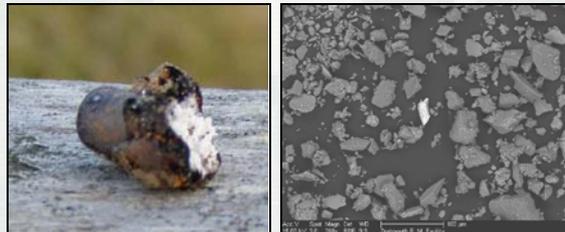
# ***Tungsten: Characteristics & Military Applications***

- Only small percentage of earth metals  
~1 mg/kg (ppm)
- Found in ores in multiple oxidative states ( $W^{-4}$ ,  $W^{-2}$ ,  $W^{-1}$ ,  $W^{+3}$ ,  $W^{+5}$ ,  $W^{+6}$ )
- 2nd most dense metal
- Highest melting point
- Highest tensile strength
- Military uses:
  - Small arms munitions
  - Penetration ammunition
  - Protective armor plates

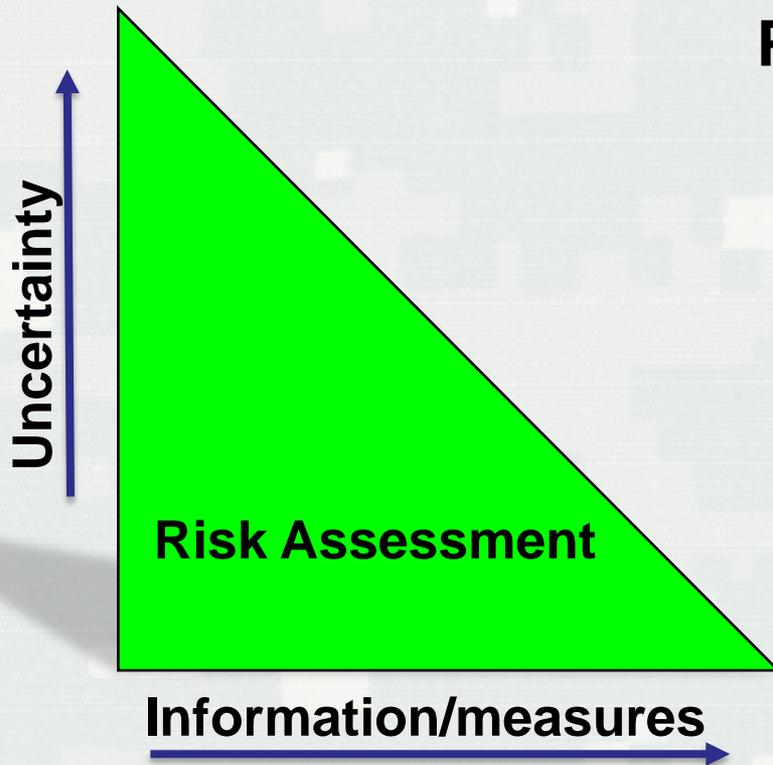


# Problems with Tungsten: Environmental Mobility

- “Green bullets” used for training in late 1990s & early 2000s as alternative to lead bullets
- Tungsten powder (~1 mm) in nylon matrix
- “Environmentally benign”
- Tungsten detected in groundwater
- Concern of ingestion from drinking water
- Inconclusive health effects
- Unknown environmental effects



# ***Reducing Uncertainty in Risk Assessment***



**Problem:** Need to increase knowledge of the potential impacts of military unique compounds and industrial compounds on aquatic and terrestrial wildlife species

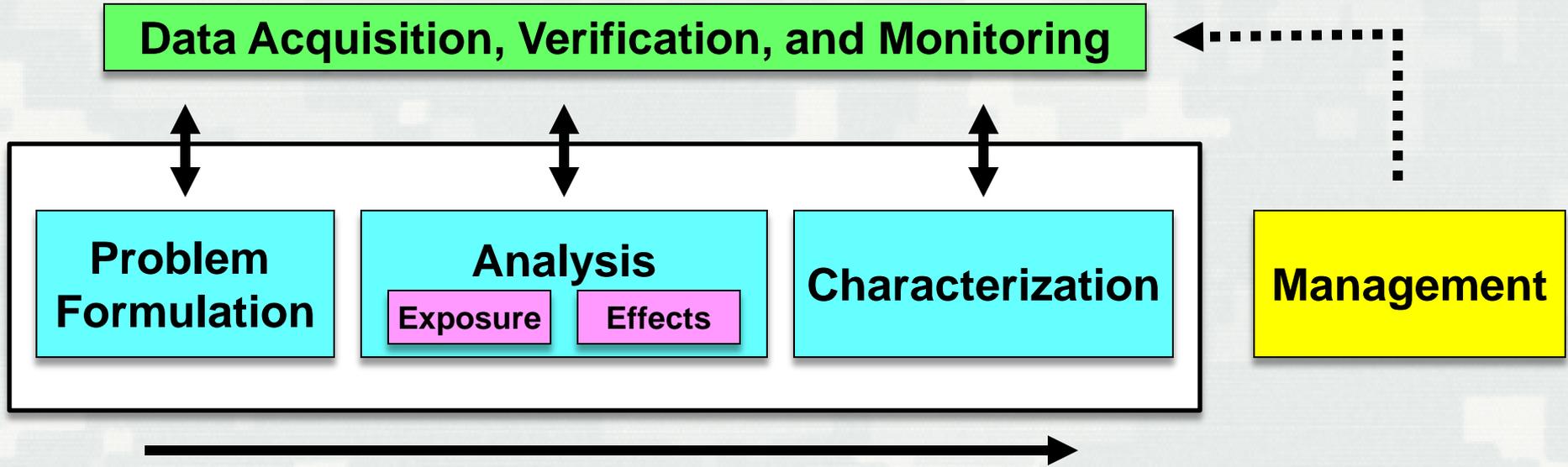
***UNCERTAINTY = \$ COST \$***

***SOLUTION:***

***MORE KNOWLEDGE = IMPROVED ASSESSMENTS =  
MORE TRAINING = BETTER SOLDIERS***



# Ecological Risk Assessment Framework



- Process that evaluates the likelihood that adverse effects may occur or are occurring as a result of exposure to one or more stressors (USEPA, 1997)
- Risk management is an approach to consider the outcome and uncertainty of an assessment and mitigate risk through a range of alternatives.



# ***Relevance: Are Environmental Tungsten Levels Likely to Cause Biochemical Effects?***

**Dietary uptake:** ~0.01 mg  
0.2-16 mg/kg (vegetables)

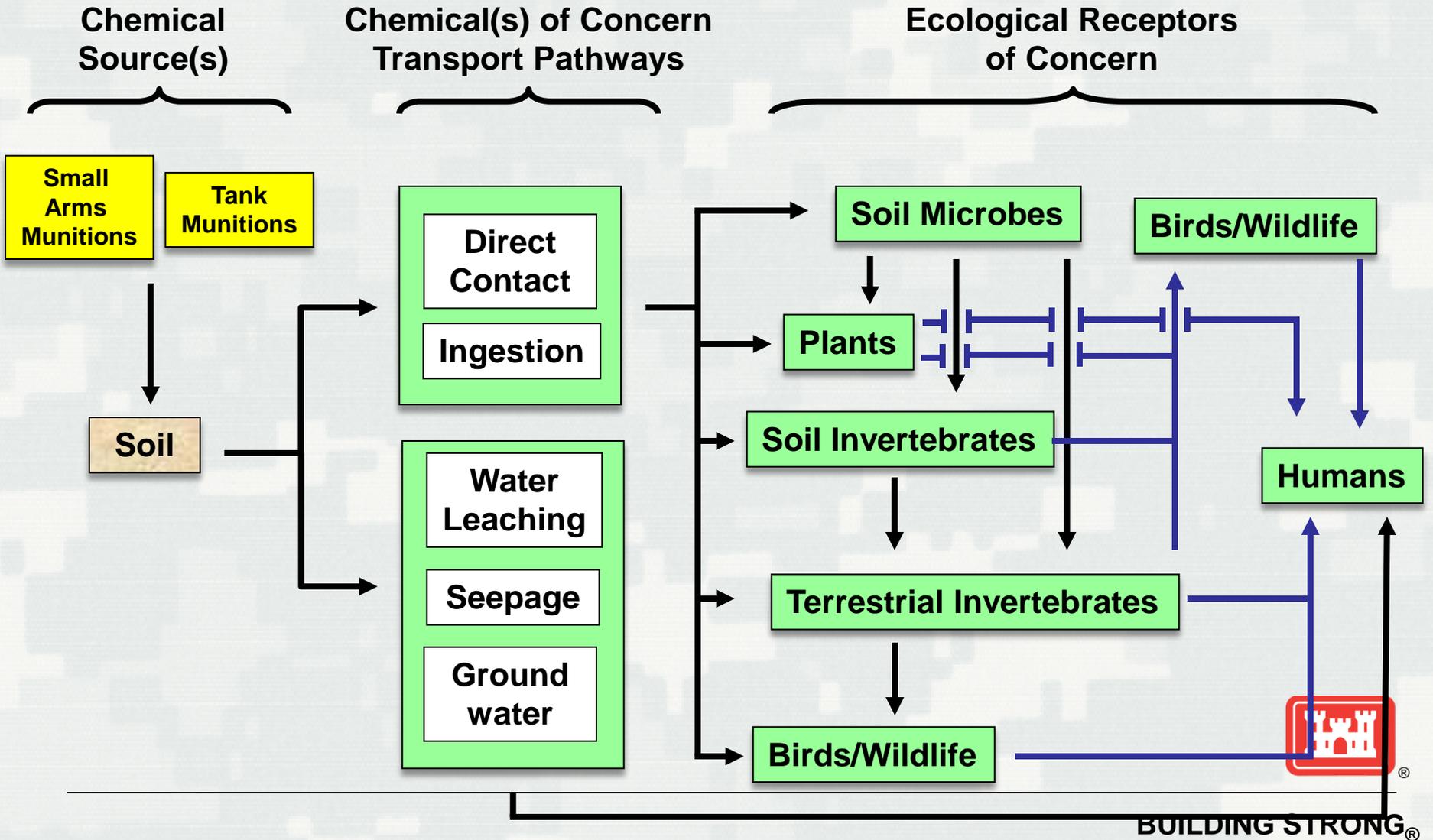
**Drinking water:** generally not measured  
0-217 µg/L (Fallon, NV)  
groundwater > surface water

**Soil:** 1-1.3 mg/kg (earth's crust)  
1-22 mg/kg (agriculture fields)  
0-5,500 mg/kg (tungsten mines, military ranges) 

**Air:** < 10 ng/m<sup>3</sup> (ambient)  
5 mg/m<sup>3</sup> (industry, OSHA)

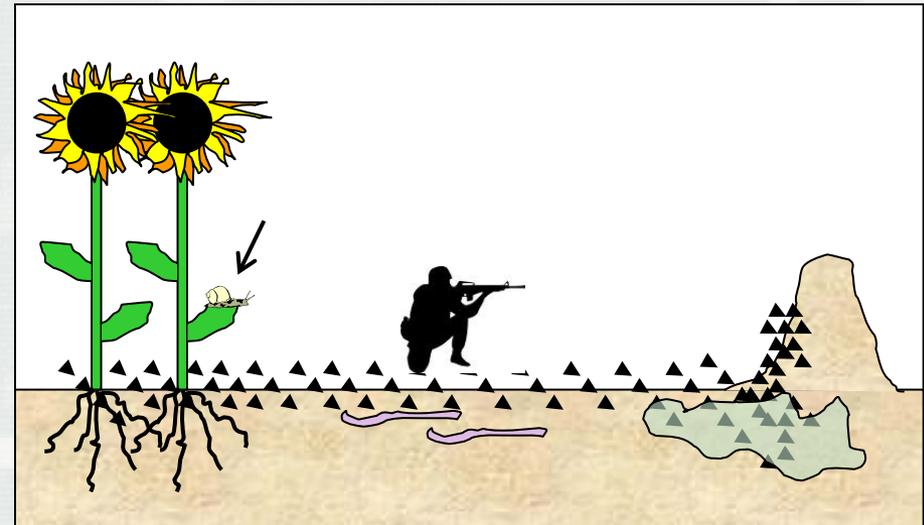


# Tungsten: Ecological Risk Assessment Conceptual Model



# ***Tungsten Research To Assess Exposure and Effects on Flora & Fauna***

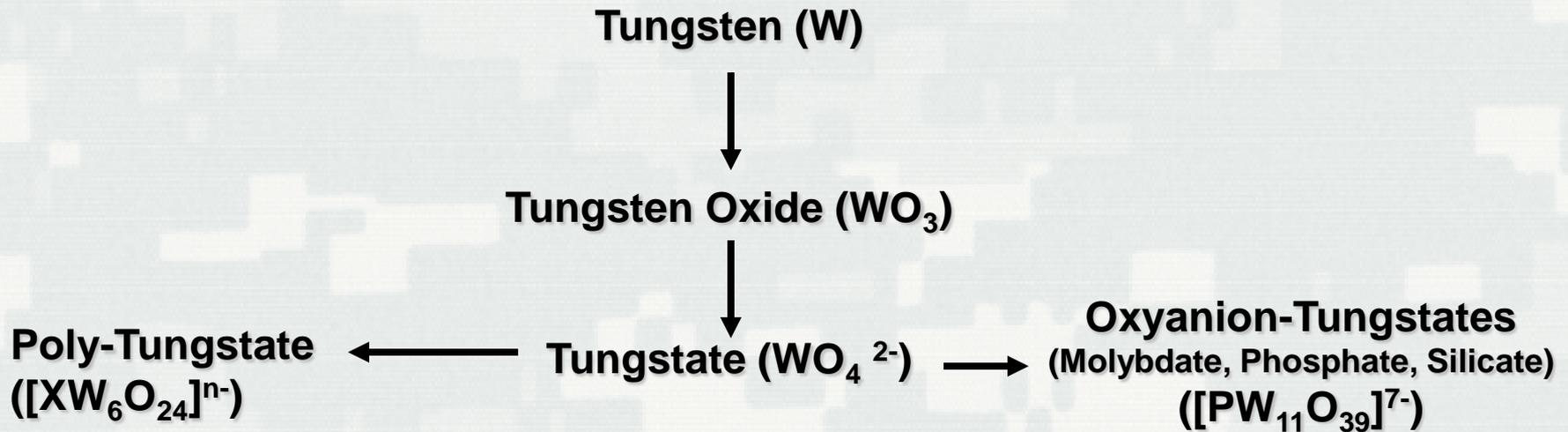
- **Geochemistry**
- **Soil microbial communities**
- **Plants**
- **Soil invertebrates**
- **Higher order animals**
- **Additional studies**



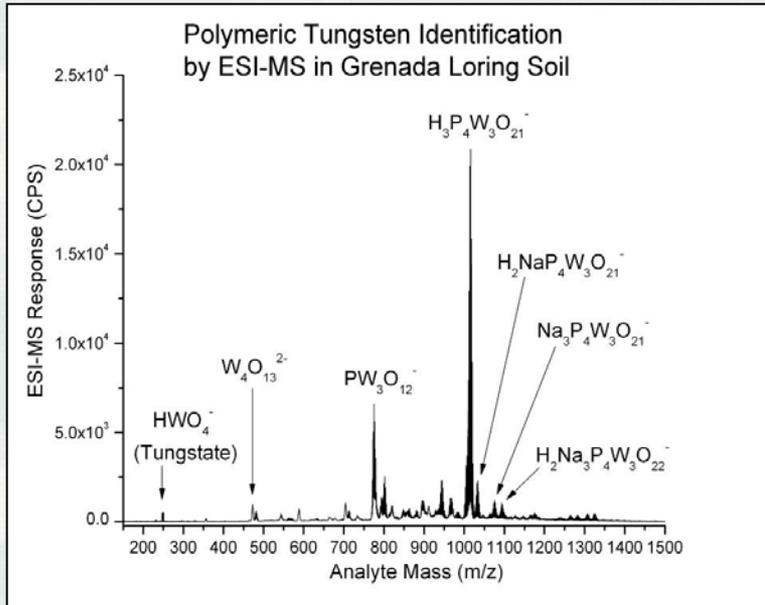
# Tungsten Geochemistry

Geochemistry of tungsten in soils will affect:

- Speciation
- Mobility/sorption in soil
- Microbe, plant, and invertebrate uptake
- Differential toxicity from parent compound and chemical species



# Tungsten Geochemistry: Chemical Speciation in Soil



Tungsten Compounds	$K_d$ 3 Days	$K_d$ 4 Months
Tungstate	284	845
Polytungstate	92	135
Phosphotungstate	112	500
Tungstosilicic Acid	103	97

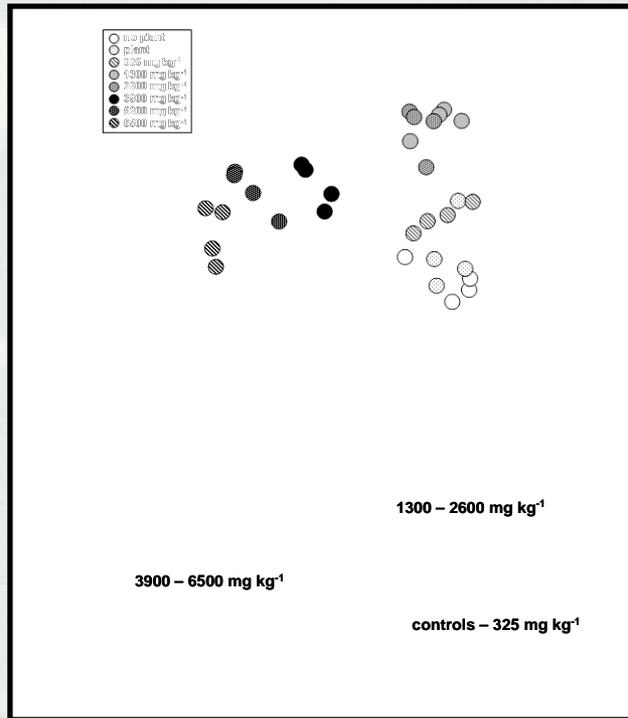
★ 1 yr aged soil  $K_d = 110$

Partition coefficients ( $K_d$ ), a measure of sorption, suggest that different species will have different mobility in soil

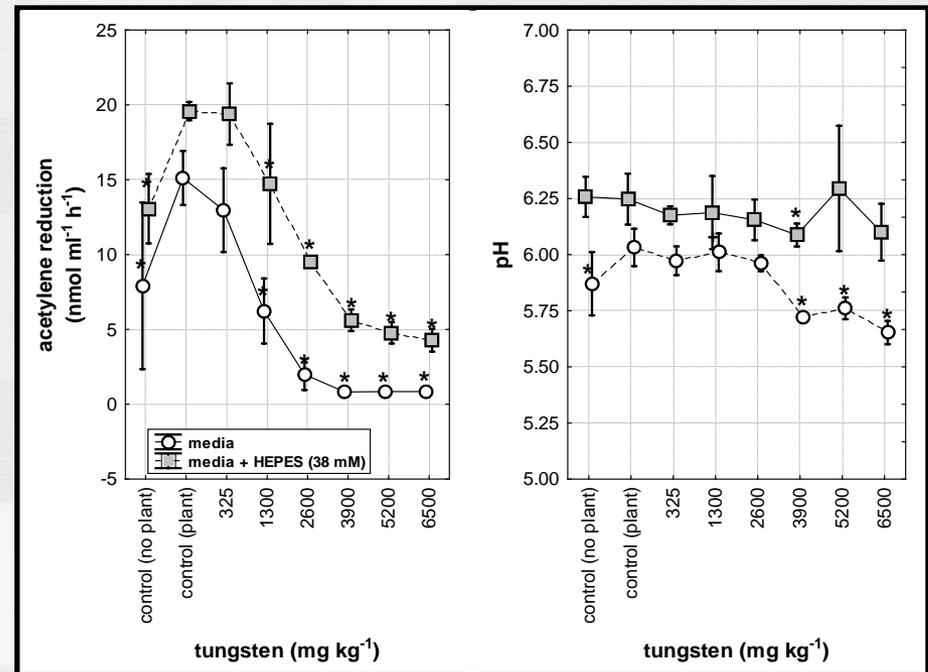


# Tungsten Effects on Soil Microbial Communities

- W caused significant shifts within the *in situ* microbial community with increasing soil W concentrations
- W significantly decreased nitrification activity in a pH-independent manner



Shift in microbial community structure w/ increasing [W]



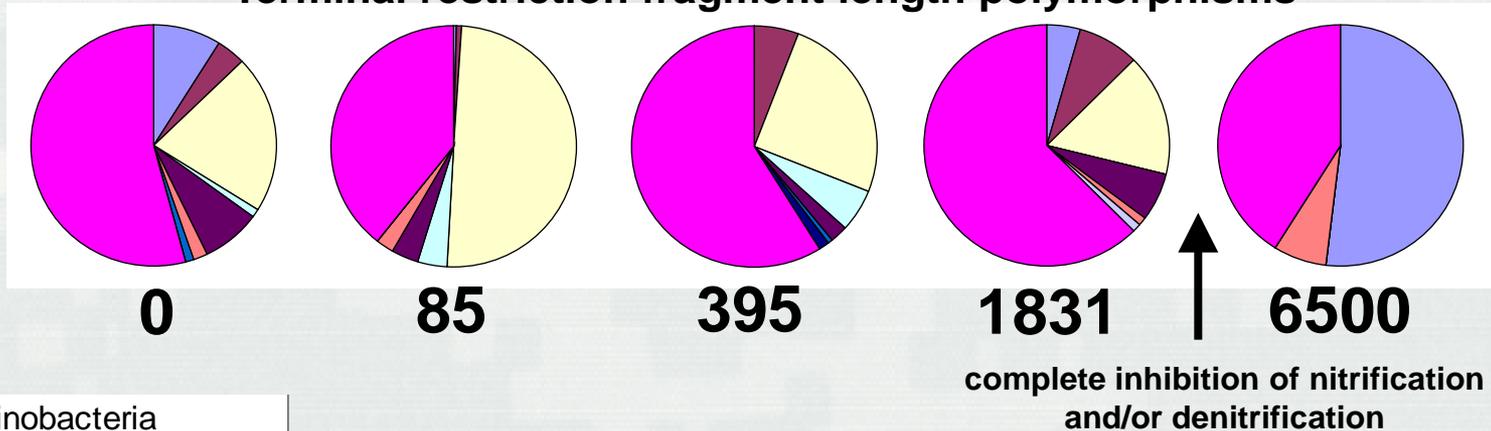
Nitrification activity inhibited by increasing [W] at neutral pH



# Tungsten Effects on Soil Microbial Communities

- We then characterized the observed community shifts and identified a loss in species diversity

Terminal restriction fragment length polymorphisms



- ★ Actinobacteria
- Bacteroidetes
- Firmicutes
- alpha-Proteobacteria
- beta-Proteobacteria
- ★ ■ gamma-Proteobacteria
- delta-Proteobacteria
- Nitrospira
- Thermotogae
- ★ ■ unknown

## Increasing soil [W] resulted in:

- Loss in diversity
  - Effect on Soil Quality
- Persistence of Actinobacteria & gamma-Proteobacteria
  - Actinobacteria – includes the actinomycetes
  - $\gamma$ -Proteobacteria – includes a variety of microbes



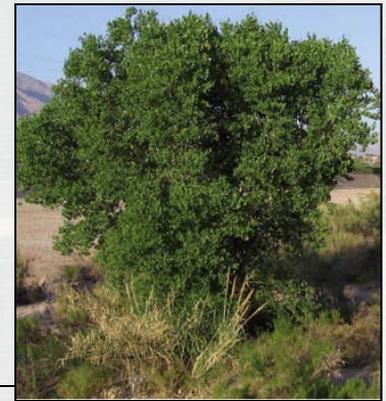
# ***Bioaccumulation of Tungsten in Plants***

## **Natural Sources**

- Trees & shrubs in Rocky Mountain region, USA
- Siberian pine, willows, mosses & lichen in tungsten-rich fissures

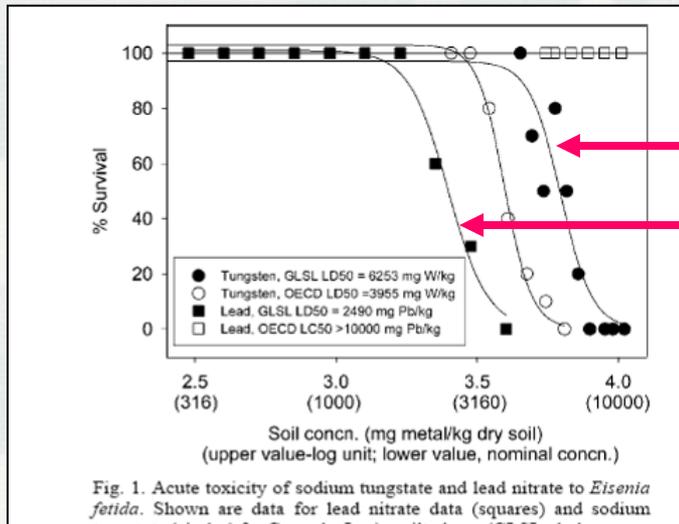
## **Anthropogenic Sources**

- Agriculture & fertilizers (e.g., chemical, municipal biosolids, incinerator ash)
- Industry (e.g., manufacturing facility wastewater discharge)
- Abandoned mines
- Military





# Effects of Tungsten on Earthworms (*E. fetida*)

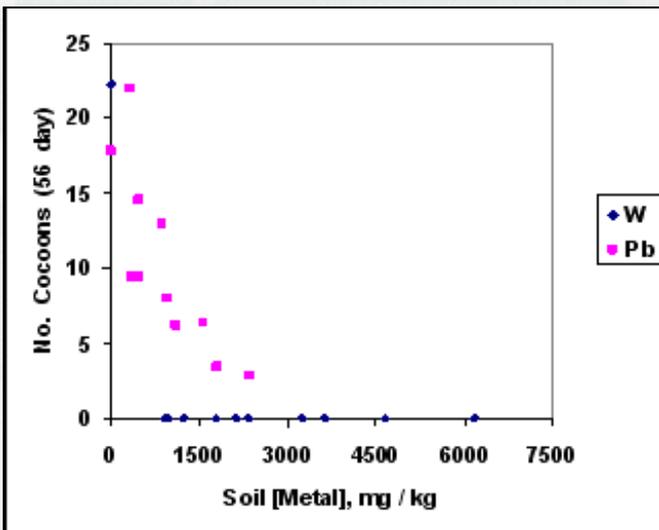


W (field soil) LD50 = 6253 mg/kg

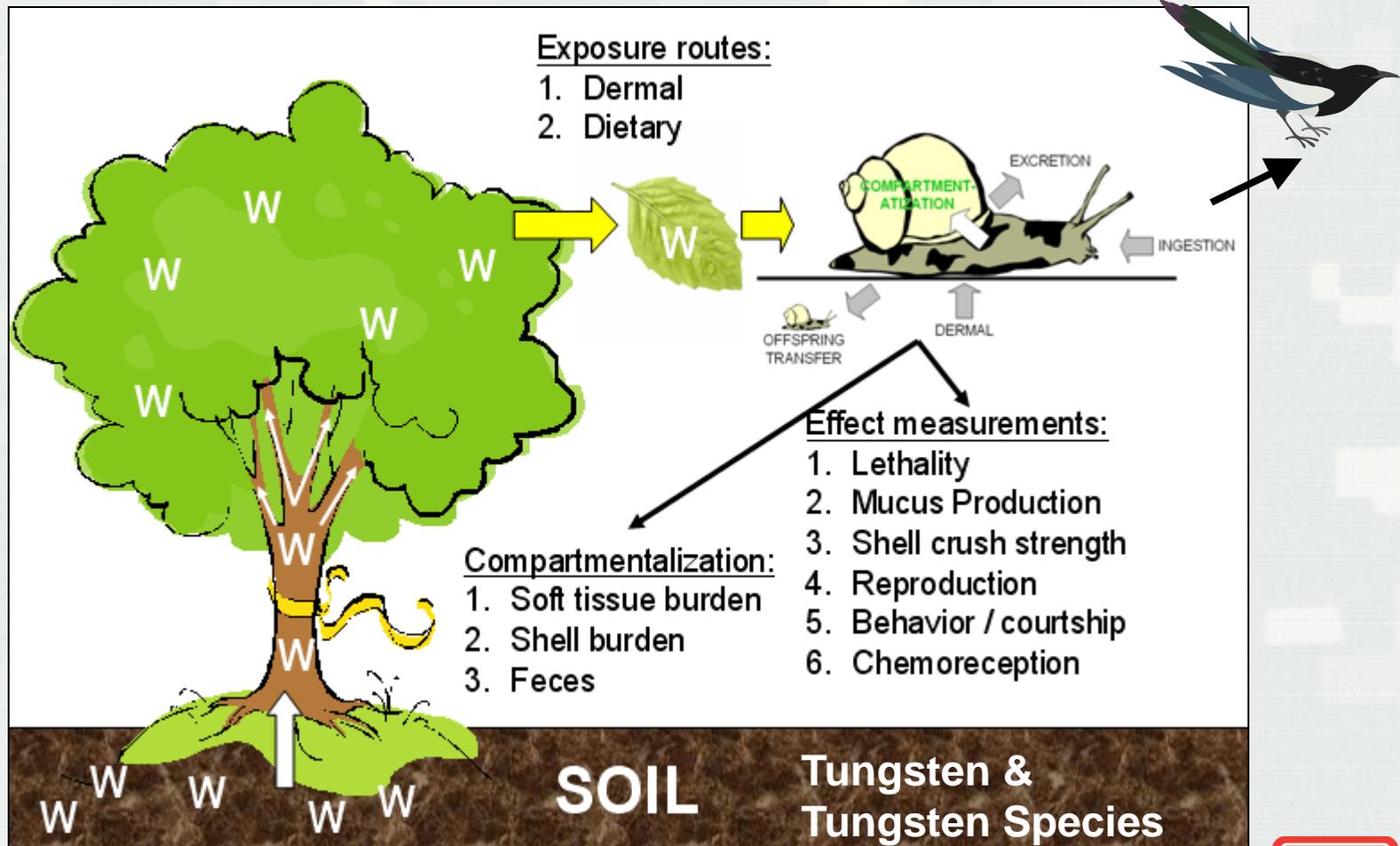
Pb (field soil) LD50 = 2490 mg/kg

- W is less acutely toxic to earthworms than lead

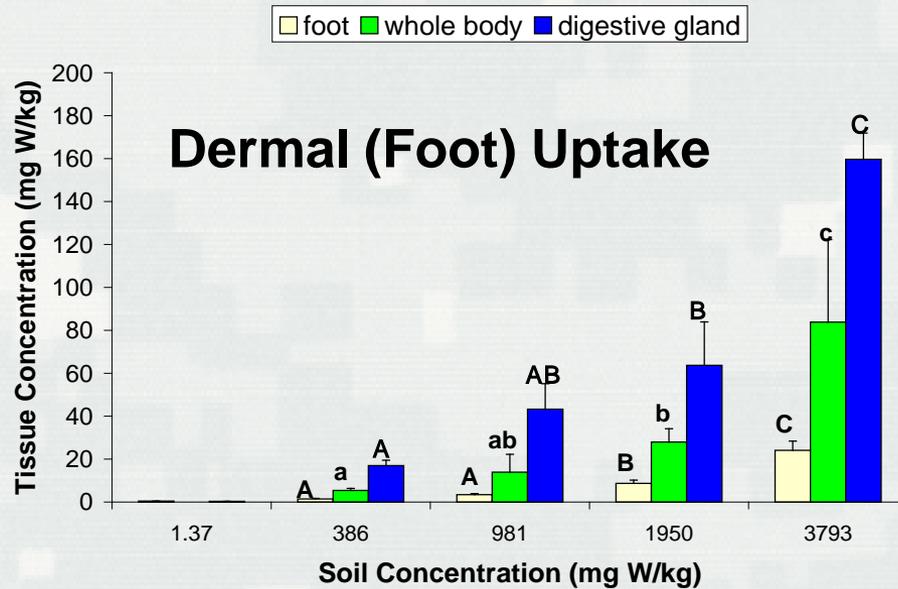
- W is a potent reproductive toxicant to earthworms after 28 day exposure



# Is Tungsten Transferred Up the Food Web?



# Uptake of W in Gastropods

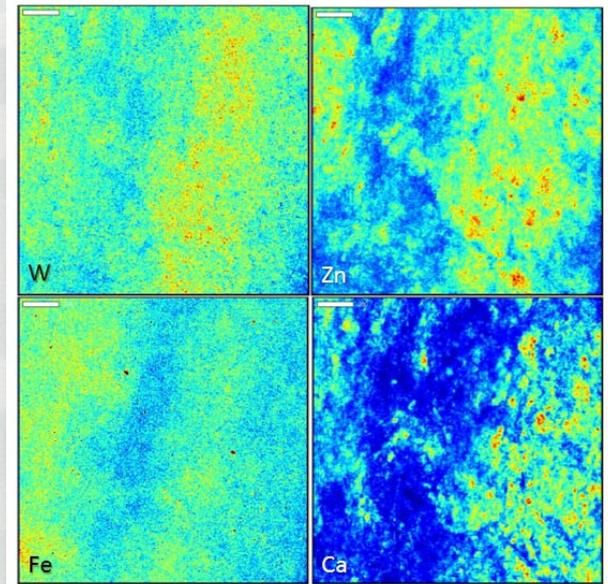


## Steady State:

Body: 14 days

Hepatopancreas: 23 days

BAF: 0.09



**Synchrotron analysis of  
Snail hepatopancreas**

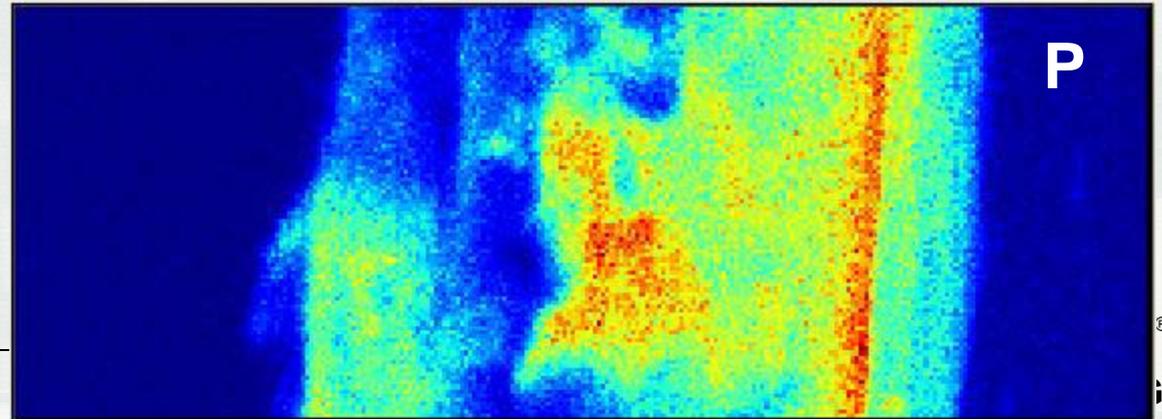
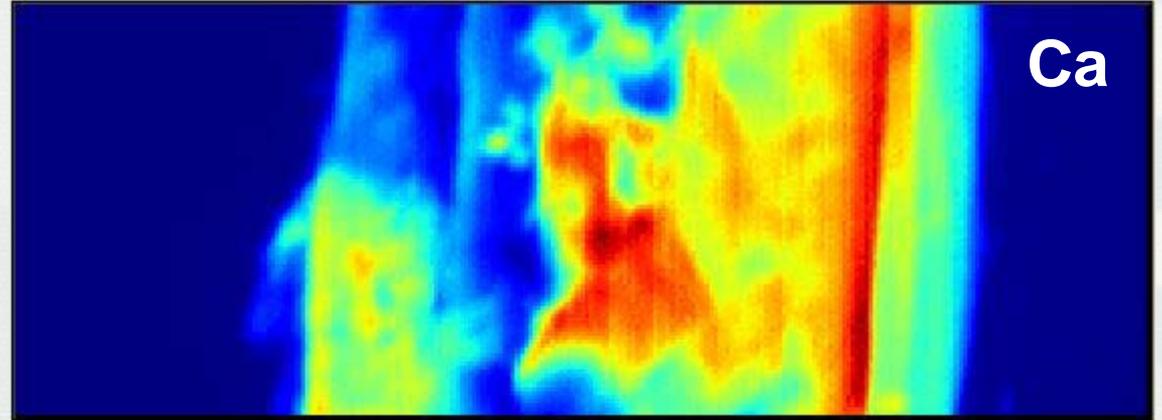
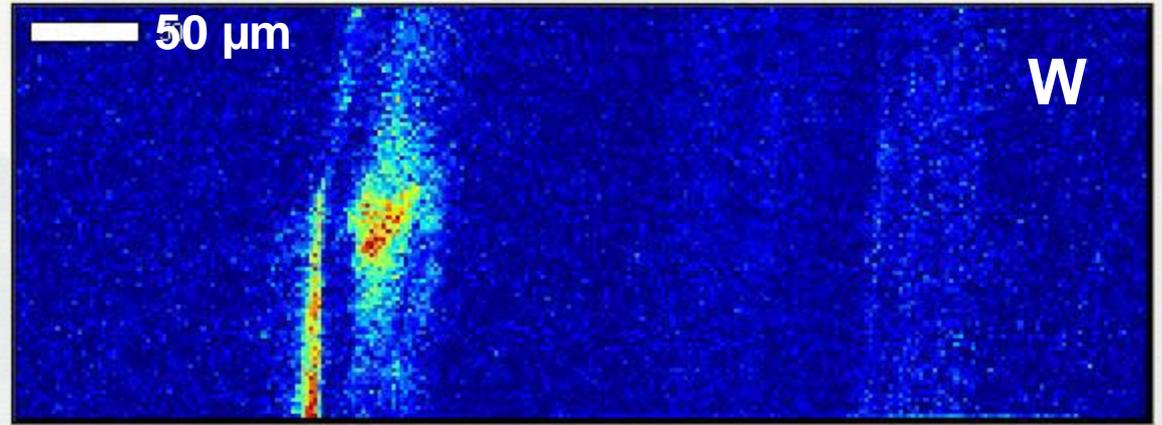
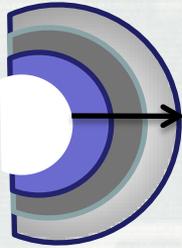


# Dermal Uptake of W in Gastropods

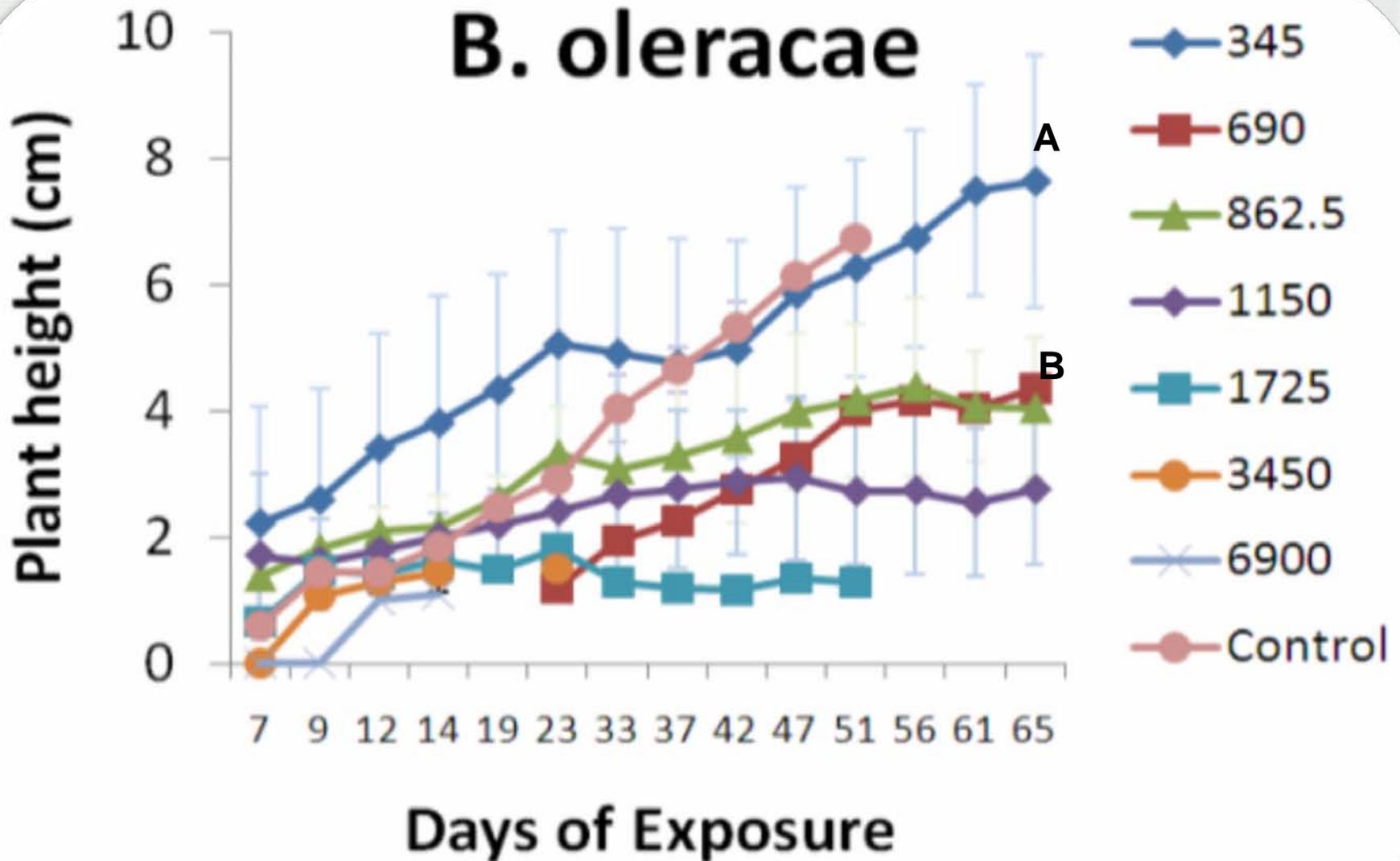
Snail Exposed to W



Shell Cross Section



# *Uptake of W in Gastropod Food Source*



# Uptake of W in Gastropod Food Source

Exposed to

Cabbage (251 mg/kg)

Soil ( $547 \pm 34$ ) mg/kg soil

Rates

Hepatopancreas

Uptake ( $k_u$ ):  $0.23 \pm 0.23$  g/g/d  
( $p=0.40$ )

Elimination ( $k_e$ ):  $0.63 \pm 0.68$  1/t  
( $p=0.43$ )

Steady state: 5-days, 85.9 mg/kg

BAF = 0.36

Body

Uptake ( $k_u$ ):  $0.05 \pm 0.03$  g/g/d  
( $p=0.15$ )

Elimination ( $k_e$ ):  $0.35 \pm 0.21$  1/t  
( $p=0.19$ )

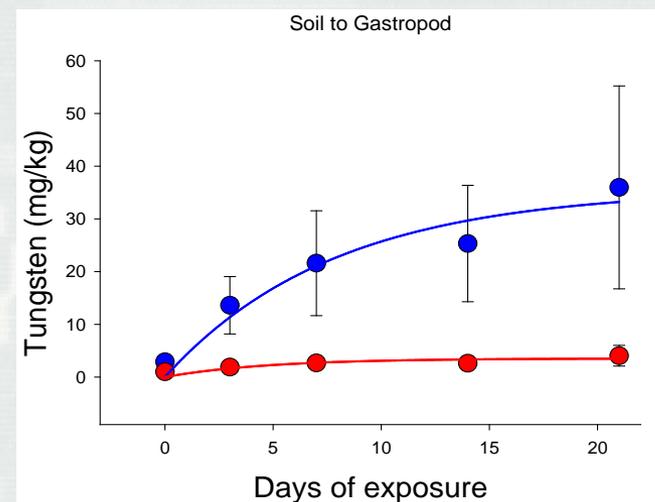
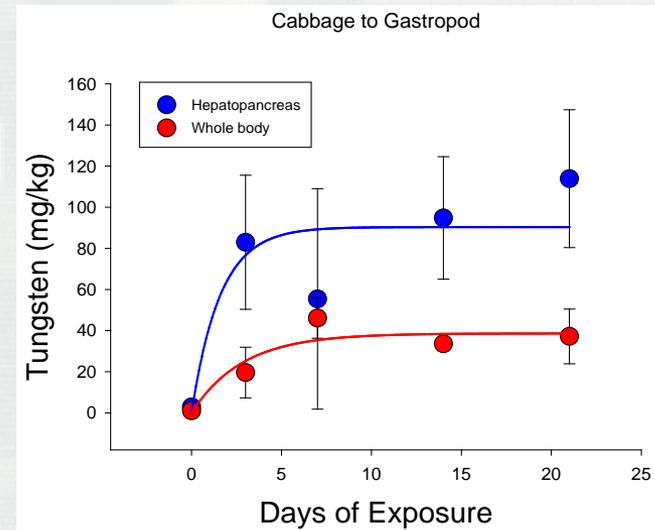
Steady state: 9-days, 36.7 mg/kg

BAF = 0.15

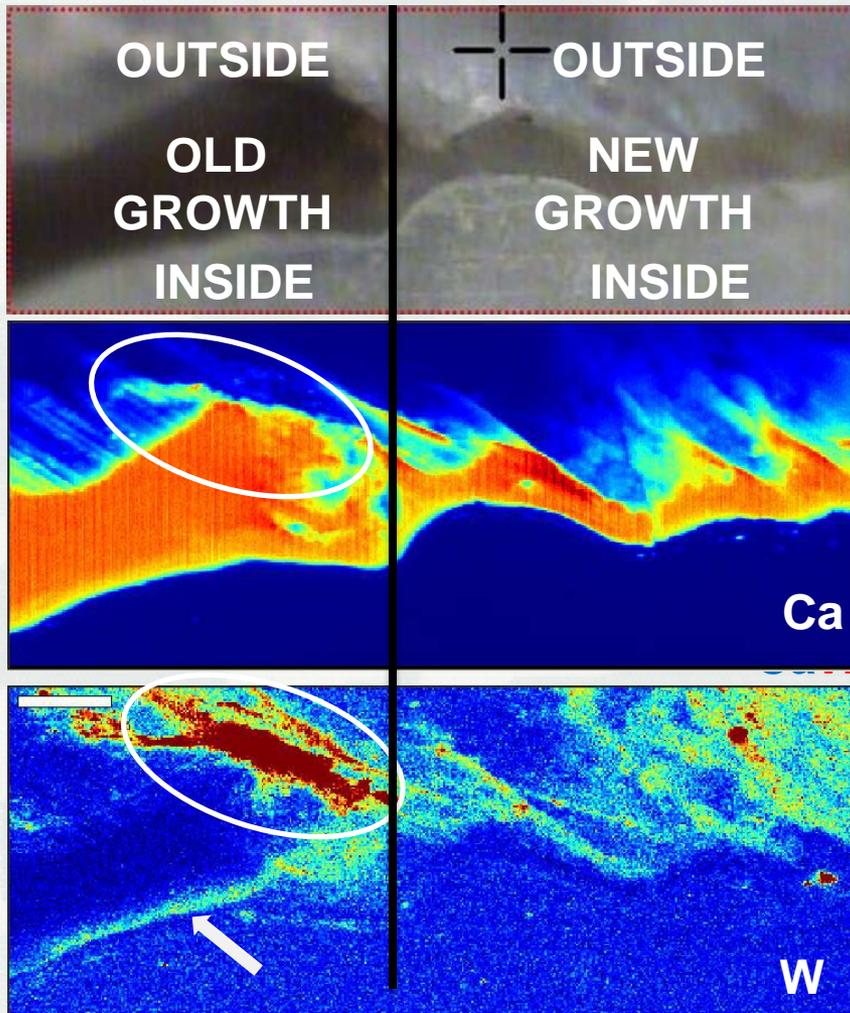
Body/liver = 0.43

Only 0.09 in soil exposure

Assimilation efficiency greater



# ***Uptake of W in Gastropod Food Source: effect on gastropod shell***



Cross section of shell  
Ca map clearly shows  
face

W clearly on the inside of  
the shell

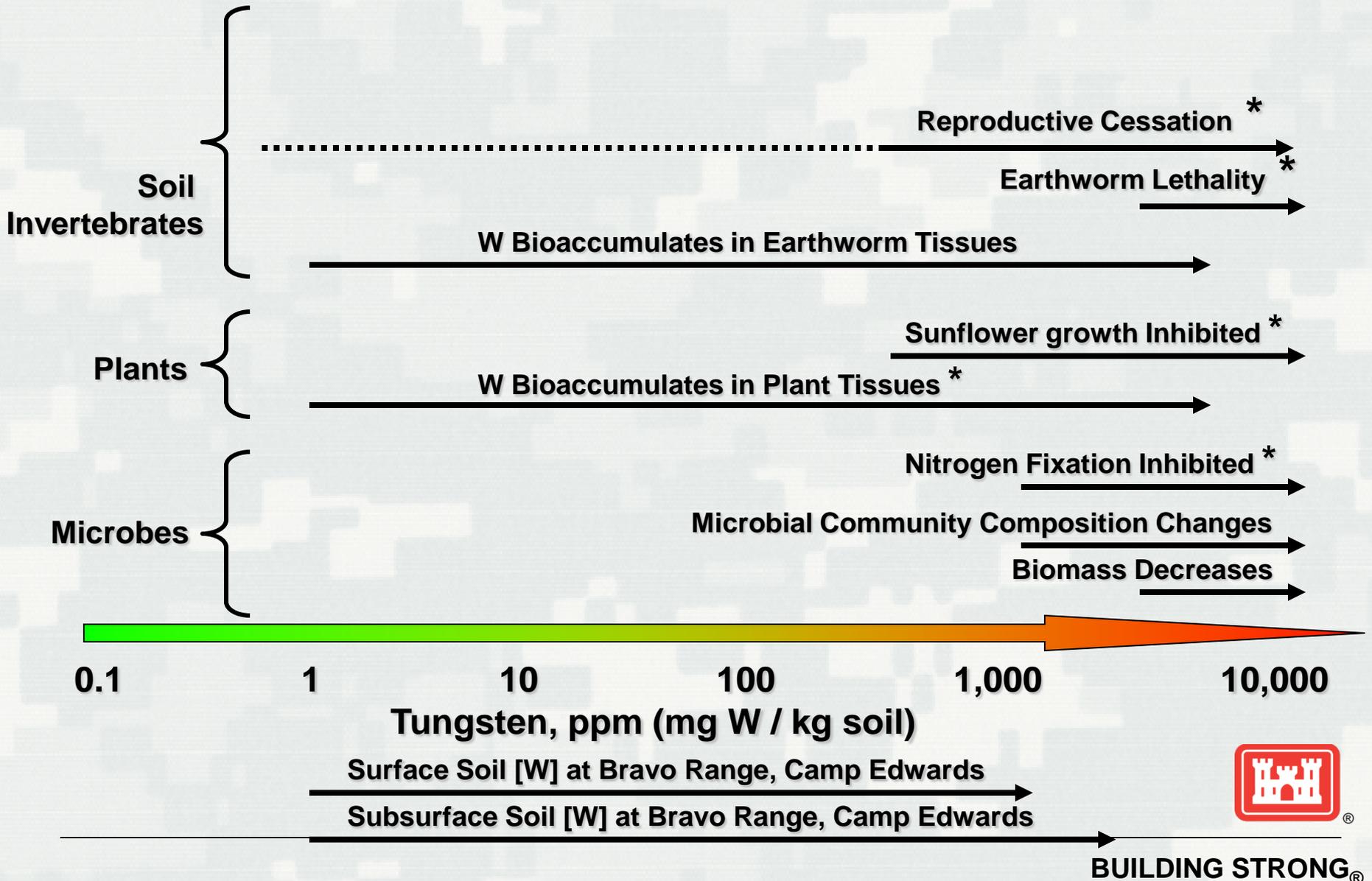
Hot spot

ICP-MS:

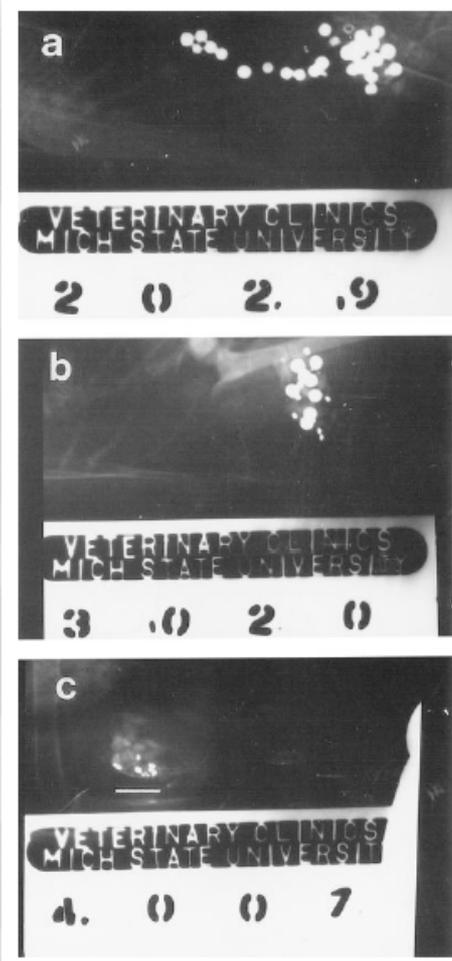
5.7 vs. < 0.1 mg/kg



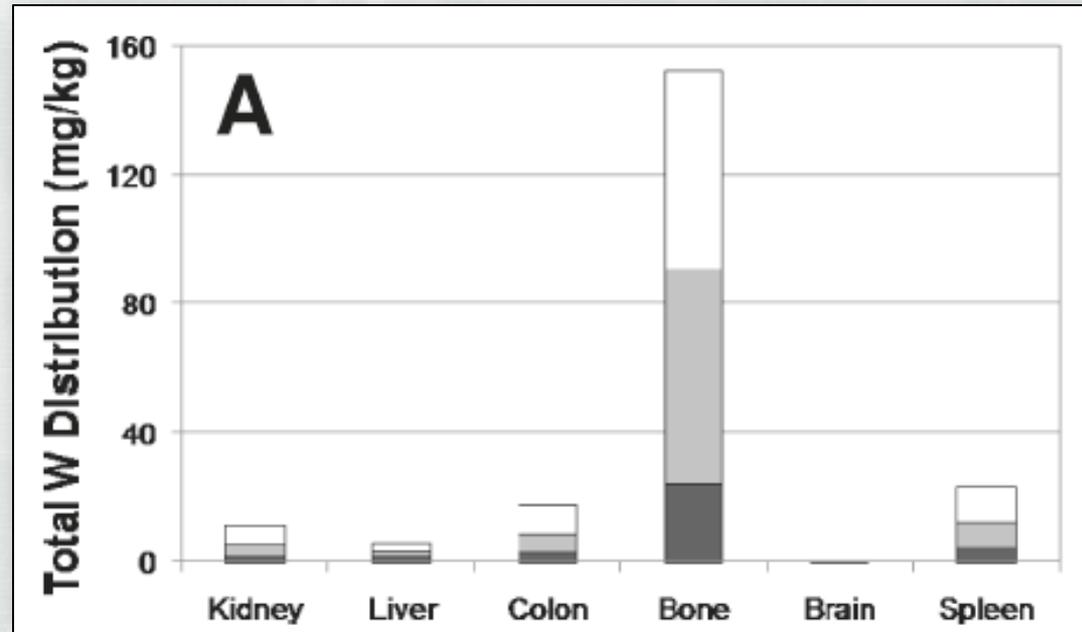
# Tungsten Ecotoxicity: Fate & Effects



# Tissue Distribution of W Uptake in Higher Organisms



Mitchell et al. 2001



Guandalini et al. 2011

Steel: 50 % erosion  
 W-FE: 64% erosion  
 W-polymer: 98% erosion



# ***Is Tungsten Affecting Cellular Biochemistry and Physiological Processes in Liver Cells?***

- **Moderate W concentrations in liver after acute exposure**
- **Direct route to liver for oral ingestion**
- **Liver contains high levels of Mo-containing enzymes... competition at Mo-binding sites?**
- **Glucose metabolism pathways affected by W**
- **Tungsten binds to oxyanions (i.e., phosphates) in soil... does it happen in the body too?**
- **If tungsten binds oxyanions, is it affecting/ interfering phosphate-dependent pathways?**



# Tungsten Bioaccumulation & Effects on Phosphate-Dependent Biochemical Pathways in the HepG2 Hepatic Cell Line

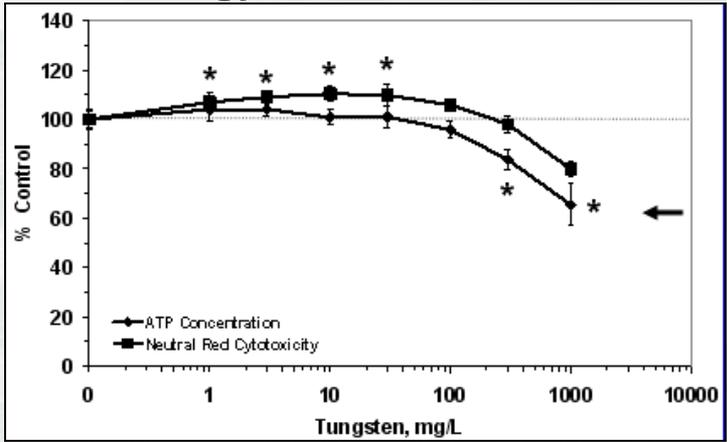
## Uptake

	Dissolved W <sup>a</sup> (ug/L) (ppb)	Tungstate <sup>b</sup> (ug/L) (ppb)	Polytungstate <sup>b</sup> (ug/L) (ppb)
<b>Control</b>	< 20	<10	<10
<b>1000 ppm W</b>	1100	871	34

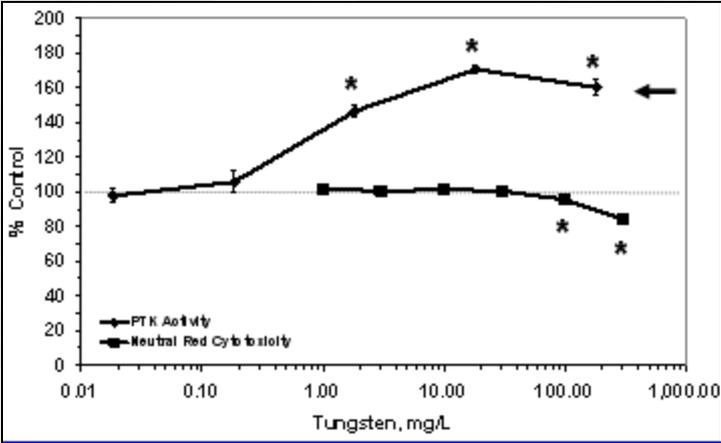
<sup>a</sup> Analyzed by ICP-MS

<sup>b</sup> Analyzed by SEC-ICP-MS

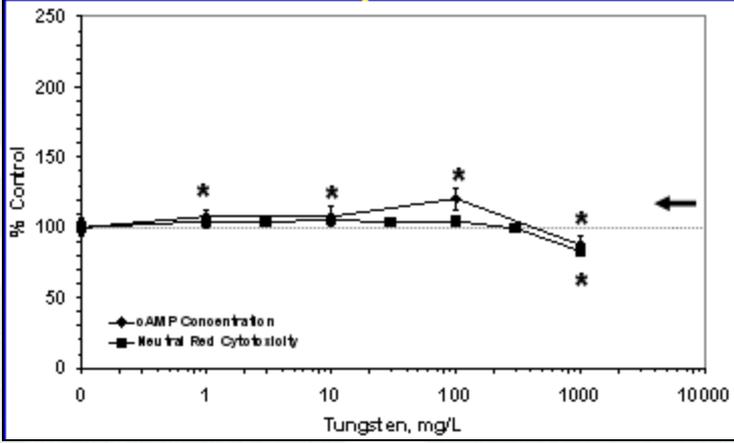
## Energy Production: ATP



## Cell Signaling: Tyrosine Kinase



## Secondary Messengers: cAMP



# ***Toxicogenomic Effects of Tungsten on Rat Hepatocytes***

1,822 Up-Regulated genes

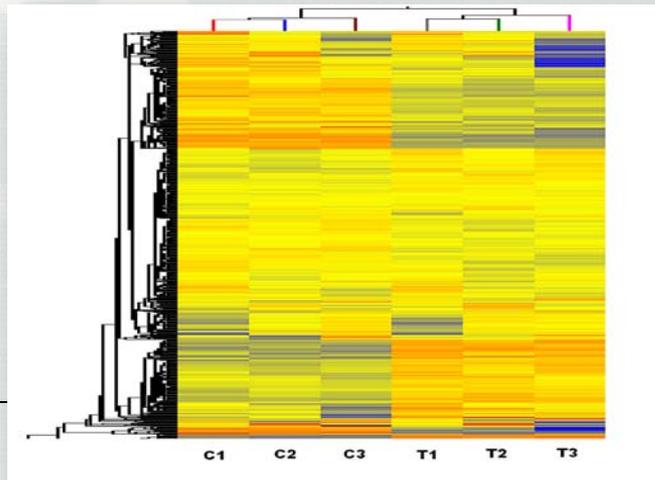
## **Major pathways affected:**

- Nucleic acid metabolism
- Macromolecule synthesis
- Caspases / apoptosis
- Cell proliferation
- Transitional metal ion binding
- Peptidase activity
- DNA & protein binding

1,802 Down-Regulated genes

## **Major pathways affected:**

- Lipid metabolism
- Glycoprotein metabolism
- Oxidoreductase activity
- Stress response
- Transferase activity
- Catalytic activity
- Membrane-bound organelles
- Membranes
- Regulating apoptosis
- Developmental processes
- Protein modification
- Mitochondria



# ***Conclusions***

## **Geochemistry:**

- **Aging of tungsten in soil results in heteropolymeric speciation**

## **Microbes:**

- **Tungsten significantly decreases nitrification, potentially affecting plant health**
- **Tungsten causes a decrease in microbial community diversity, resulting in poorer soil quality**

## **Plants:**

- **Tungsten significantly affects sunflower growth**
- **Tungsten (species) bioaccumulates in plant tissues**

## **Invertebrates:**

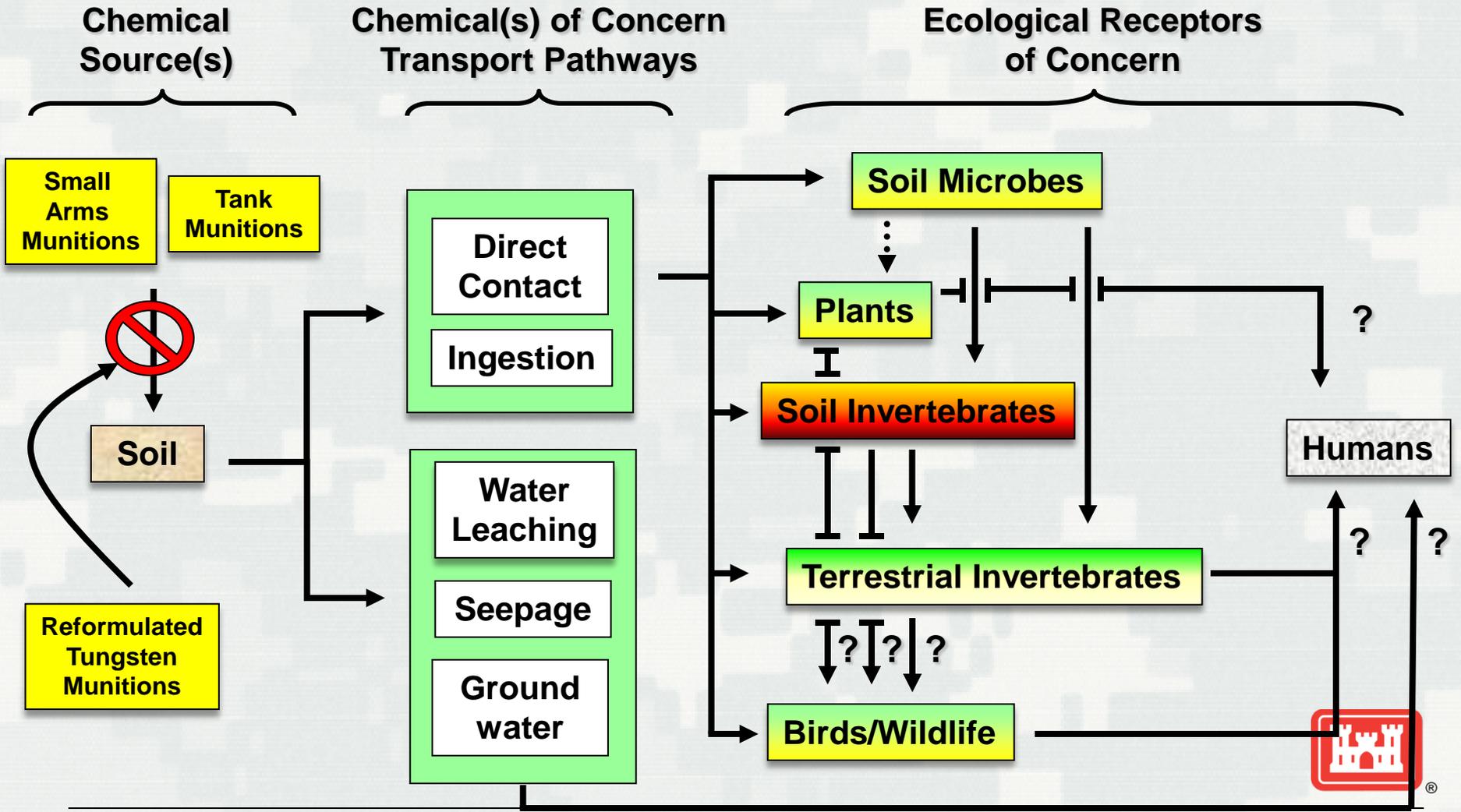
- **Earthworm reproduction blocked by tungsten**
- **Tungsten bioaccumulates in snails via foot exposure and diet**
- **Tungsten bioaccumulates in snail shell**

## **Higher Organisms:**

- **Tungsten (at medium to high concentrations) significantly affects phosphate-dependent cell signaling pathways and secondary messengers in a liver cell culture**



# Tungsten: Ecological Risk Assessment Conceptual Model



Low Concern    Moderate Concern    High Concern

# ***Thank You for Your Time and Attention***

- **Anthony Bednar & Will Jones (EL): Environmental Chemistry**
- **Mark Chappell & Jen Seiter (EL): Soil geochemistry**
- **Chris McGrath (EL): Geochemical modeling**
- **David Ringelberg (CRREL): Microbiology**
- **Linda Winfield (retired): Plant Biology**
- **Robert Boyd (EL): Terrestrial Ecotoxicology (plants & earthworms)**
- **Alan Kennedy & Jay Lindsay (EL): Terrestrial Ecotoxicology (gastropods)**
- **ChooYaw Ang (BTS): Cellular Biology**
- **Laura Inouye (Washington State Dept. of Ecology): Terrestrial Ecotoxicology & Cellular Biology**

**This project was funded by the Army's Environmental Quality & Installations Basic Research Program (projects # 04-16 & 06-27)**

**The findings of this presentation are not to be construed as an official Department of the Army position unless so designated by other authorized documents.**

**Permission was granted by the Chief of Engineers to distribute this information.**





---

**BUILDING STRONG®**